Benzyne as a Monomer for Polymerization: Alternating Copolymerization of Benzyne and Pyridine To Give Novel Polymers with *o*-Phenylene and 2,3-Dihydropyridine Units in the Main Chain

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ABSTRACT: Benzyne generated from fluoride-induced reaction of *o*-trimethylsilylaryl triflates was found to be copolymerized with pyridine to give novel alternating copolymers bearing *o*-phenylene and 2,3-dihydropyridine units in the main chain. The unique polymer structures were confirmed from the elemental analyses, MALDI−TOF-MS, and IR, although ^{1}H NMR spectra of the polymers did not exhibit the signals of protons on the pyridine-derived rings. The copolymers obtained as HCl adducts of pyridine-derived rings can be converted to neutral forms via treatment with NaOH aqueous solution, where nucleophilic attack of hydroxide anion to the pyridine-derived rings resulted in the incorporation of hydroxy and imine groups on the cyclic structure. The mechanism of the copolymerization and the transformation with the alkaline treatment thereafter was proposed. This is the first example that benzyne generated from *o*-trimethylsilylaryl triflates can be used as a monomer for polymerization.

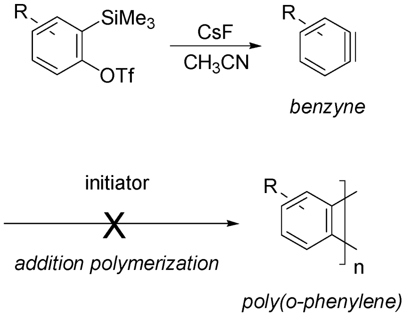
Introduction

Dehydrobenzene, so-called benzyne or aryne, has been recognized as a highly reactive intermediate and has played important roles in some fundamental organic transformations.[1−4] In particular, since a very convenient method for the fluoride-induced generation of benzyne from *o*-trimethylsilylaryl triflate under mild conditions was established,[5] efficient additions of various reagents to benzyne have been reported.[6−13] However, despite the high reactivity of benzyne toward such additions, there has been no report that investigates the reactivity of benzyne toward addition polymerizations, to our knowledge so far, except that the nucleophilic addition to benzyne was suggested to be involved in the formation of polyphenylene frameworks.[14,15]

Thus, on the assumption that the reactivity of benzyne is high enough to be polymerized to give poly(*o*-phenylene), we have examined the reaction of benzyne generated in situ in the aforementioned fluoride-induced method with various initiators for addition polymerizations. Although none of the reagents promoted the homopolymerization of benzyne, we have found that a novel alternating copolymerization of benzyne with pyridine proceeds to afford new polymers having *o*-phenylene and 2,3-dihydropyridine units in the main chain.

Results and Discussion

Scheme 1. Attempt To Synthsize Poly(*o*-phenylene) via Addition Polymerization of Benzyne



initiator = nucleophiles, transition metals, radicals

At first glance, because of the reported high reactivity of benzyne, we expected that benzyne could be polymerized via consecutive additions to its carbon−carbon triple bond to give poly(*o*-phenylene), if an appropriate initiator is employed. Thus, as shown in Scheme 1, after benzyne was generated from trimethylsilylaryl triflate in the presence of cesium fluoride (CsF) in acetonitrile (MeCN), it was reacted with a catalytic amount (ca. 0.05 equiv with respect to benzyne) of various nucleophiles (Grignard reagents, amines, and phosphines), transition-metal compounds ($MoCl_5$, WCl_6, $PdCl_2$, and Ni(acetylacetonate)$_2$), and radical initiators (AIBN and V-70). Nevertheless, no polymerization took place in these experiments at all.

In contrast, we have found that benzyne reacted with pyridine to give polymeric materials. For example, benzyne **1b** was generated from the reaction of 4-methyl-2-trimethylsilylphenyltriflate (**1a**) with 2 equiv of CsF in MeCN, and pyridine (5 equiv with respect to **1a**) was added to the mixture at room temperature (Table 1, run 2). The initial colorless suspension gradually turned to a deep purple suspension, which suggested that a reaction took place between **1b** and pyridine. After the mixture was stirred at room temperature overnight, volatiles were removed and extractive workup with 1 N HCl(aq) and $CHCl_3$ was carried out for the residual deep purple solid.[16] Purification with preparative recycling gel permeation chromatography (GPC) afforded a polymeric product, whose M_n was estimated to be 1730 ($M_w/M_n = 1.39$) by GPC analysis based on poly(methyl methacrylate) (PMMA) standards. The ^{1}H NMR spec-

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Table 1. Alternating Copolymerization of Benzyne and Pyridine Derivatives[a]

run	monomer precursor (M) mol	pyridine derivatives (Py)	[Py]/[M]	product	yield[b] (%)	M_n[c]	M_w/M_n[c]	elemental analysis[d] found calcd (x HCl, y H_2O per repeating unit)
1	**1a**, 1.60	pyridine	10	**1c**	21.9	1530	1.44	C, 69.39; H, 5.95; N, 8.54 C, 70.07; H, 5.88; N, 6.81 ($x = 1.00, y = 0.0$)
2	**1a**, 1.64	pyridine	5	**1c**	19.1	1730	1.39	C, 67.57; H, 5.39; N, 7.35 C, 68.01; H, 5.61; N, 6.61 ($x = 1.00, y = 0.4$)
3	**1a**, 3.25	pyridine	3	**1c**	33.7	2220	1.27	C, 69.93; H, 5.87; N, 7.76 C, 70.07; H, 5.91; N, 6.87 ($x = 0.95, y = 0.0$)
4	**1a**, 3.23	pyridine	1	**1c**	38.4	1526	1.25	C, 72.60; H, 6.05; N, 8.67 C, 72.65; H, 6.00; N, 7.06 ($x = 0.80, y = 0.0$)
5	**1a**, 6.41	pyridine	0.5	**1c**	41.7	1881	1.20	C, 75.63; H, 6.13; N, 7.33 C, 75.42; H, 6.12; N, 7.33 ($x = 0.60, y = 0.0$)
6	**2a**, 1.52	pyridine	5	**2c**	25.6	2170	1.33	C, 60.91; H, 4.91; N, 5.14 C, 60.53; H, 4.91; N, 5.88 ($x = 1.00, y = 0.3$)
7	**3a**, 1.44	pyridine	5	**3c**	17.5	1540	1.27	C, 67.47; H, 4.50; N, 5.29 C, 68.20; H, 5.19; N, 5.30 ($x = 1.00, y = 1.3$)
8	**4a**, 3.37	3-*n*-Bu-pyridine	3	**4c**	14.5	1314	1.14	C, 71.50; H, 6.92; N, 6.14 C, 71.94; H, 6.90; N, 5.99 ($x = 1.00, y = 0.0$)

[a] Benzyne (actual monomer) was generated by the reaction with 2 equiv of cesium fluoride. Acetonitrile (20−40 mL) was used as a solvent. Polymerization was conducted at room temperature for 15−22 h, except for run 8 at 40 °C for 18 h. [b] Yields were calculated based on the amount of the monomer precursor, except for run 5, where it was calculated based on the amount of pyridine. [c] M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF. [d] Caculated value of the elemental analyses were based on the structure of alternating copolymers of the structure with *o*-phenylene and 2,3-dihydropyridine with x HCl per repeating unit as shown in Scheme 2.

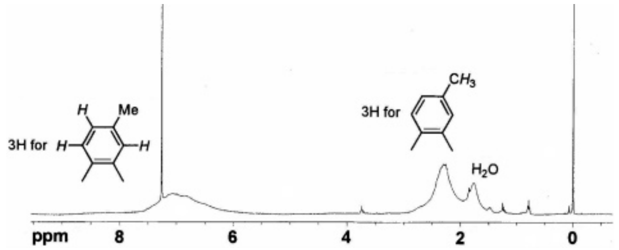
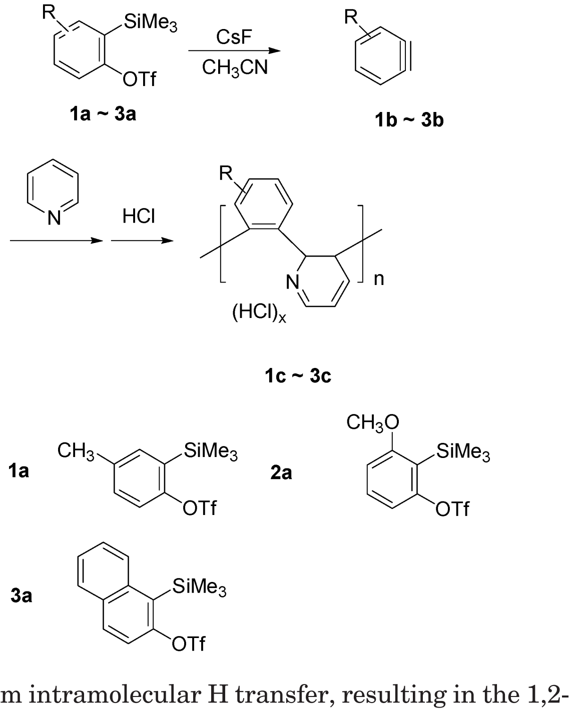


Figure 1. ^{1}H NMR spectrum of **1c** (Table 1, run 2).

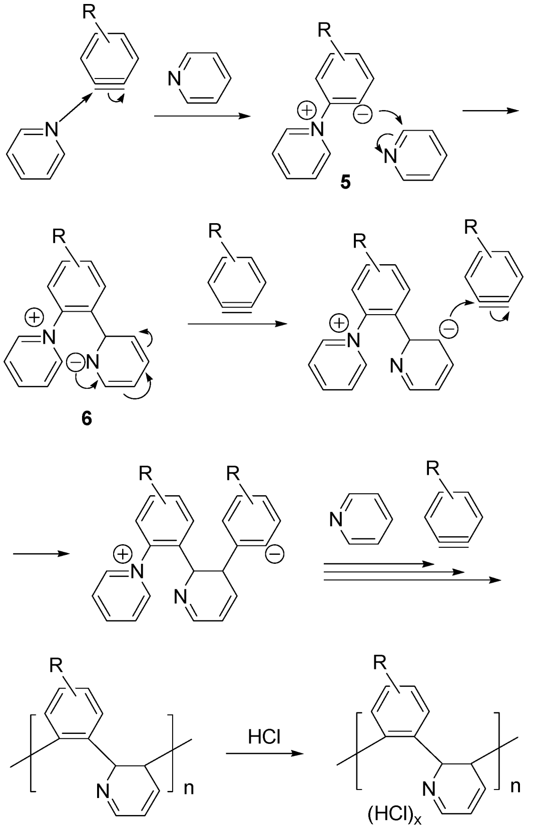
trum of the product exhibited two broad signals at 2.0−3.0 and 5.5−8.0 ppm, which should derive from methyl and aromatic protons of **1b**, respectively (Figure 1). Although the signals derived from pyridine were not observed,[17] the high N content (7.35%) in the elemental analysis of the product obviously indicated the presence of pyridine-derived units in the polymeric structure. We have found that the most reasonable structure for the CHN content is an alternating copolymer of benzyne and pyridine, where *o*-phenylene and 2,3-dihydropyridinium hydrochloride constitute the main chain alternatively as shown in Scheme 2. As summarized in runs 1−5 in Table 1, reactions with various **1a**:pyridine feed ratios resulted in the formation of the products with the CHN values corresponding to the same alternating structure with a different degree of HCl attachment, and ^{1}H NMR spectra of these products are identical. In addition, **1b** was not homopolymerized with a small amount of basic compound such as Grignard reagents, triethylamine, triphenylphosphine, or the reaction of pyridine with anionic initiators such as phenyllithium and *n*-butyllithium did not give any polymeric product. From these experimental results, we presume that the products are the complete or partial HCl adducts of 1:1 alternating copolymers of **1b** and pyridine.

Our proposed mechanism for the polymerization is described in Scheme 3. The initiation will be a nucleophilic attack of nitrogen of pyridine to the C−C triple bond of benzyne, which should result in the formation of a zwitterionic compound **5**. As reported in the literature,[11] if the nucleophile is a primary or secondary amine, the corresponding zwitterionic intermediates perform intramolecular H transfer, resulting in the 1,2-addition of the amine to benzyne. On the other hand, in the case of pyridine, because there is no H source available for the H transfer, the anionically charged carbon of **5** would attack the 2-position of another pyridine molecule nucleophilically, affording **6** having an anionic charge on the pyridine nitrogen. Our assumption for the next step is that the anionic species **6** would attack another benzyne nucleophilically, in a manner leaving 1-azadiene in the pyridine-derived six-membered ring, furnishing a 2,3-dihydropyridine unit in the main chain. Although we cannot rule out the possibility of nucleophilic attacks from the other resonance forms of the anionic species, the one described in Scheme 3 affording the 1-azadiene framework seems most probable. Accordingly, polymerization takes place through alternation of the two kinds of nucleophilic attacks as

Scheme 2. Alternating Copolymerization of Benzyne and Pyridine



Scheme 3. Proposed Mechanism for Copolymerization of Benzyne and Pyridine



propagation, giving the alternating copolymer that accepts HCl during workup with HCl aqueous solution. On the basis of the proposed mechanism, the gradual increase of the yield of **1c** with the decrease of the relative amount of pyridine in the feed ratios can be ascribed to the lower concentration of the initiator (a part of pyridine that takes part in the initiation) because the lower concentration of the initiator would decrease the relative amount of low molecular weight products, which would be removed by purification with the preparative recycling GPC.

Benzynes **2b** and **3b**, generated from trimethylaryl triflate precursors **2a** and **3a**, respectively, can be used as monomers for the alternating copolymerization. Both monomers reacted with 5 equiv of pyridine under the same conditions as those for **1b**, giving polymeric products as shown in runs 6 and 7 in Table 1. As well as the case with **1b**, although the signals derived from pyridine were not observed in their ^{1}H NMR spectra,[17] the presence of the 2,3-dihydropyridinium unit in the main chain and the 1:1 stoichiometry of the benzyne- and pyridine-derived units were confirmed from the results of the elemental analyses.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF−MS) analysis of **3c** afforded another evidence for the structure of the repeating unit. As shown in Figure 2, we observe a main set of peaks (m/z = 615.33, 820.49, 1026.99, 1231.91) in the MS spectrum of **3c**. The average interval of the four peaks is m/z = 205.53, which is close to the MW of the repeating unit in a neutral form ($C_{15}H_{11}N$; MW = 205.26). In addition, the m/z value of the lowest peak (m/z = 615.33) is close to the MW (616.78) of an oligomer bearing a pyridinium cation at the α-chain end and H at the ω-chain end. Considering the broad signals appeared in its ^{1}H NMR spectrum and the M_n value measured by the GPC analysis (although the M_n value based on the PMMA standards cannot be reliable for **3c**), we presume that the peaks observed in Figure 2 are a low molecular weight part of **3c**, which would be relatively easy to be detected in the MS analyses, and the peaks does not reflect the exact distribution of the whole product accordingly.

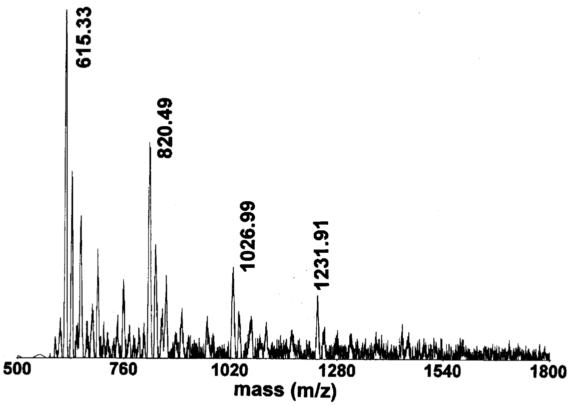


Figure 2. MALDI−TOF−MS spectrum of **3c**.

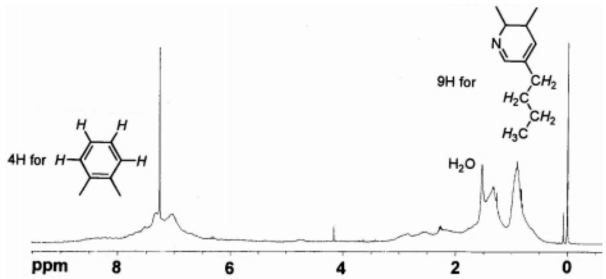


Figure 3. ^{1}H NMR spectrum of **4c**.

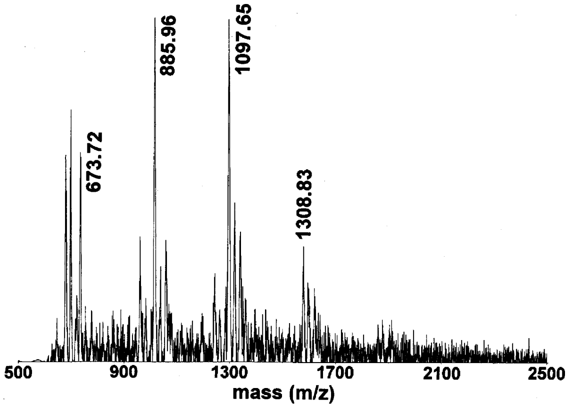
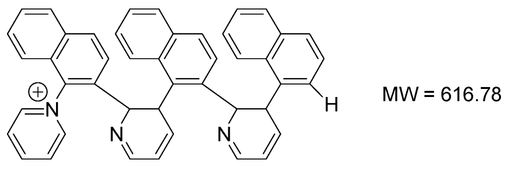


Figure 4. MALDI−TOF−MS spectrum of **4c**.



Unsubstituted benzyne **4b** can be used for the polymerization. To improve the solubility of the resulting product, 3-n-butylpyridine (3-BuPy) was used as a pyridine derivative. As shown in run 8 in Table 1, the resulting polymer **4c** has the alternating structure as well as **1c**−**3c** judging from the elemental analysis. The ^{1}H NMR spectrum of **4c** exhibits signals derived from

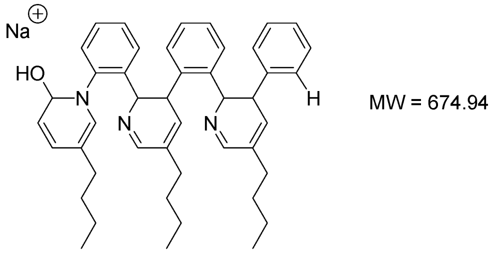
Table 2. Alternating Copolymerization of Benzyne and Pyridine Followed by Alkaline Treatment[a]

run	monomer precursor (M) mol	product	yield[b] (%)	M_n[c]	M_w/M_n[c]	elemental analysis[d] found calcd (y H_2O per repeating unit)
1	**1a**, 6.41	**1d**	38.6	1200	1.70	C, 76.08; H, 6.19; N, 8.43 C, 76.97; H, 6.99; N, 7.48 ($y = 0$)
2	**3a**, 2.99	**3d**	31.8	1280	1.54	C, 78.17; H, 5.28; N, 5.71 C, 78.12; H, 5.94; N, 6.07 ($y = 0.3$)
3	**4a**, 5.54	**4e**	16.1	1280	1.14	C, 71.90; H, 6.87; N, 5.49 C, 72.84; H, 8.56; N, 5.66 ($y = 0$)

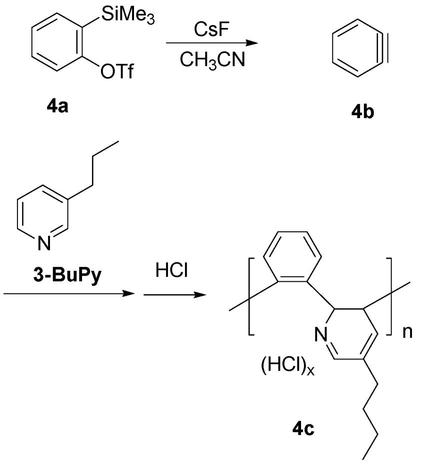
[a] Benzyne (actual monomer) was generated by the reaction with 2 equiv of cesium fluoride. [Pyridine]/[M] = 5. Acetonitrile (20 mL) was used as a solvent. Polymerization was conducted at 40 °C for 13−15 h. [b] Yields were calculated based on the amount of the monomer precursor. [c] M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF. [d] Caculated value of the elemental analyses were based on the structure of alternating copolymers of benzyne and pyridine shown in Scheme 5 for runs 1, 2 and Scheme 6 for run 3.

the *n*-butyl group on 3-BuPy as shown in Figure 3, where the integral ratio of *n*-butyl to aromatic signals corresponds to the alternating structure.

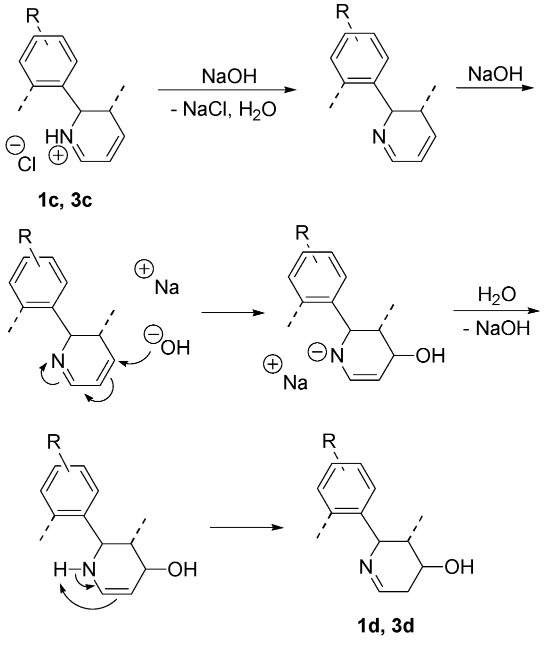
In the MALDI−TOF−MS spectrum of **4c** (Figure 4), we observe a main set of peaks (*m/z* = 673.72, 885.96, 1097.65, 1308.83) with an average interval of *m/z* = 211.70, which is close to the MW of the neutral repeating unit of **4c** ($C_{15}H_{17}N$; MW = 211.31). The *m/z* value of the lowest peaks (673.72) is close to the MW of a Na^+ adduct of an oligomer with the structure described below, where the initiating pyridinium moiety is neutralized with an attack of OH^- and the oligomerization was terminated with H^+ (MW = 674.94).



Scheme 4. Alternating Copolymerization of 4b and 3-BuPy



Scheme 5. Alkaline Treatment of Benzyne−Pyridine Copolymer

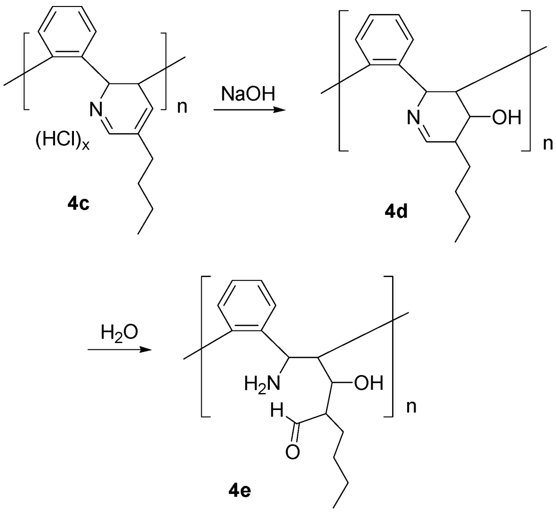


Next, we attempted to neutralize the dihydropyridinium hydrochloride unit in the copolymers by the treatment with aqueous NaOH solution. Thus, after the polymerization of **1b** and pyridine was quenched by the treatment with 1 N HCl(aq), the $CHCl_3$ solution containing **1c** was washed thoroughly with 10% NaOH aqueous solution. Although the resulting deep purple solid[16] with a GPC-estimated M_n of 1200 ($M_w/M_n = 1.70$) exhibited almost the same signals as those of the dihydropyridinium polymer **1c**, its CHN contents from elemental analyses were apparently different from those of **1c** (Table 2, run 1). We have found that the observed CHN values agree well with the calculated values of an 1:1 alternating copolymer of benzyne and pyridine **1d**, in which the pyridine-derived six-membered ring consists of a hydroxy-substituted carbon and a C=N double bond. We can propose the plausible mechanism for the formation of **1d**, as shown in Scheme 5. After HCl was removed from the dihydropyridinium salt to form a 1-azacyclobutadiene structure, 1,4-addition of a hydroxy anion would occur on the α,β-unsaturated imine to form vinylamine via protonation and then followed by isomerization to result in the formation of the 4-hydroxy-1-azacyclobutene structure.

In a similar manner, benzyne **3b** afforded an alternating copolymer by the treatment with the alkaline solution after the polymerization (Table 2, run 2). On the other hand, judging from the result of elemental analysis, the alkaline treatment of the copolymer **4c** resulted in the formation of **4e**, which should be obtained through hydrolysis of C=N bond of initially formed **4d** (Scheme 6). The signals for *n*Bu protons of **4e** were observed in its ^1H NMR spectra. In accord with the generation of imine (**1d**, **3d**) and aldehyde (**4e**) in their structures, corresponding absorptions derived from C=N and C=O were observed in their IR spectra at 1640 (**1d**), 1627 (**3d**), and 1664 cm^{-1} (**4e**).

To get more accurate information about the molecular size of the copolymers than the relative M_n values

Scheme 6. Formation of 4e



obtained with GPC measurements based on PMMA standards, we tried to carry out vapor pressure osmometry (VPO) measurements. For that purpose, **1c** was prepared under the same conditions as in run 3 in Table 1 with a much larger scale by using 11.77 mmol of **1a**. The polymerization gave **1c** in 39.4% yield (GPC-estimated $M_n = 1860$ and $M_w/M_n = 1.52$), whose VPO measurement in $CHCl_3$ gave $M_n = 665$. Then, the **1c** sample was subjected to the alkaline treatment, which afforded **1d** (GPC-estimated $M_n = 1530$ and $M_w/M_n = 1.51$) in 22.1% yield on the basis of the amount of **1a** used for the polymerization. According to the VPO measurement, M_n of the **1d** is 1364, which indicates that the VPO-determined M_n for the **1c** is low because of the dissociation of Cl anions from the main chain. More importantly, these results suggest that GPC-estimated M_n values in Tables 1 and 2 are somewhat reliable.

Conclusions

We have demonstrated that benzynes generated from trimethylsilylaryl triflates can be copolymerized with pyridine, affording the 1:1 alternating copolymers with novel structures. To our knowledge, this is a rare example in which benzyne and pyridine are used as monomers for polymerization and at least is the first example of the polymerization of benzynes generated from the trimethylsilylaryl triflates.

Experimental Section

Materials. Acetonitrile (MeCN) (Wako, 99.8%) was dried over CaH_2 and used without further purification. Pyridine (Wako, 99%) was dried over CaH_2 and distilled before use. CsF (Aldrich, 99%) was used as received. Bezyne precursors **1a**,[8,12] **2a**,[6] **3a**,[7] and **4a**[5] were prepared according to the reported procedures.

Measurements. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer using tetramethysilane as an internal standard in chloroform-*d* ($CDCl_3$) at 50 °C. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured by means of gel permeation chromatography (GPC) on a Jasco-Bowin system (version 1.50) equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with a poly(MMA) standard (Shodex M-75, $M_n = 2190$, $M_w/M_n = 1.08$) and dibutyl sebacate (MW = 314.5). The column used for the GPC analyses was KF-802 (Shodex; 300 mm × 8 mm i.d., 6 μm average particle size, exclusion molecular weight of 5K for polystyrene). Purification by preparative recycling GPC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H (600 mm × 20 mm i.d., exclusion molecular weight of 70K for polystyrene) and a JAIGEL-2H (600 mm × 20 mm i.d., exclusion molecular weight of 20K for polystyrene) using $CHCl_3$ as eluent at a flow rate of 3.5 mL/min at 25 °C. The sample solution (3 mL containing ca. 0.3 g of the crude product) was injected and recycled before fractionation.

MALDI–TOF–MS analyses were performed on a PerSeptive Biosystems Voyager RP equipped with 1.3 m linear flight tubes and a 337 nm nitrogen laser (pulse width, 3 ns). All experiments were carried out at an accelerating potential of 20 kV in linear mode mode under the pressure of ca. $(2-3) \times 10^{-7}$ mmHg. In general, mass spectra from 100 laser shots were accumulated to produce a final spectrum. Angiotensin I (human; MW = 1296.5) (Sigma, 97%) and insulin (bovine pancreas, MW = 5733.50) (Nacalai, 28.0 U/mg) were used as internal standards to calibrate the mass scale. A 1.5 μL portion of the mixture consisting of a polymer solution (100 μL, 10 mg/mL in THF), a matrix, 3-indoleacrylic acid (TCI, >97%) for **1c**, 1,8-dihydroxy-9(10*H*)-anthracenone (Nacalai, 95%) for **4c**, solution (300 μL, 30 mg/mL in THF), and a cationizing agent, sodium trifluoracetate (TCI, >98%), solution (100 μL, 10 mg/mL in THF) was deposited onto a sample target plate and allowed to dry in air at room temperature.

The vapor pressure osmometry measurements for **1c** and **1d** were carried out on a Gonotec Osmomat 070 in chloroform at 45 °C. The cell constant for the measurement was determined with benzil (TCI, >99.9%). Four solutions of the samples in $CHCl_3$ with different concentrations (**1c**; 3.932, 8.341, 16.136, and 24.145 g/kg $CHCl_3$, **1d**; 2.932, 5.828, 11.952, and 18.108 g/kg $CHCl_3$) were used for the measurements.

Elemental analyses were performed on a YANAKO MT-5 analyzer at Integrated Center for Science (INCS) in Ehime University.

Copolymerization of Benzyne 1b and Pyridine. As a typical procedure for the copolymerization, the procedure for run 3 in Table 1 is described as follows. Under a nitrogen atmosphere, a MeCN solution (20 mL) of the benzyne precursor **1a** (1.01 g, 3.25 mmol) was added to a suspension of CsF (1.05 g, 6.92 mmol) in MeCN (20 mL) at room temperature to generate the monomer **1b**, and the mixture was stirred at room temperature for 5 min. Pyridine (0.65 mL, 8.0 mmol) was added to the mixture, and it was stirred at room temperature for 18 h. After volatiles were removed from the resulting deep purple mixture under reduced pressure, the residual solid was dissolved into $CHCl_3$ (30 mL), and it was washed with 1 N HCl (aq) (50 mL). After the organic layer was washed with 50 mL of water twice, it was dried over Na_2SO_4. Filtration and removal of $CHCl_3$ gave a deep purple solid, which was subjected to the purification using preparative recycle GPC. The yield of **1c** as a deep purple solid was 33.7% (0.210 g). Other polymerizations in Table 1 were carried out in similar procedures.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) for **1c**: δ 2.0–3.4 (br, 3H, CH_3–Ar), 5.5–8.0 (br, 3H, *H*–Ar), **2c**: δ 3.0–4.1 (br, 3H, CH_3O–Ar), 6.0–8.0 (br, 3H, *H*–Ar), **3c**: δ 6.0 – 8.5 (br, 6H, *H*–Ar), **4c**: δ 0.5–1.0 (br, 3H, CH_3–$CH_2CH_2CH_2$–Py), 1.0–3.2 (br, 6H, CH_3–$CH_2CH_2CH_2$–Py), 6.0–8.5 (br, 4H, *H*–Ar). IR (KBr pellet, cm^{-1}) for **1c**: 2924, 1604, 1508, **2c**: 2959, 1605, 1491, **3c**: 1624, 1595, 1508, **4c**: 2956, 2928, 1596, 1491.

Copolymerization of Benzyne and Pyridine with Alkaline Treatment. As a typical procedure for the alkaline treatment of the copolymers, the procedure for run 1 in Table 2 is described as follows. The copolymerization using **1a** (2.00 g, 6.41 mmol), CsF (2.01 g, 13.2 mmol), and pyridine (1.55 mL, 19.2 mmol) was carried out in a similar manner as described above, except that the copolymerization was conducted at 40 °C. The resulting product after removal of volatiles was first treated with $CHCl_3$ (50 mL) and 1 N HCl(aq) (100 mL), and then the $CHCl_3$ solution was washed thoroughly with 200 mL of 10% NaOH(aq). After the organic layer was washed with 50 mL of water twice, it was dried over Na_2SO_4, and $CHCl_3$ was removed under reduced pressure to give a crude product, which was purified with the preparative recycling GPC. The yield of **1d** as a deep purple solid was 38.6% (0.370 g). Other polymerizations in Table 2 were carried out in similar procedures.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) for **1d**: δ 1.8−3.0 (br, 3H, CH_3−Ar), 5.8−7.6 (br, 3H, *H*−Ar), **3d**: δ 6.0−8.2 (br, 6H, *H*−Ar), **4e**: δ 0.5−1.1 (br, 3H, CH_3−$CH_2CH_2CH_2$−Py), 1.1−2.7 (br, 6H, CH_3−$CH_2CH_2CH_2$−Py), 6.0−8.5 (br, 4H, *H*−Ar). Signals for hydroxy, amino, and aldehyde groups of **1d**, **3d**, and **4e** could not be identified. IR (KBr pellet, cm^{-1}) for **1d**: 3421, 3029, 2921, 1640, 1604, 1510, **3d**: 3565, 3055, 2926, 1627, 1597, 1508, **4e**: 3421, 3061, 2955, 1664, 1596, 1493.

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(16) As one of the reviewers pointed out, the deep purple color of the copolymers in this study is strange for their chemical structures, and it was suspected that the color derived from oxidation of the nitrogen moiety. However, the copolymerization under thoroughly deoxidized conditions gave the same results with respect to the color and the polymerization behavior. Thus, the origin of the intense color of the copolymers is not clear at present.

(17) At present, it is not clear why some signals derived from pyridine are not observed in ^{1}H NMR spectra of the copolymers. As broadening of the observed signals in the spectra indicates, the main chain structure of the copolymers should be highly rigid. We suppose that ring current effects of the aromatic rings in the rigid main chain conformation might cause the disappearance of the signals.

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