ionic bands remains constant. However, beyond 30.0 mbar pressure, the molecular jet exhibits the deflected jet flow which distort the optical alignment into the spectrometer, resulting in decrease of the reproducibility of the experiments.

In summary, we have developed a graphite tube nozzle by which a metastable He atom was generated. The nitrogen molecules initially excited in Engelking type nozzle were further excited by collisional energy transfer of a metastable He atom. The excitation of nitrogen molecules to nitrogen molecular ions were monitored by observing the emission intensity of the bands in the spectra from the nitrogen jet. From the observation, it has been found that the excitation of the nitrogen molecules at the excited state is more effective for the generation of nitrogen molecular ions, suggesting that the effective energy transfer by molecular collision may be useful for the generation of the highly excited species.

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Polymerization of Anisole Derivatives Containing Allyl or Chloromethyl Group Through Aromatic Electrophilic Substitution Reaction

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4-Allylanisole was polymerized with AlCl₃ as a catalyst. The polymerization was carried out in nitroethane at various temperatures with changing the ratio of the initiator to the monomer concentration. The weight average molecular weights measured by gel permeation chromatography in chloroform with polystyrene standards were between 1,500 and 4,700. ^{1}H NMR spectroscopy showed that the polymerization proceeded through a stepwise aromatic electrophilic substitution reaction along with a minor chain-reaction, resulting in a branched polymer. 4-Chloromethylanisole was also polymerized with AlCl₃ in nitroethane through an aromatic electrophilic substitution reaction to give a high molecular weight polymer (Mw=88,000).

Introduction

A few aromatic compounds having electrophiles are polymerized through aromatic electrophilic substitution reactions.[1,2] The reactions are accelerated by presence of elec-

tron donating groups on the aromatic rings. In the polymerization of a phenol-formaldehyde under basic conditions, the benzene ring of the phenol is activated by an oxide group and reacts easily with formaldehyde.[3-5] Certain aromatic compounds with alkyl halide substituents are po-

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lymerized with Friedel-Craft catalysts.[6-11] For example, benzyl chloride is polymerized with strong Lewis acids, where a benzylic carbocation acts as an electrophile.

On the contrary, the carbocation formed from the vinyl group of styrene with a Lewis acid does not react with the aromatic ring electrons. Only the chain-reaction polymerization occurs at the vinyl group.[12] The polymerization of a styrene derivative having a 1-chloroethyl group at the meta position was also reported to proceed through a chain reaction in the presence of $SnCl_4$.[13] The carbocation resulted from the 1-chloroethyl group and the Lewis acid initiated the chain-reaction polymerization. No significant aromatic electrophilic substitution reaction was observed. Obviously, the reactivity of an aromatic ring toward a carbocation is greatly influenced by its substituent.

In this work, we studied the polymerization of the aromatic compounds with ring activating substituents and latent electrophiles. The anisole derivatives having an allyl group or a chloromethyl group were polymerized with $AlCl_3$. The polymerization of the latter proceeded through a stepwise aromatic electrophilic substitution reaction, while in the polymerization of the former, an aromatic electrophilic substitution reaction was accompanied with a chain reaction, resulting in a branched polymer. The polymerization pathways were investigated by structural analysis of the polymers.

Experimental Section

Materials and Instrumentation. All reagents were purchased from Aldrich. Chloroform and nitroethane were distilled over $CaCl_2$. The other reagents were used as received. The ^1H and ^{13}C NMR spectra were recorded on a Varian-Gemini 200 spectrometer. IR spectra were obtained with the use of a Nicolet Magna-IR 550 spectrometer. Gel permeation chromatography was carried out with a Waters 150C GPC with a M410 refractive index detector. Elemental analyses were performed by a Fisons 1108 elemental analyzer.

Polymerization of 4-Allylanisole. To a solution of 4-allylanisole (2 mL, 13 mmole) in nitroethane (10 mL) was added an appropriate amount of $AlCl_3$ (0.65-13 mmole) at room temperature. The reaction mixture was stirred at various temperatures (−40 °C-0 °C) under nitrogen. After concentration by evaporating the solvent, the polymer was isolated by precipitation in methanol and further purified by being reprecipitated in methanol from the chloroform polymer solution. The polymerization results are summarized in Table 1 and the ^1H NMR spectrum of the polymer in $CDCl_3$ is shown in Figure 1.

^{13}C NMR ($CDCl_3$): δ=157.8, 155.5, 134.8, 132.8, 130.0, 127.2, 113.9, 110.0, 55.2, 44.0, 42.8, 34.0, 21.8, 20.0. IR (KBr, cm^{-1}): 2966, 2941, 2868, 2841, 1617, 1518, 1505, 1472, 1249.

Polymerization of 4-Chloromethylanisole. To a solution of 4-chloromethylanisole (3 mL, 22.1 mmole) in nitroethane (10 mL) was added $AlCl_3$ (0.15 g, 1.1 mmole) at room temperature. The reaction mixture was stirred at the same temperature for 1 h under nitrogen. After concentration by evaporating the solvent, the polymer was isolated by precipitation in methanol and further purified by being reprecipitated in methanol from the chloroform polymer solution (yield 90%).

^1H NMR ($CDCl_3$): δ=6.50-7.20 (br, 3H, Ar-H), 3.76 (br, 3H, O-CH_3), 3.62 (br, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ= 155.4, 132.8, 130.9, 129.7, 127.2, 113.8, 110.2, 55.2, 35.0. IR (KBr, cm^{-1}): 3001, 2941, 2908, 2840, 1611, 1506, 1466, 1255.

Polymerization of Allylbenzene. To a solution of allylbenzene (2 mL, 15 mmole) in nitroethane (10 mL) was added $AlCl_3$ (0.2 g, 1.5 mmole) at room temperature. The reaction mixture was stirred at the same temperature for 24 h under nitrogen. After concentration by evaporating the solvent, the oily product was isolated by precipitation in methanol (yield 20%).

Results and Discussion

4-Allylanisole was polymerized with $AlCl_3$ as a catalyst. Lewis acids have been widely used for the cationic polymerization of the vinyl monomers.[12] It is not fully understood how $AlCl_3$ initiates the polymerization. One suggested mechanism is that aluminum trichloride molecules are self-ionized to yield $[AlCl_2]^+$ and $[AlCl_4]^-$.[14] The aluminum dichloride cation takes electrons from the vinyl group in the initiation step. The cocatalyst initiation by $AlCl_3$ and a trace of water in the polymerization system is also likely to occur.[15] Since the carbocation is a strong electrophile, an interesting question arises whether it can react with the aromatic ring electrons along the chain propagation, especially when the ring is activated. The aromatic electrophilic substitution reaction may compete with the chain propagation reaction, leading to branched polymers. The reactivity of the vinyl group and the aromatic ring toward the carbocation will depend on the nature of substituents on them. The polymerization of styrene monomers is known to follow the chain reaction mechanism to give linear polymers. Branching by aromatic electrophilic substitution has not been reported even in the cationic polymerization of 4-vinylanisole. This result is attributable to that the carbocation at the benzylic position is resonance-stabilized, which enhances the vinyl group reactivity.

Unlike in the case of the styrene monomers, the reaction of 4-allylanisol with $AlCl_3$ gives the secondary carbocation which is not resonance-stabilized. Three possible reaction pathways are described in Scheme 1. In reaction 1, the carbocation takes electrons from the vinyl group as in the usual chain propagation step of the cationic vinyl polymerization. Reaction 2 involves the aromatic electrophilic substitution. The carbocation reacts with the ring electrons to yield an arenium ion. In the following step, the proton is removed to complete the substitution. As a result, the carbocation is consumed and a new protonic acid, $H^+AlCl_4^-$ is formed, which will generate another carbocation. The third reaction is the rearrangement of the secondary carbocation to the more stable benzylic carbocation. In that case, an aromatic electrophilic substitution reaction is unlikely expected as observed in the polymerization of 4-vinylanisole. The chain propagation after the rearrangement of the carbocation will result in the linear polymer with a different repeating unit from that of the polymer obtained by reaction 1.

The polymerization was carried out in nitroethane at vari-
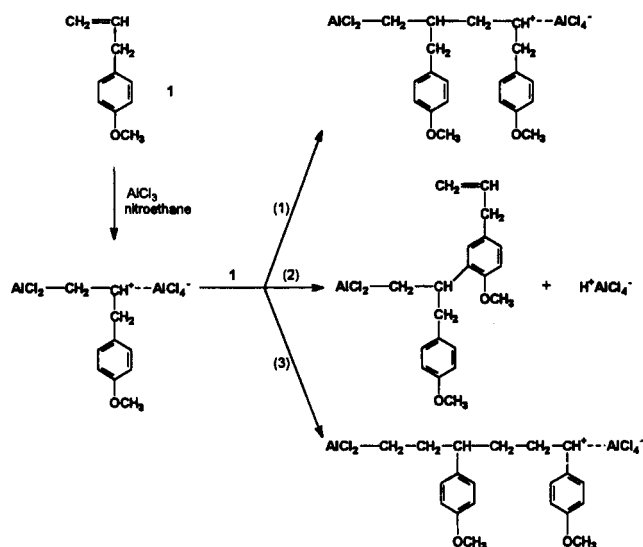
Scheme 1.

Figure 1. The ^1H NMR spectrum of the polymer obtained from monomer 1 (polymerization No. 6) in $CDCl_3$.
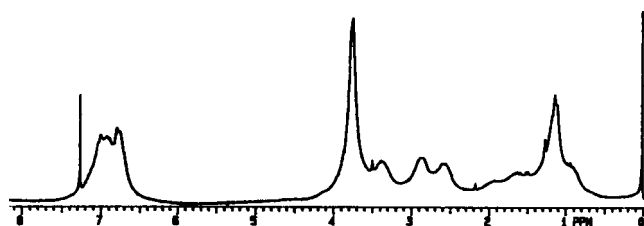
ous temperatures with changing the ratio of the initiator to the monomer concentration. The resulting polymers were isolated by precipitation in methanol. The weight average molecular weights measured by gel permeation chromatography in chloroform with polystyrene standards were between 1,500 and 4,700. When 10 mole% of the initiator to the monomer was used at 0 °C, the polymer of the highest molecular weight was obtained. The polymerization results are summarized in Table 1. Figure 1 shows the ^1H NMR spectrum of the polymer obtained at 0 °C with [I]/[M] =10%. The methylene and methine protons at the backbone of the polymer expected from reaction 1 appeared at 1.2-2.0 ppm. There also appeared two broad peaks at 0.8-1.4 ppm for the methyl protons and at 3.3 ppm for the methine protons adjacent to the aromatic ring, indicating the polymerization also proceeded through reaction 2. The peaks at 2.4-3.1 ppm were assigned to the methylene protons at the benzylic positions of the polymers resulted from reaction 1 and 2. The peaks for the aromatic ring protons and the methoxy protons appeared at 6.5-7.4 ppm and 3.7 ppm, respectively. According to the ^1H NMR results, we concluded that reaction 1 and 2 occurred simultaneously. The aromatic electrophilic substitution reaction favored over the chain propagation. Based on the peak areas, the structural

Table 1. The polymerization results of monomer 1 ([M]=13.2 mole/L in nitroethane)

No.	[I]/[M]	Time (h)	Temp.	Yield (%)	Mw^a
1	100	24	−40	65	–
2	100	24	−20	60	1,500
3	100	24	0	62	1,700
4	10	20	−40	65	2,000
5	10	20	−20	70	2,300
6	10	20	0	80	4,700
7	.5	16	−40	78	2,600
8	5	16	−20	85	3,900

^{a} Weight average molecular weight measured by gel permeation chromatography in chloroform with polystyrene standards.

units formed by the former were estimated to be about four times more than those by the latter. It seems that the carbocation rearrangement did not take place. The polymerization at a lower temperature (− 40 °C) also showed the similar results.

For comparison, allylbenzene which does not have a strong activating group, was polymerized with $AlCl_3$ in nitroethane at room temperature. Only an oligomer was isolated as an oil in a low yield by precipitation in methanol. In the ^1H NMR spectrum of the oligomer in $CDCl_3$, the peaks at 1.5-2.4 ppm were assigned to the methylene and the methine protons at the backbone and the peaks at 2.6-3.1 ppm to the benzylic protons. The area ratio of the former to the latter was about 3, which was two times larger than the calculated value, 1.5 based on the polymer structure formed exclusively by the 1,2-polymerization. Accordingly, the chain propagation seemed to occur in part after rearrangement of the carbocation. The peaks at 0.7-1.1 and 3.6-4.2 ppm also appeared, probably for the end group protons. The area of the ring proton peaks at 6.7-7.4 ppm was almost same as the total area of the peaks in the aliphatic region, proving that an aromatic electrophilic substitution reaction did not occur. Fast termination of the chain-polymerization resulted in an oligomer of a low molecular weight, which is attributable to unstability of active centers and impurities in the polymerization system.

The polymerization of 4-chloromethylanisole with $AlCl_3$ ([I]/[M]=0.05) was carried out in nitroethane at room temperature. Within 1 h, complete conversion of the monomer to the polymer was achieved. In the ^1H NMR spectrum, the peaks at 6.50-7.20, 3.76, and 3.62 ppm appeared for the ring protons, the methoxy protons, and the benzylic protons, respectively. The area ratio of the ring proton peaks to the methoxy and the benzylic proton peaks was 0.6 as expected from the polymer structure formed by the aromatic electrophilic substitution reaction. The weight average molecular weight measured by gel permeation chromatography in chloroform with polystyrene standards was 88,000. Higher molecular weight of the resulting polymer compared to the polymerization results of benzyl chloride in the literature[16] is ascribed to the benzene ring activation by a methoxy group.

In summary, we investigated the polymerization of an aromatic monomer having an allyl or a chloromethyl group with $AlCl_3$. The polymerization of 4-chloromethylanisole proceeded through the step-wise aromatic electrophilic substitution. In contrast to the chain-reaction polymerization of 4-vinylanisole with a Lewis acid, the polymerization of 4-allylanisole proceeded through the aromatic electrophilic sub-

stitution along with the minor chain propagation, resulting in a branched polymer. This result suggests that the polymerization of a vinyl monomer having an activating aromatic ring with a Lewis acid should yield a highly branched polymer if the reactivities of the aromatic ring and the vinyl group toward the carbocation are controlled properly.

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Catalytic Dehydropolymerization of Di-*n*-butylstannane *n*-Bu₂SnH₂ by Group 4 and 6 Transition Metal Complexes

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The catalytic dehydrocoupling of di-*n*-butylstannane *n*-Bu₂SnH₂ by the Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) and M(CO)₆/Red-Al *in situ* combination catalysts yielded a mixture of two kinds of catenated products: one is a cross-linked insoluble solid, and the other is a non-cross-linked soluble solid (≈Sn₅) or viscous oil (≈Sn₂). The soluble oligostannanes could be produced by simple dehydrocoupling of *n*-Bu₂SnH₂, whereas the insoluble polystannanes could be obtained *via* disproportionation/dehydrocoupling combination process of *n*-Bu₂SnH₂. The disproportionation/dehydrocoupling combination process may initially produce a low-molecular-weight oligostannane with partial backbone Sn-H bonds which could then undergo an extensive cross-linking reaction of backbone Sn-H bonds, resulting in the formation of an insoluble polystannane.

Introduction

For many special applications, inorganic polymers possessing various superior properties over organic polymers have been employed.[1] In particular, polysilanes with unique optoelectronic and chemical properties attributed to σ electron-conjugation along the one-dimensional silicon polymer backbone have received extensive attentions as SiC preceramic polymers,[2a] electroluminescent materials,[2b] deep-UV photoresists of positive image,[2c] electroconductors,[2d] and photoinitiators.[2e-f] The Wurtz coupling reaction of organodichlorosilanes using an alkali metal dispersion in toluene-re-

fluxing temperature is the conventional method for synthesizing polysilanes. However, the synthetic method has several disadvantages such as intolerance of some functional groups, lack of reproducibility, and danger due to the strongly reduced reaction conditions.[3] Other synthetic methods include anionic polymerization of masked disilenes,[4a] ring-opening polymerization of cyclic oligosilanes,[4b] electroreductive polymerization of organodichorosilanes,[4c] sonochemical polymerization of organodichlorosilanes,[4d] and electrochemical polymerization of hydrosilanes.[4e] Harrod recently dicovered an alternative group 4 metallocene-catalyzed dehydropolymerization of hydrosilanes, resulting in