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The cationic oligomerization of *p*-aminostyrene
2. Dimerization in the intial stage

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Summary

It was found that p-aminostyrene (PAS) could be oligomerized by using several aminium perchlorates as catalysts in acetonitrile to give a dimer **D** in the initial stage of the reaction and finally the isomerization oligomer **1** at the end, in quite similar manner to the preceding paper (1), where dimerization (hydroamination) is the main reaction in the initial stage. The pK_a values for the amines were evaluated by the indicator method, and the $[H^+]_0$ and $[MH^+]_0$ values were calculated from equilibrium equations. As a result, the rate increased with decreasing pK_a of the catalytic amine used and reached an overall constant value. From the relationships between the rate of the reaction and the $[H^+]_0$ or $[MH^+]_0$ values calculated numerically, however, it was determined that the rate was more affected by the $[H^+]_0$ or $[M^+]_0$ values rather than the pK_a of the catalyst. It was assumed that the reaction would be initiated by the electrophilic attack of MH^+ on the double bond of the monomer. Three successive reactions were proposed for the dimerization step: slow protonation followed by subsequent fast reactions; amine addition to the resultant styryl cation and proton elimination. It was assumed that oligomerization might proceed via the same three successive reactions as proposed for the dimerization step.

Introduction

In the preceding paper (1), we reported that the low molecular weight oligomer having the unique structure **1** ($\mathbf{P_n}$) was produced when PAS was reacted with a catalytic amount of trifluoroacetic acid (TFA) in carbon tetrachloride (CCl_4). Structural analyses showed the selective formation of **1** without any other product by conventional chain reaction. It was suggested that the reaction was a kind of "hydrogen transfer reaction" and the proton played an important role during the reaction. When a strong Brönsted acid is used as a catalyst, almost all of the protons released from the acid are presumably sequestered by the large amount of monomeric amine existing in solution. This idea encouraged us to examine whether PAS could be polymerized by an anilinium salt initiator rather than TFA. As expected, PAS was found to be oligomerized by aminium perchlorates (2) as easily as with TFA. Furthermore, the reaction rate was found to be dependent on the pK_a of the amine catalyst.

In this paper, we examine the features of the reaction of PAS with a variety of aminium perchlorates in order to clarify the reaction mechanism. Acetonitrile was used as the solvent, because of the ease with which it dissolves aminium perchlorates. The pK_a values for amines in acetonitrile were measured by the indicator method (3).

Experimental

Reagents

The PAS monomer was prepared in the same manner as described in the preceding paper (1). Acetonitrile was purified according to the method of Kolthoff et al (4). Technical grade acetonitrile (Wako Co. Ltd.) was shaken with activated alumina followed by drying over anhydrous calcium chloride and magnesium sulfate. This was then distilled over calcium hydride at 81.0 ± 0.5 °C. The solvent was stored in a glass stoppered bottle in the dark. The water content of the solvent was determined by the Karl Fischer method and found to be 0.0025 %.

Aminium perchlorates

Several aminium perchlorates were prepared by the addition of 71 % aqueous perchloric acid

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to the ether solution of amines. The resultant precipitate was separated by suction filtration and recrystallized several times from an appropriate solvent. Anilinium perchlorate (recrystallized from n-amyl alcohol): ^{1}H NMR (DMSO-d6) δ 7.35 (d, 5H, aromatic), 8.76 (br s, 3H, NH_3^+). p-Chloroanilinium perchlorate (recrystallized from ethyl acetate-ether mixed solvent): ^{1}H NMR (DMSO-d6) δ 7.15-7.60 (m, 4H, aromatic), 8.58 (s, 3H, NH_3^+). p-Nitroanilinium perchlorate (recrystallized from ethanol-benzene mixed solvent): ^{1}H NMR (DMSO-d6) δ 6.44 (s, 3H, NH_3^+), 6.62 (AB, J_{AB}=7.2 Hz, 2 aromaticH, o-H to -NH_3^+), 7.95 (AB, J_{AB}=7.2 Hz, 2 aromaticH, m-H to -NH_3^+). o-Nitroanilinium perchlorate (recrystallized from ethanol-benzene mixed solvent): ^{1}H NMR (DMSO-d6) δ 6.06 (br s, 3H, NH_3^+), 6.62 (t, J=8.6 Hz, 1 aromaticH, 4-H to -NH_3^+), 7.02 (d, J=8.6 Hz, 1 aromaticH, 2-H to -NH_3^+), 7.40 (t, J=8.6 Hz, 1 aromaticH, 3-H to -NH_3^+), 7.96 (d, J=8.6 Hz, 1 aromaticH, 5-H to -NH_3^+). 4-Vinylanilinium perchlorate (recrystallized from acetone-ether): ^{1}H NMR (DMSO-d6) δ 4.60 (br s, 3H, -NH_3^+), 5.35 (dd, J=1.0 Hz, J'=10.8 Hz, 1H, Ph-CH=C$\underline{\text{H}}$, syn), 5.89 (dd, J=1.0 Hz, J'=18.1 Hz, 1H, Ph-CH=C$\underline{\text{H}}$, anti), 6.77 (dd, J=10.8 Hz, J'=18.1 Hz, 1H, Ph-C$\underline{\text{H}}$=CH_2), 7.35 (AB, J_{AB}=6.6 Hz, 2 aromaticH, o-H to -NH_3^+), 7.62 (AB, J_{AB}=6.6 Hz, 2 aromaticH, m-H to -NH_3^+). N-Methylanilinium perchlorate (recrystallized from chloroform): ^{1}H NMR (DMSO-d6) δ 2.95 (s, 3H, CH_3), 7.43 (s, 5H, aromatic), 8.76 (br s, 2H, NH_2^+). N,N-Dimethylanilinium perchlorate (recrystallized from n-amyl alcohol): ^{1}H NMR (DMSO-d6) δ 3.15 (s, 6H, CH_3), 7.47 (s, 5H, aromatic), 8.60 (br s, 1H, NH^+). Pyridinium perchlorate (recrystallized from ethanol): ^{1}H NMR (DMSO-d6) δ 7.92-9.05 (m, 5H, heterocyclic), 11.28 (br s, 1H, NH^+). 3-Methylpyridinium (ß-picoline) perchlorate (recrystallized from ethanol-ether mixed solvent): ^{1}H NMR (DMSO-d6) δ 2.51 (s, 3H, CH_3), 7.80-8.82 (m, 4H, heterocyclic), 11.18 (br s, 1H, NH^+). 2,4-Dimethylpyridinium (lutidine) perchlorate (recrystallized from n-amyl alcohol): ^{1}H NMR (DMSO-d6) δ 2.55 (s, 3H, 4-CH_3 to NH^+), 2.66 (s, 3H, 2-CH_3 to NH^+), 7.72 (AB, J=6.0 Hz, 1H, 5-H to NH^+), 7.78 (s, 1H, 3-H to NH^+), 8.62 (AB, J=6.0 Hz, 1H, 6-H to NH^+), 11.95 (br s, 1H, NH^+). 2,4,6-Trimethylpyridinium (γ-collidine) perchlorate (recrystallized from ethanol-ether mixed solvent): ^{1}H NMR (DMSO-d6) δ 2.48 (s, 3H, 4-CH_3 to NH+), 2.61 (s, 6H, 2 and 6-CH_3 to NH^+), 7.53 (s, 2H, 3 and 5-H to NH^+), 11.50 (s, 1H, NH^+). Morpholinium. perchlorate (recrystallized from ethanol-ether mixed solvent): ^{1}H NMR (DMSO-d6) δ 3.08 (t, 4H, 3 and 5-CH_2 to O), 3.75 (t, 4H, 2 and 6-CH_2 to O), 8.62 (br s, 2H, NH_2^+).

Measurement of pK_a values for several amines in acetonitrile

The pK_a of several amines were evaluated by the method of Blackwell et al. (3) using indicators, the pK of which in acetonitrile are already well known (5, 6). Indicators used for the measurement are shown in Table 1. The calculated pK_a values of several amines are summarized in Table 2 (7).

Table 1. pK_{HI} and Spectrophotometric Characteristics of Indicators in CH_3CN

Indicator	λ / nm$^{a)}$	ε x 10^{-4}	pK_{HI} $^{b)}$
Methyl red	560	3.25	10.2
Picric acid	440	1.50	11.0
Phenol red	390	2.28	13.7
Neutral red	532	3.90	15.6
2,6-Dinitrophenol	463	1.85	16.45

a) Wavelengths in measurement. b) Ref. 5.

The reaction procedure

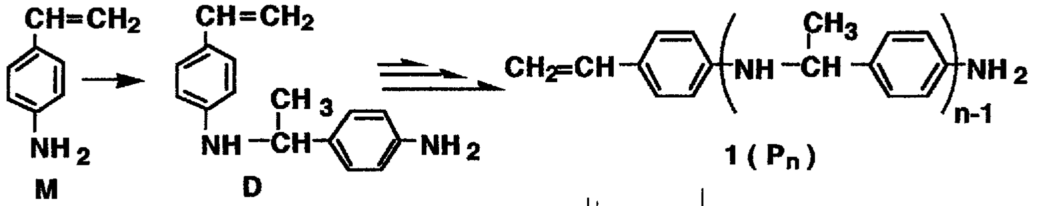
The reaction was carried out under dry nitrogen in a glass tube equipped with a three-way stopcock in acetonitrile at 25 °C. The reaction was initiated by adding an initiator to the monomer solution. The conversion was measured by liquid chromatography (LC), using a p-nitroacetophenone as a standard (Shimadzu LC-10AS; Asahipack ODP-50, 4.6 mm i.d. x 150 mm). The molecular weight of the product was evaluated as a number-average molecular weight from the GPC analysis (Shim-pack HSG-20H; 7.9 mm i.d. x 300 mm) and VPO measurement (Hitachi Perkin-Elmer 115 molecular weight apparatus). NMR spectra were measured using Varian Gemini (300 MHz).

Results

The features of the reaction of PAS with aminium perchlorates in acetonitrile

It was found that PAS could be easily oligomerized by a variety of aminium perchlorates. In order to clarify the behavior of the reaction, it was followed by measuring the NMR in CD_3CN. The spectral changes were similar for all catalysts used and were comparable to those observed for TFA in CCl_4 in the preceding paper (1). Figure 1 shows the NMR spectra of the solution in the initial stages of the reaction (catalyst: anilinium perchlorate (ANP)). The two characteristic peaks at 1.4 and 4.3 ppm were assigned to the methyl and methine protons respectively due to the formation of the unit, -(CH$_3$)CH-NH-, as confirmed from their chemical shifts and peak ratio (3 : 1) as explained in the preceding paper (1). It was found that the two sharp peaks at 1.4 ppm (doublet) and 4.35 ppm (quartet) in Figure 1A respectively are in good agreement with the methyl and methine protons of the p-aminostyrene dimer, N-(1-(4-aminophenyl)ethyl)-4-vinylaniline, **D** (1). Therefore, dimer **D** is also formed in acetonitrile in a similar manner to CCl$_4$ (1). Oligomer **1** is believed to be produced from the fact that the intensities of these two characteristic peaks are enhanced while their peak ratio remaines approximately 3:1 throughout the reaction (Fig. 1B and 1C). At the same time, the signals ascribable to the vinylic protons (-C=CH$_2$) of **D** and **1** appeared at positions slightly higher upfield, about 0.07 ppm, than those of the monomer. These were initially observed to increase but later decreased in the latter half of the reaction. Figure 2 shows the GPC curves for the solution in the initial stages of the reaction. The molecular weight of the product appears rather low suggesting the main portion is either a dimer or a trimer. These two portions were later separated by preparative GPC and were identified to be dimer **D** and trimer **P$_3$** from the structural analyses in the same manner as reported in the preceding paper (1). The dimer peak is observed to increase first but then decreases via a maximum. The molecular weight of the product was found to be about pentamer at the end of the reaction from GPC analysis and VPO measurements.

From the above results, we can say that the dimerization step is the main reaction resulting in up to 50 % conversion and that the reaction proceeds stepwisely even in polar solvents such as acetonitrile, in the same manner observed in CCl$_4$ (1) as follows:



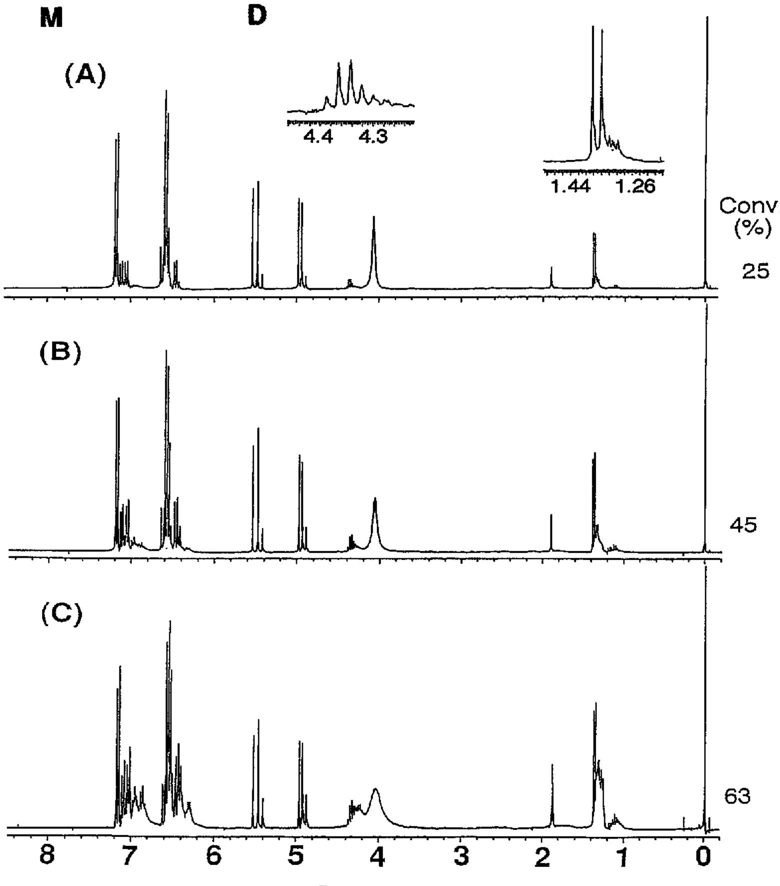


Fig. 1. ^{1}H NMR spectra for the reaction of PAS with ANP in CD$_3$CN at 25 °C ([PAS] = 1.0 M, [ANP] = 0.01M) at the conversion of (A) 25, (B) 45, and (C) 63 %.

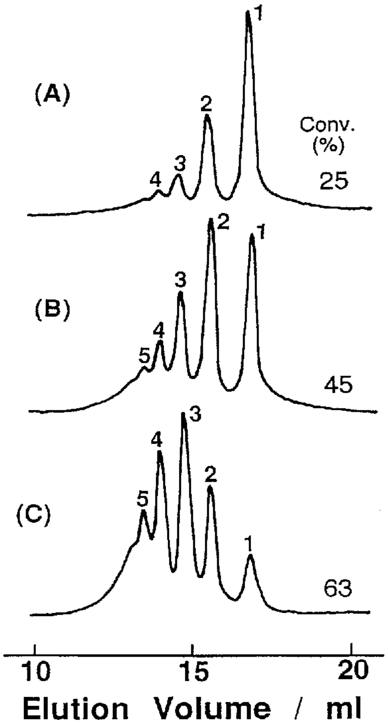


Fig. 2. The GPC curve for the reaction solution of PAS with ANP in CD$_3$CN at 25 °C ([PAS] =1.0 M, [ANP] = 0.01 M) at the conversion of (A) 25, (B) 45, and (C) 63 %. The numbers indicate the degree of polymerization.

The result of none of solvent effect on the molecular weight and structure seems to be strange because it is well known that generally the molecular weight becomes larger in the more polar solvent in the cationic polymerization. These results suggest that this reaction is remarkably different from the conventional chain reaction mechanism.

The reaction of PAS with several aminium perchlorates

The amount of monomer consumption was monitored by LC for the reaction where various aminium perchlorates were used as catalysts (see Experimental part). Time-conversion curves for these experiments are shown in Figure 3. The initial rate decreased in the order of p-nitroaniline ~ o-nitroaniline ~ p-chloroaniline ~ aniline > pyridine > 4-methylpyridine > 2,4-dimethylpyridine > 2,4,6-trimethylpyridine > morpholine among the catalytic amines used. This order is in reverse to the strengthening basicity of the amine. Tetrabutylammonium perchlorate has no available labile protons and as such gave no product even after prolonged reaction times. The apparent rate constants k_{obs} are summarized in Table 2. It can be seen that the k_{obs} increases with decreasing pK_a of the catalytic amine and becomes almost constant for catalysts with pK_a values smaller than that of PAS. In other words, k_{obs} no longer increases even when the strength of the conjugate acid of the amine becomes stronger than that of PAS. The relationship between k_{obs} and the pK_a of the catalytic amines is shown in Figure 4.

The analysis of equilibrium equations

The equilibrium equations were analyzed in order to evaluate the concentrations of various ionic species existing in the solution at the start point of the reaction. Knowing the pK_a values of the conjugate acids of PAS and the amines, $[H^+]_0$, $[BH^+]_0$ and $[MH^+]_0$ can be calculated by treating the equilibrium equations numerically. For our experimental system, the hydrogen ion concentration in the solution at the start point will be calculated as follows :

In our reaction system, there exists two types of base, a catalytic amine (**B**), added as the perchlorate, and the PAS monomer (**M**). The dissociation reactions of their conjugate acids BH^+ and MH^+ are

$$BH^+ \rightleftharpoons B + H^+ \qquad (1)$$

$$MH^+ \rightleftharpoons M + H^+ \qquad (2)$$

The equilibrium constants K_1 and K_2 corresponding to equations 1 and 2 are expressed by equations 3 and 4, respectively.

$$K_1 = \frac{[B]\,[H^+]}{[BH^+]} \qquad (3) \qquad\qquad K_2 = \frac{[M]\,[H^+]}{[MH^+]} \qquad (4)$$

From the initial concentration of the aminium perchlorate C_S and monomer C_M, the following conservations are applied.

$$C_S = [B] + [BH^+] \qquad (5)$$

$$C_M = [M] + [MH^+] \qquad (6)$$

In addition, electroneutrality rule yields

$$C_S = [ClO_4^-] = [BH^+] + [MH^+] + [H^+] \qquad (7)$$

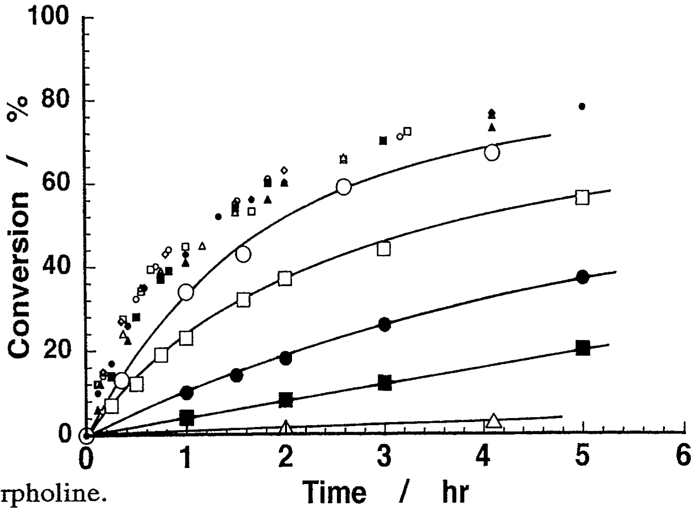


Fig. 3. The oligomerization of PAS with a variety of aminium perchlorates in CH_3CN at 25 ℃ ([PAS] = 1.0 M, [Perchlorate] = 0.01 M). Amine: (○): p-Nitroaniline, (◇): o-Nitroaniline, (□): p-Chloroaniline, (△): p-Aminostyrene, (●): Aniline, (■):N-Methylaniline, (▲): N,N-Dimethylaniline, (○): Pyridine, (□): 3-Methylpyridine (β-picoline), (●): 2,4-Dimethylpyridine (lutidine) , (■): 2,4,6-Trimethylpyridine (γ-collidine), (△): Morpholine.

Substituting equation 5 into equation 3 and combining equations 4 and 6 yields

$$[BH^+] = \frac{C_S\,[H^+]}{(K_1 + [H^+])} \qquad (8) \qquad\qquad [MH^+] = \frac{C_M[H^+]}{(K_2 + [H^+])} \qquad (9)$$

Substituting equations 8 and 9 into equation 7 and rearranging for $[H^+]$, we get equation 10.

$$[H^+]^3 + (K_1+K_2+C_M)[H^+]^2 + K_1(K_2+C_M-C_S)[H^+] - C_SK_1K_2 = 0 \qquad (10)$$

$C_M >> K_1$, K_2 and $C_M >> C_S$ from experimental conditions ; hence, by neglecting the highest-order term, we obtain upon simplification

$$C_M(H^+)^2 + K_1C_M(H^+) - C_SK_1K_2 = 0 \qquad (11)$$

Solving for $[H^+]$, we have

$$[H^+] = \frac{-C_MK_1 \pm \sqrt{C_M^2K_1^2 + 4C_SC_MK_1K_2}}{2C_M} \qquad (12)$$

simplifying, equation 13 results.

$$[H^+] = \frac{K_1}{2}\left\{\sqrt{1 + \frac{4C_SK_2}{C_MK_1}} - 1\right\} \qquad (13)$$

Knowing the values of K_1 and K_2, the hydrogen ion concentration can be calculated from equation 13 using the analytical concentrations of C_S and C_M. If $K_1 \geq K_2$, we obtain equation 14 as a first approximation by applying equation 13 a binominal theorem.

$$[H^+] = K_2\frac{C_S}{C_M} = 10^{-2}K_2 \qquad (14)$$

This implies that if the acidity of the conjugate acid of the catalytic amine becomes stronger than that of PAS, $pK_1 \leq pK_2$, the hydrogen ion concentration of the solution becomes constant 10^{-2}x K_2 M. In other words, the concentration of H^+ is controlled only by the equilibrium equation 2 independent of the acidity of the catalytic amine, because almost all of the released protons from BH^+ are captured by the monomeric amine due to its stronger basicity. The values of $[H^+]_0$ of the start point of the reaction were calculated from either equations 13 or 14 using the amine pK_a values and substituting 1.0 and 0.01 for C_M and C_S respectively. These results are summarized in Table 2 together with the $[BH^+]_0$ and $[MH^+]_0$ values calculated from equations 8 and 9.

From Table 2, it can be seen that $[H^+]_0$ or $[MH^+]_0$ also increases with decreasing amine pK_a and becomes constant at the region where $pK_1 \leq pK_2$. This behavior is remarkably similar to the relationship between k_{obs} and the pK_a of the catalytic amines. This suggests that a good correlation might exist between the k_{obs} and $[H^+]_0$ or $[MH^+]_0$ in the system. Their relationship is depicted in Figures 5 and 6. Linear relationships were observed between the log k_{obs} and log $[H^+]_0$ or log $[MH^+]_0$. We can say that the rate is rather better correlated with the $[H^+]_0$ or $[MH^+]_0$ rather than with the pK_a values for the catalytic amines. The linear relationship between log k_{obs} and log $[H^+]_0$ is quite interesting in terms of the related literature. For acid-catalyzed hydration (9) and acid addition (10) to olefins, as shown later, the linear relationship between the rate constant and acidity function (H_0) have been generally constructed. After all, the invariance of the rate at $pK_1 \leq pK_2$ might well be explained by the maximum constant concentration of $[MH^+]_0$ (or $[H^+]_0$) attained, no matter how stronger the acid strength of the catalytic amine becomes with regards to that of PAS.

Table 2. The apparent rate constant and the hydrogen ion concentration at the initial stage

Amine	pKa a)	$[H^+]_0x10^{13}$ b) $mol \bullet l^{-1}$	$[MH^+]_0x10^2$ c) $mol \bullet l^{-1}$	$[BH^+]_0x10^2$ d) $mol \bullet l^{-1}$	$k_{obs}x10^4$ sec^{-1}
p-Nitroaniline	3.6	3.98	1.0	$1.6x10^{-9}$	2.70
o-Nitroaniline	4.9 e)	3.98	1.0	$3.2x10^{-8}$	2.72
p-Chloroaniline	9.6	3.98	1.0	0.001	2.65
p-Aminostyrene	10.4	3.98	1.0	—	2.57
Aniline	10.6	3.98	0.98	0.02	2.31
N-Methylanilene	11.0	3.85	0.96	0.04	2.17
N,N-Dimethylaniline	11.3	3.71	0.92	0.08	1.93
Pyridine	12.3	2.61	0.66	0.34	1.39
3-Methylpyridine	13.1	1.56	0.39	0.61	0.84
2,4-DimethylPyridine	14.2	0.47	0.15	0.85	0.33
2,4,6-Trimethylpyridine	15.1	0.17	0.04	0.96	0.13
Morpholine	16.1	0.056	0.01	0.99	0.03

a) pKa was evaluated by indicator method (7). b) $[H^+]_0$ was calculated from eq. 13 or 14.
c) $[MH^+]_0$ was calculated from eq. 9. d) $[BH^+]_0$ was calculated from eq. 8. e) From Ref. 8.

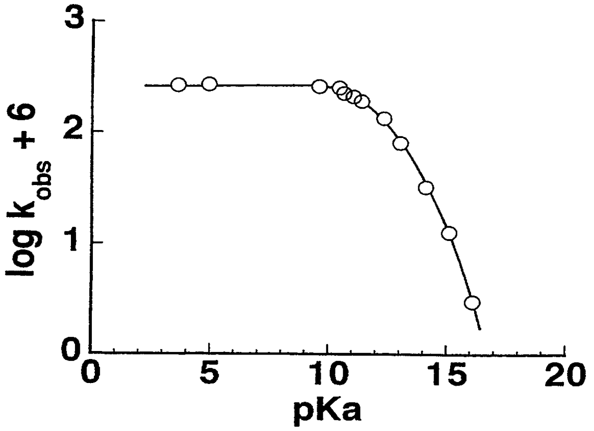


Fig. 4. The relationship between log kobs and pKa of catalitic amine.

Discussion

As observed in the results section (Figs. 1 and 2), it is clear that dimerization occurs in the initial stages of the reaction. It is what is called "hydroamination reaction" that an amine molecule adds to the double bond of an olefin. The hydroamination of olefins is caused by several types of catalyst such as hydrogen halides (11), aluminium phenoxide (12), and rhodium complexes (13). Both "oxidative amination" and "anti-Markovnikov hydroamination" are also encountered simultaneously in the case of rhodium complex catalysts (13).

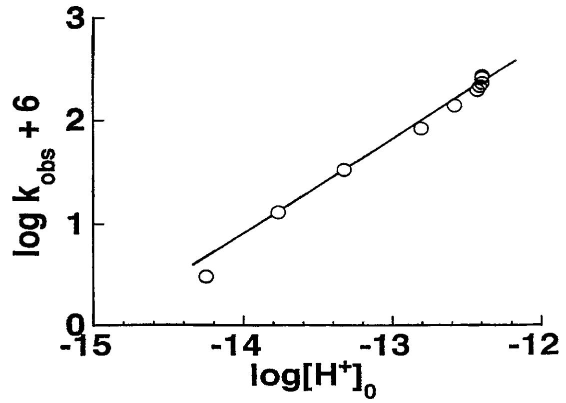


Fig. 5. The relationship between log kobs and log $[H^+]_0$.

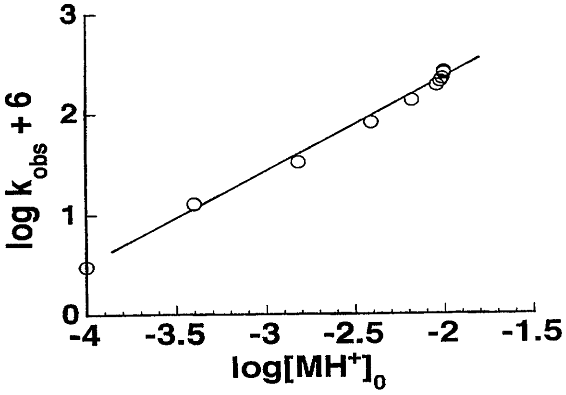
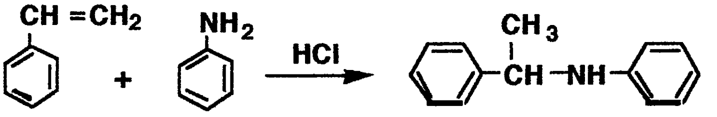


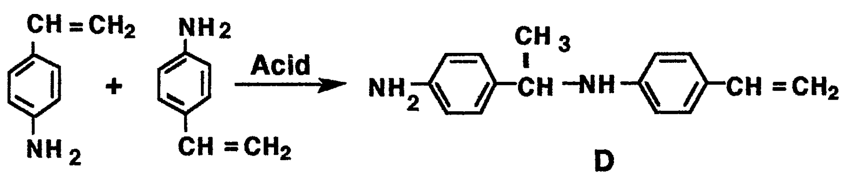
Fig. 6. The relationship between log kobs and log $[MH^+]_0$.

Hart et al. (11a) and Hickinbottom et al. (11b) found that the N-alkylated aniline (α-phenethylamine) was produced by the reaction of styrene with aniline (catalyst: anilinium chloride), the ring-alkylated aniline being produced simultaneously. The hydroamination step



(15)

supposedly occurs in the reaction between a styrene and an aniline derivative. From the above explanation, our results for the dimerization (hydroamination) step seems not so strange. For the



(16)

addition reaction to an alkene other than hydroamination, the acid-catalyzed hydration (9) and acid addition (10) have been quite numerously examined so far. It is now clear that these reactions proceed cationically; a slow protonation (rate-determining process) and subsequent fast nucleophilic addition to the resultant carbocation. Furthermore, an important and interesting point worth mentioning is that a linear relationship between the rate constant (log k) and the acidity function (H_0) has been observed for many reactions (9, 10). Schubert et al. studied the acid-catalyzed hydration of p-aminostyrene in detail (9d). They observed a linear relationship between the rate constant and H_0, which was derived from the rate-determining protonation of the double bond and subsequent nucleophilic addition of an H_2O molecule to the resultant styryl cation. They also found that the rate was dependent on the concentration of MH^+, which increased with increasing acidity in the system. We also observed similar relationships, as shown in Figures 5 and 6. These facts suggest that our hydroamination reaction may proceed in a similar manner to a hydration or an acid addition to an alkene.

In our case, the following three reactions may be conceivable as the protonation process.

Among them, equation 17 might be neglected, because the concentration of [H^+] is extremely low, $4x10^{-13}$ - $5.6x10^{-15}$ M in the initial stage (Table 2). The participation of equation 18 is supposed to be small for the following reasons; In the case of the strong acidic catalyst, the concentration of BH^+ is remarkably low; for instance, $3.2x10^{-10}$ and $1.6x10^{-11}$M for o- and p-nitroaniline, respectively (Table 2). In the case of weak acidic catalysts, $pK_1 \geq pK_2$, the reactivity of BH^+ will become smaller with increasing pK_1 due to the increasing basicity of amine **B**. Equation 19 is therefore the most plausible representation, especially when a fairly strong acid is used as the catalyst.

$$M + H^+ \longrightarrow M^* \qquad (17)$$

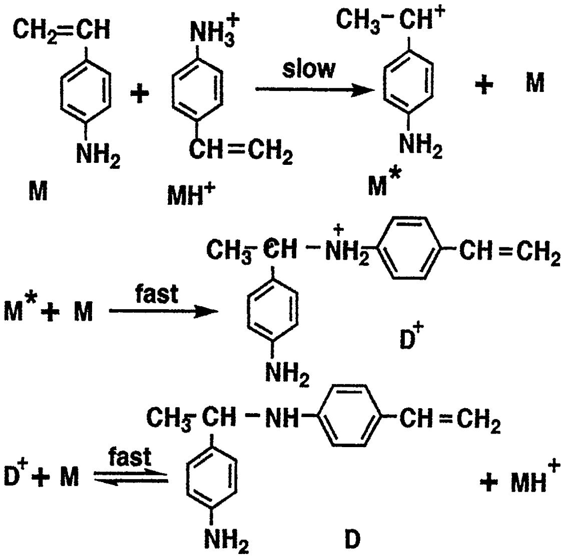
$$M + BH^+ \longrightarrow M^* + B \qquad (18)$$

$$M + MH^+ \longrightarrow M^* + M \qquad (19)$$

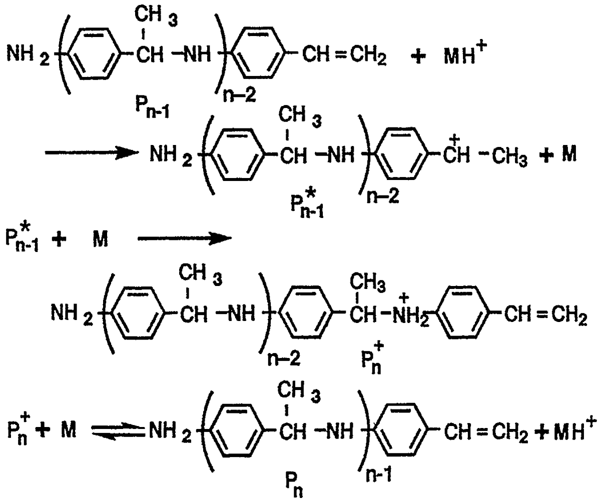
On the basis of these facts, we propose the following scheme (Scheme 1) for the dimerization of PAS in order to explain our experimental results well. These reactions contain the slow protonation step followed by two subsequent fast reactions; the first is the nucleophilic addition of monomeric amine to the resultant styryl cation **M***, and the second is the proton release from the formed ammonium ion **D**$^+$.

For the cationic polymerization of styrene and styrene derivatives, many catalysts have been developed to date (14 - 16). However, aminium perchlorates have never previously been used as initiators because of their low catalytic activity. The ease of reaction of PAS with aminium perchlorates is probably due to the high reactivity of the PAS monomer elevated by the inductive and mesomeric effects through the electron-donating amino group; the former enhances the electrophilicity of the double bond while the latter promotes the formation of the styryl cation. The resultant p-aminostyryl cation (**M***) is stabilized on contact with the monomeric amino group, the combination of which gives rise to dimer **D**$^+$. The stabilization of the carbocation weakens the interaction between the cation and the counteranion, and suppresses the formation of a linear unsaturated product (15). The neutral dimer **D** is produced by the proton dissociation from **D**$^+$. The MH^+ (or H^+) is exhausted by the initiation process and is later regenerated by the proton release from the ammonium ion, which further initiates the reaction. The hydroamination dimer is produced exclusively in this way (Scheme 1). The resultant dimer **D** and oligomer **1** have still two reactive groups (-CH=CH_2 and -NH_2) at both ends within their respective molecules. So the stepwise reaction might progressively proceed via quite the same three successive reactions as proposed for the dimerization step (Scheme 2).

Scheme 1 : Dimerization



Scheme 2 : Oligomerization



Conclusion

The features of this reaction are considered as follows : When a catalytic amount of acid is added to the PAS solution, MH^+ is produced, the concentration of which increases with increasing acid strength of catalyst used and reaches a constant at $pK_1 \leq pK_2$. The initiation (protonation) reaction is caused by the electrophilic attack of MH^+ to the double bond of the PAS monomer. The resultant styryl cation is stabilized on contact with the monomeric amino group, combining to form dimer **D**$^+$. The neutral dimer **D** is then produced following proton dissociation from **D**$^+$ (Scheme 1). The resultant dimer **D** and oligomer **1** have still two reactive groups (-CH=CH$_2$ and -NH$_2$) at both ends of their respective molecules. The stepwise reaction might therefore progressively proceed via quite the similar three successive reactions to the dimerization (Scheme 2).

Conclusively, the most striking event in this reaction is that the formed p-aminostyryl cation (**M***) or oligostyryl cation (**P**$_n^*$) reacts more favorably with an amino group than a double bond, and is stabilized as an ammonium ion (**D**$^+$ or **P**$_n^+$). This is reasonable since it is well known that amines are useful inhibitors for such cationic polymerization reactions (17) and it is generally said that the carbocation is more reactive to n-nucleophiles rather than π-nucleophiles (18). This is the reason why the reaction proceeds stepwisely to give isomer **D** and **1** (**P**$_n$) exclusively, a remarkably different mechanism from the conventional chain polymerization reaction (14 - 16).

An overall kinetic study is needed in order to clarify a more detailed mechanism, which we couldn't treat in this paper. This reaction, however, is very interesting and important among related studies such as hydration, addition of acid, hydroamination and cationic polymerization etc. Further examinations are desired to establish more detailed kinetics, the production of higher molecular weight isomers, its application as a "reactive oligomer" and so on.

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