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The cationic oligomerization of *p*-aminostyrene
1. Trifluoroacetic acid-catalyzed polyaddition

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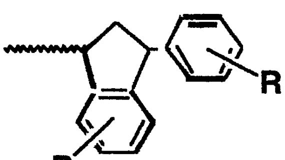
Summary

It was found that p-aminostyrene (PAS) was easily oligomerized by CF_3COOH (TFA) in CCl_4 to give a low molecular weight oligomer **4** including phenylene, ethylidene and secondary amine groups in the backbone, i.e., the isomer of poly-p-aminostyrene **5**. The NMR and IR spectra of the product are quite different from those of polymer **5** produced by 2,2'-azobisisobutyronitrile (AIBN) in toluene. The dimer **D** and trimer **T** were separated from the reaction solution through the preparative GPC. The reaction seems to proceed stepwisely to give **D** in the initial stage and finally the near pentameric oligomer **4** at the end of the reaction.

Introduction

For the cationic oligomerization of styrene and styrene derivatives with acid catalysts, there are two well known transfer reactions; one is intramolecular cyclization leading to the formation of an oligomer with a cyclic end group **1** and the other is β-proton elimination which leads to give an isomer with a terminal double bond **2**. Higashimura and Sawamoto et al. (1) have determined that the molecular weight and the structure of the product can be controlled by varying the reaction conditions such as the nature of the catalyst, solvent or the temperature etc. For instance, metal halides such as BF_3OEt_2, $SnCl_4$ and $EtAlCl_2$ are apt to give the higher oligomer or the indanic terminal **1**, while oxo acids such as CF_3SO_3H, CH_3SO_3H, $CH_3C_6H_4SO_3H$ and acetyl perchlorate ($AcClO_4$) yield either the lower oligomer **2** or the linear unsaturated dimer (1,3-diphenyl-1-butene) selectively in a nonpolar solvent at high temperature. To the contrary, TFA, one of the oxo acid, gives the oligoester **3** with a trifluoroacetate end group in a nonpolar solvent, though it needs the use of fairly large amount of acid (2). On the other hand, we have recently found (3) that PAS is easily oligomerized by a variety of Brönsted acids to give the isomeric oligomer **4** exclusively, the features of which are extremely different from the results observed above for the cationic oligomerization of styrene and styrene derivatives by an acid.



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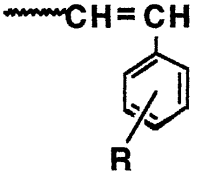

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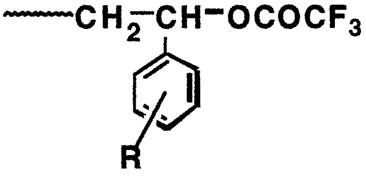

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Here we will describe these results in more detail. The oligomerization of PAS was conducted using TFA in CCl_4 at 25 °C.

Experimental

General Procedure

TFA and CCl_4 were purified by distillation (the latter; over calcium hydride) at least twice just before use. Molecular weight distribution (MWD) was measured by gel-permeation chromatography (GPC) in THF on a Shimadzu LC-10AS chromatograph with a refractive index detector. When necessary, some fractions were separated from the solution using the same apparatus. The analytic (7.9 mm i.d. x 300 mm) and preparative columns (20 mm i.d. x 300 mm) were packed with HSG-20H polystyrene gel. The molecular weight (MW) of the product was evaluated as a number-average molecular weight from the GPC analysis and VPO measurement (Hitachi Perkin-Elmer 115). ^{1}H NMR spectra were measured using Varian Gemini (300 MHz). IR spectra were measured using a Jasco FTIR-5300 spectrophotometer. Conversion was determined from the residual monomer concentration measured by LC (Shimadzu LC-10AS, Asahipak ODP-50) using p-nitroacetophenone as a standard (elution solvent: acetonitrile).

*PAS monomer **M***

PAS monomer **M** was prepared by the procedure of Kamogawa (4). Colorless liquid, bp 80 - 82 °C/2.5 mmHg (lit. (5) 80 °C/2.5 mmHg). ^{1}H NMR ($CDCl_3$) δ 3.64 (s, 2H, -NH_2), 5.03 (dd, J=1.0 Hz, J'=10.5 Hz, 1H, Ph-CH=C$\underline{H}$, syn), 5.53 (dd, J=1.0 Hz, J'=17.5 Hz, 1H, Ph-CH=C$\underline{H}$, anti), 6.59 (AB, J_{AB}=8.5 Hz, 2 aromaticH, o-H to -NH_2), 6.60 (dd, J=10.5 Hz, J'=17.5 Hz, 1H, Ph-C$\underline{H}$=CH_2), 7.21 (AB, J_{AB}=8.5 Hz, 2 aromaticH, m-H to -NH_2).

*Separation of dimer **D** and trimer **T** from reaction solution*

The dimer and trimer peak fractions (Fig. 1) were separated from the reaction solution in the initial stage by preparative GPC. Viscous liquids were obtained from both fractions by evaporating the solvent and drying in vacuo, respectively. From the structural analyses, they were identified to be a PAS dimer, N-(1-(4-Aminophenyl)ethyl)-4-vinylaniline **D** and trimer **T** as follows; **D**: ^{1}H NMR ($CDCl_3$): δ 1.46 (d, J=6.6 Hz, 3H, -CH_3), 3.58 (br s, 3H, -NH_2 and -NH), 4.40 (q, J=6.6 Hz, 1H, -CH), 4.96 (dd, J=1.0 Hz, J'=10.5 Hz, 1H, Ph-CH=C$\underline{H}$, syn), 5.47 (dd, J=1.0 Hz, J'=17.7 Hz, 1H, Ph-CH=C$\underline{H}$, anti), 6.46 (AB, J_{AB}=8.7 Hz, 2 aromaticH, o-H to -NH), 6.62 (AB, J_{AB}=8.7 Hz, 2 aromaticH, o-H to -NH_2), 6.56 (dd, J=10.5 Hz, J'=17.7 Hz, 1H, Ph-C$\underline{H}$=CH_2), 7.12 (AB, J_{AB}=8.7 Hz, 2 aromaticH, m-H to -NH_2), 7.17 (AB, J_{AB}=8.7 Hz, 2 aromaticH, m-H to -NH), IR (NaCl): 3453, 3411, 3370, 3002, 2975, 2919, 2868, 1613, 1512, 1321, 1179, 828, 787, 762 cm^{-1}. Anal. Calcd. for $C_{16}H_{18}N_2$: C, 80.67; H, 7.56; N, 11.76. Found. C, 80.25; H, 7.68; N, 11.69. Mass: m/z 238. **T**: ^{1}H NMR ($CDCl_3$): δ 1.38 - 1.48 (m, J=6.9 Hz, 6H, -CH_3), 3.74 (br s, 4H, -NH_2 and -NH), 4.27 - 4.45 (m, J=6.9 Hz, 2H, -CH), 4.95 (dd, J=1.0 Hz, J'=10.8 Hz, 1H, Ph-CH=C$\underline{H}$, syn), 5.46 (dd, J=1.0 Hz, J'=17.7 Hz, 1H, Ph-CH=C$\underline{H}$, anti), 6.56 (dd, J=10.8 Hz, J'=17.7 Hz, 1H, Ph-C$\underline{H}$=CH_2), 6.44 - 7.18 (m, 12 aromaticH), IR (NaCl): 3407, 3002, 2967, 2924, 2866, 1613, 1518, 1318, 1179, 824, 787, 763 cm^{-1}. Anal. Calcd. for $C_{24}H_{27}N_3$: C, 80.67; H, 7.56; N, 11.76. Found. C, 79.82; H, 7.14; N, 11.13. Mass: m/z 357.

Reaction procedure

The reaction was carried out in CCl_4 at 25 °C under dry nitrogen in a glass tube equipped with a three-way stopcock. The reaction was initiated by adding TFA to a solution of the PAS monomer in CCl_4 ([PAS]=1.0 mol/L, [TFA]: 0.01mol/L). Aliquots of the reaction solution were diluted with $CDCl_3$ under dry nitrogen and were subjected to NMR, GPC, and LC analysis at the appropriate time intervals. At the end of the reaction, the solution was poured into a large amount of petroleum ether and the resultant solid product was further reprecipitated from an acetone-petroleum ether system. As a comparison, radical polymerization of PAS was also carried out. 5 g of PAS (0.042 mol) and 30 mg of AIBN (1.83 x 10^{-4} mol) were dissolved in 20 ml of toluene in a Pyrex glass ampoule. The contents of the ampoule were frozen under liquid nitrogen and subjected to a freezing and thawing operation and finally sealed under reduced pressure. The ampoule was kept in a shaking bath at 70 °C for 24 h. The solid product was dissolved in acetone and the polymer was precipitated by pouring the solution into a large amount of ethyl ether. The resultant solid was reprecipitated again from an acetone-ether system.

Results

The oligomerization of PAS with TFA in CCl_4

The reaction of PAS with TFA in CCl_4 was analyzed by GPC and ^1H NMR spectroscopy. In these experiments, a catalytic amount of TFA was added to PAS ($[M]_0$ =1.0 M, $[TFA]_0$ =0.01 M) and a series of GPC and NMR spectra were recorded during the reaction.

The GPC curves

Figure 1 shows the GPC curves of the reaction solution during the reaction. At first, the dimer peak increases gradually with decreasing monomer peak. The peaks of a trimer and higher oligomers then increase with decreasing monomer and dimer peak. The dimer peak seems to change via maximum. The molecular weight of the product is comparatively low; the trimer is the main product even at 85% conversion, and the near pentamer was produced at the end of the reaction. In the initial stage, dimerization occurs as the main reaction, the reaction then seems to proceed in a stepwise manner.

The NMR changes

Figure 2 shows the NMR spectra of the solutions during the reaction. In the initial stage of the reaction (Fig. 2A), three characteristic new signals appeared at 1.5 ppm as doublet, 4.3 ppm as quartet, and 5.0 and 5.5 ppm as two doublets. From their splitting patterns and chemical shifts and especially good agreement to absorptions of PAS dimer

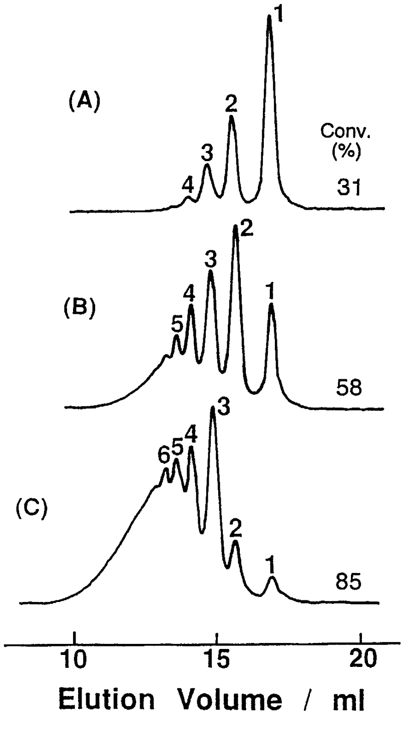


Figure 1. GPC curves of the reaction solution of PAS with TFA in CCl_4 at 25 °C ([PAS]: 1.0 M, [TFA]: 0.01 M). Conversion is (A) 31, (B) 58, and (C) 85 %. The numbers indicate the degree of polymerization.

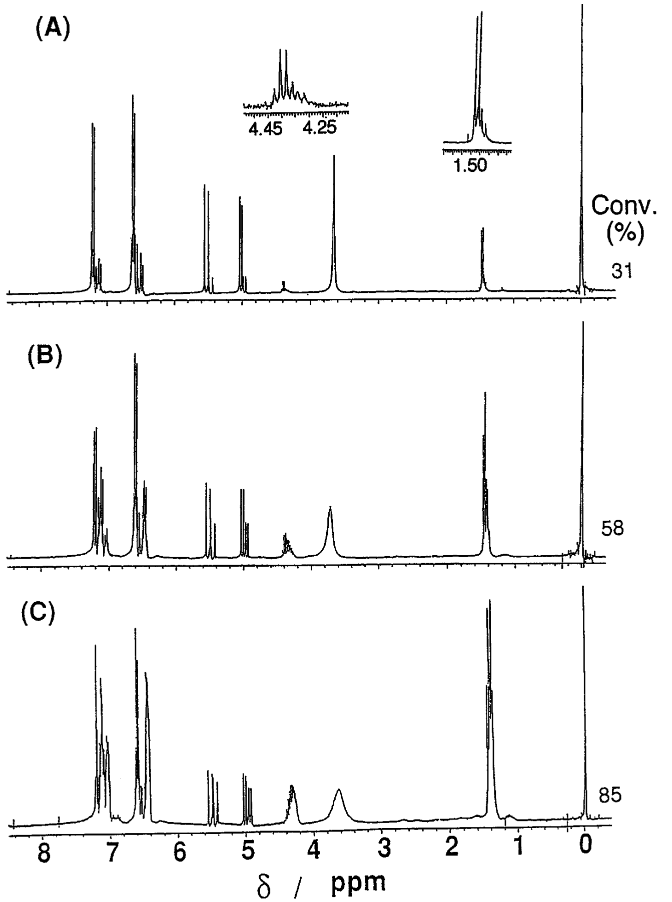
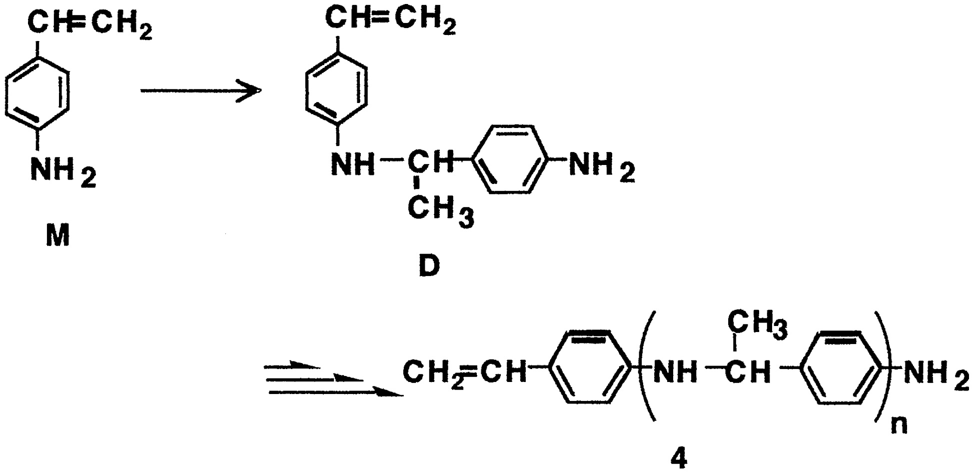


Figure 2. ^1H NMR spectra of the reaction solution of PAS with TFA in CCl_4 at 25 °C ([PAS]:1.0 M, [TFA]: 0.01 M). The solution was diluted one-fifth by $CDCl_3$ and subjected to measurement. Conversion is (A) 31, (B) 58, and (C) 85 %.

(vide infra), they were assigned to the methyl, methine and vinyl (=CH$_2$) protons of PAS dimer **D**, respectively. The vinyl protons (=CH$_2$) appear approximately 0.07 ppm more upfield than those of monomer. The methyl and methine signals gradually increased with conversion and became more complicated and broadened. These complicated signals might be due to the progressive formation of trimer **T** and higher oligomer **4**, because the methyl and methine proton of the trimer are located in a slightly upfield (about 0.02 ppm) than those of dimer as multiplet (see the next section) and both are overlapped (Fig. 2B and 2C). The vinyl (=CH$_2$) protons of **T** appear also about 0.07 ppm further upfield than those of the monomer and overlapped with those of the dimer **D**. The vinyl protons (=CH$_2$) of dimer and trimer increased with time and finally decreased via maximum. These changes synchronize quite well to those of dimer and trimer peak in GPC traces; newly appearance, gradually increase and decrease via maximum (Fig. 1).

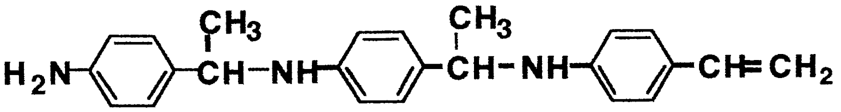
Conclusively, the dimer **D** is formed first, and then trimer **T** and oligomer **4** are produced progressively after. The reaction appears to proceed stepwisely, as shown below. The molecular weight of the product is not as high as expected. The main product is dimer at cnv. 58% and is trimer even at cnv. 85% (Fig. 1B and 1C). About pentamer was produced at the end of the reaction, which was evaluated from GPC and VPO methods.



It should also be noted that no characteristic signals assignable to the other dimer or the oligomer **1**, δ 3.3 (m, ArCH) (6), **2**, δ near 6.3 (m, -CH=CH-) (1b), and **3**, δ near 5.5 (m, -CHO-) (2a) could be detected during the reaction (Fig. 2). The integration ratio of the methyl to methine proton remained constant 3:1 throughout. These results indicate the selective formation of **4** with none of the oligomers having indanic, linear-unsaturated, or trifluoroacetate end groups.

*Separation of the dimer **D** and trimer **T** from the reaction solution*

D and **T** were separated from the initial reaction solution by preparative GPC. Their structures were determined by elemental analysis, NMR, IR, and mass spectroscopy etc. (see Experimental part). Figure 3 illustrates their ^{1}H NMR spectra along with that of the monomer. The phenyl protons of **D** show typical two kinds of AB patterns. The vinyl protons (=CH$_2$) of **D** and **T** are located at quite similar positions, though ca. 0.07 ppm

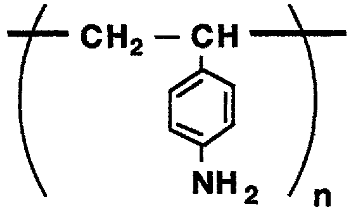


T

further upfield than those of the monomer **M**. In contrast, the methyl and methine protons of **T** appear slightly more upfield than those of **D**, about 0.02 ppm, which is the reason that both signals (methyl and methine) become more complicated and broadened in the latter half of the reaction (Fig. 2B and 2C).

The comparison of the structure between the product obtained by TFA and the polymer produced by AIBN

The NMR spectrum of the product obtained by TFA in CCl_4 was shown in Figure 4 compared with that of poly-p-aminostyrene produced by AIBN in toluene (MW: about 550 and 4000 from GPC analysis, respectively). Both are quite different from each other. The NMR spectrum of poly-p-aminostyrene (Fig. 4B) is quite similar to that of conventional polystyrene except for the amino group and is assigned to **5** from the following NMR spectral analysis:



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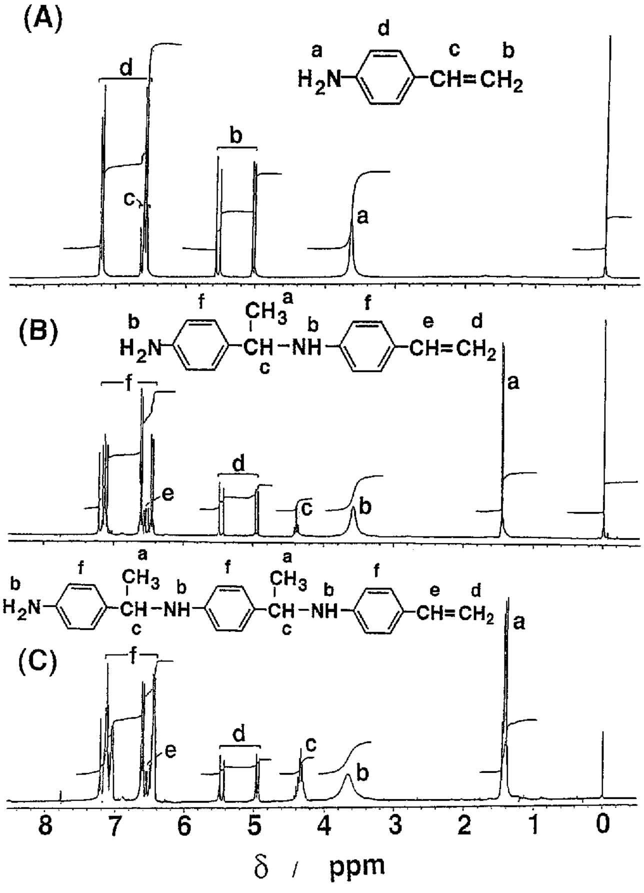


Figure 3. ^1H NMR spectra of products separated from the reaction solution by preparative GPC method. ^1H NMR spectrum of monomer was also depicted as a comparison (A) monomer, (B) dimer, and (C) trimer in $CDCl_3$.

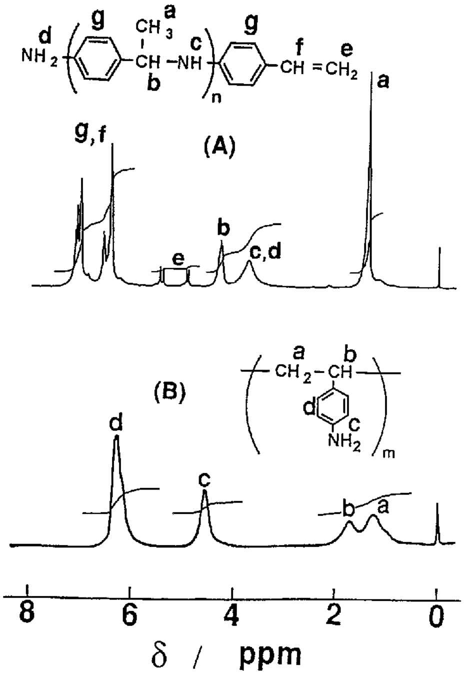


Figure 4. The comparison of ^1H NMR spectrum of the reaction products at the end of the reaction. (A) The oligomer obtained by TFA in CCl_4, which was reprecipitated by acetone-petroleum ether system (MW: 550) Solvent: $CDCl_3$. (B) The polymer produced by AIBN in toluene, reprecipitated by acetone-ether (MW: 4000).
Solvent: DMSO(d6).

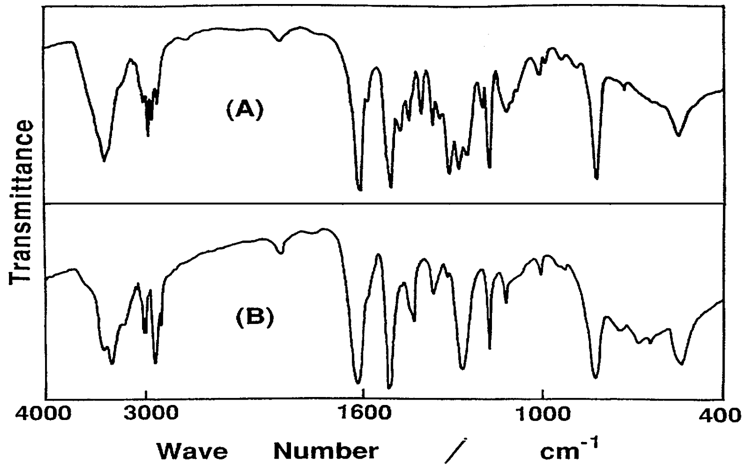


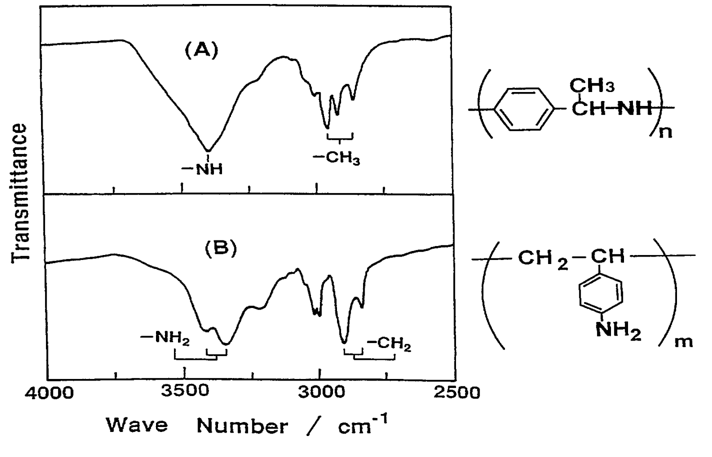
Figure 5. The comparison of IR spectrum (KBr) of the reaction product at the end of the reaction. (A) The oligomer obtained by TFA in CCl4. (B) The polymer produced by AIBN in toluene.

^{1}H NMR (DMSO-d6): δ 0.80-1.53 (br 2H, -CH_2), 1.53-2.30 (br 1H, -CH), 4.40-4.90 (br 2H, -NH_2), 6.00-6.60 (br 4H, Ph(H)). To the contrary, Figure 4A shows two rather broad bands at 1.4 ppm and 4.3 ppm, the integration ratio of which is 3:1. These two chemical shifts are quite similar to the methyl and methine proton of dimer **D** or trimer **T**. Furthermore the vinyl proton (=CH_2) of the end group is still observed between δ 4.85 and 5.50. From these results, therefore the production of the oligomer **4** was confirmed. The integration of the vinyl proton (=CH_2) indicates a DP of about 5, which is quite consistent with the results of the GPC and VPO methods. The structure **4** includes a unit of phenylene, ethylidene and secondary amine group in the backbone and also is an isomer of **5**. This unique structure of **4** was further confirmed from the comparison of their IR spectra (Fig. 5 and 6). The differences between them are particularly noteworthy for the amine stretching (3300-3500 cm $^{-1}$) and hydrocarbon stretching (2800-3000 cm^{-1}) regions (Fig. 6). The sharp singlet band at 3407 cm^{-1} (-NH) and strong doublet bands at 2969 and 2868 cm^{-1} (-CH_3) observed in Figure 6A are quite different from the doublet bands at 3356 and 3430 cm^{-1} (-NH_2) and doublet bands at 2920 and 2850 (-CH_2) in Figure 6B.

Discussion

For the cationic oligomerization of styrene and styrene derivatives, it has been determined that the molecular weight and the structure of the product can be controlled by the proper choice of catalysts in a nonpolar solvent at high temperature. Higashimura et al. summarized and explained these phenomena in terms of the interaction between the carbocation and the counteranion derived from the catalyst or the stability of the resultant carbocation (1); i.e., Lewis acids favorably yield the higher oligomer or the indanic terminal **1** owing to its weak interaction (or the stabilization of carbocation), while oxo

Figure 6. The magnification of the region of stretching vibration of amine and hydrocarbon in Fig. 5.



acids such as CF_3SO_3H and $AcClO_4$ preferably give the lower oligomer or the linear unsaturated end group **2** due to their strong interaction (or the unstabilization of the carbocation). For the oligomerization of styrene with oxo acids, the selective formation of the unsaturated linear dimer (1,3-diphenyl-1-butene) or the lower oligomer **2** was reported to be produced by proton elimination from the β-hydrogen of the propagating species, the end of which interacts strongly with the oxygen atoms of the counteranion (1b).

To the contrary, TFA reacts differently in the reaction of styrene compared to sulfonic acids and $AcClO_4$. TFA has generally been known to react with olefin to give an acid adduct (7). It was also found that 1-phenethyl trifluoroacetate and oligoester **3** were produced from the cationic oligomerization of styrene with TFA (2). Sawamoto et al. (2b) observed the formation of styryl and polystyryl ester **3** from the measurement of ^{19}F NMR spectra. Matyjaszewski also observed the formation of 1-phenethyl trifluoroacetate in the initial stage, which is then activated by another TFA molecule followed by the propagation reaction in the polymerization of styrene with TFA (8). However, a fairly large amount of TFA is required to cause the polymerization of styrene because its initiation ability is extremely low. We also found that the monoester and oligoester **3** were produced from the equimolar reaction between styrene (2a) or p-substituted styrenes (9) and TFA in CCl_4. The production of both the acid adduct and oligoester **3** might also be interpreted by the strong interaction between the carbocation and the counteranion. Tidwell et al. reported that the styrene and p-substituted styrenes reacted with TFA in CCl_4 to yield the acid adduct, which was caused by the slow protonation and subsequently fast nucleophilic addition of trifluoroacetate anion to the resultant styryl cation (7e). After all, in the case of TFA, an ester is supposed to be preferentially formed by the binding of a styryl or polystyryl cation with the trifluoroacetate anion, which prefers combining with carbocations rather than the β-proton of the propagating end because of its higher nucleophilicity compared to either the sulfonate or perchlorate anions.

In a series of studies, we attempted the oligomerization of PAS with TFA in CCl_4 expecting the formation of ester. However, it was found that PAS was easily oligomerized with a catalytic amount of TFA to yield an unexpected isomerization product **4** with none of the ester. The high reactivity of PAS might be interpreted by the two factors, 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 a styryl cation. For the cationic oligomerization of PAS with TFA, the existing large amounts of monomeric amino group may weaken the interaction between the resultant styryl cation and the counteranion (or stabilize the carbocation), which would suppress the formation of **2** and **3**, and finally combine with the carbocation covalently to give an amine adduct. This is a reasonable explanation since it is well known that an amine is used as an inhibitor for cationic polymerization (10). The produced dimer **D** and the oligomer **4** also have two reactive groups ($-CH=CH_2$ and $-NH_2$) at both ends of their respective molecules quite similar to the monomer. The reaction is therefore expected to further proceed through the protonation and the subsequent nucleophilic addition of monomeric amino group. This is the reason why such isomerization oligomers are produced exclusively by the reaction of PAS with TFA. The reaction appears to proceed stepwisely, which is very different from the conventional chain reaction polymerization.

This reaction is one of the so-called "hydrogen transfer polymerization reactions". An acrylamide (11), 4-vinylpyridine (12) and aliphatic branched α-olefins such as 3-methyl butene-1 (13), are well known as typical vinyl monomers which cause hydrogen transfer polymerization. Styrene derivatives such as β-methylstyrene (14), p-methylstyrene (15) and o-isopropylstyrene (16) have also been reported to cause hydrogen transfer polymerization. However, these claims were all later denied following a reexamination by Kennedy et al. (17-19). PAS might therefore be the first case of a monomer causing hydrogen transfer polymerization among styrene derivatives.

The oligomerization of PAS was attempted in several solvents using a variety of Brönsted acid catalysts (Solvent: CH_3CN, CH_2Cl_2, C_6H_6 etc.; Acid: $HClO_4$, HCl, HNO_3, CCl_3COOH, $CHCl_2COOH$, CH2ClCOOH etc.), and almost the same low molecular weight oligomer **4** was produced, irrespective of the nature of the catalyst and the solvent polarity. The effects of the reaction conditions for the cationic oligomerization of PAS will be described elsewhere in the near future. In the initiation process, acid-base equilibrium relationships are supposed to play an important role, because the monomer is a base and the catalyst is an acid. The anilinium ion of the monomer is formed first by adding TFA to the solution. In preliminary experiments, we found that the anilinium salt or similar amine analogues could easily oligomerize PAS, and that there was a good relationship between the initial rate and the pKa of the catalytic amine used. This suggests that the releasable proton is closely related to the initiation process. The details of the reaction mechanism will be described in the succeeding paper (20).

Conclusion

It was found that PAS could be easily polymerized by a catalytic amount of TFA in CCl_4 to give oligomer **4**, the structure of which includes a set of phenylene, ethylidene and secondary amine groups in the backbone, and is an isomer of polymer **5**. From the changes in GPC curve and NMR spectra, it can be seen that the reaction proceeds in a stepwise manner (dimerization being main reaction in the initial stage). The dimer **D** and trimer **T** were separated from the reaction solution. The near pentameric oligomer **4** was produced at the end of the reaction. The product presented here has two functional groups, a vinyl ($-CH=CH_2$) group and primary amino group. This species is therefore a very useful reactive, synthetic intermediate which gives valuable material and undergoes useful chemical modifications at its functional end groups.

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