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Notes

True Polyazulene: Soluble Precursor of So-Called “Polyazulene”

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So-called “polyazulene”, which has been synthesized by oxidative polymerization of azulene, is one of the most promising conductive polymers.[1,2] Although conventional “polyazulene” should be denoted by “dehydropolyazulene” or “polyazulenylene,” the wrong nomenclature, polyazulene, has been widely used, as well as polythiophene and polypyrrole, because true polyazulene has not been reported. In this note, we wish to report the first synthesis of the true polyazulene.

Azulene dissolves in strong acid to form cycloheptatrienyl cation **1**, as shown in Scheme 1.[3,4] When a trifluoroacetic acid solution of **1** was heated at 60 °C for 24 h, a brown polymeric product (M_n 3300) was obtained in 67% yield after the treatment with triethylamine.[5] ^{1}H- and ^{13}C-NMR spectra of the polymer are shown in Figure 1. Aliphatic protons and carbons are observed in these spectra. The integration ratio of the higher magnetic field region (0.5−4.2 ppm) and lower magnetic field region (4.2−9.3 ppm) was about 2:6. These observations indicate that azulene underwent addition polymerization as a conjugated olefin to afford a true polyazulene. Elemental analysis showed that the polymer was a complex of polyazulene with 29 mol % of trifluoroacetic acid. (See Experimental Section.) Polyazulene is soluble in various organic solvents including DMF, THF, dichloromethane, and toluene and is gradually oxidized in the air to afford insoluble material. Polyazulene formed a brittle film when cast from dichloromethane solution.

Apparently, this polymerization is cationic. Thus, we carried out $BF_3{\cdot}OEt_2$-initiated cationic polymerization of azulene in dichloromethane at room temperature, although only insoluble polymer was obtained in poor yield. Since the polyazulene was soluble in various solvents, $BF_3{\cdot}OEt_2$-initiated cationic polymerization of azulene might afford cross-linked polymer.

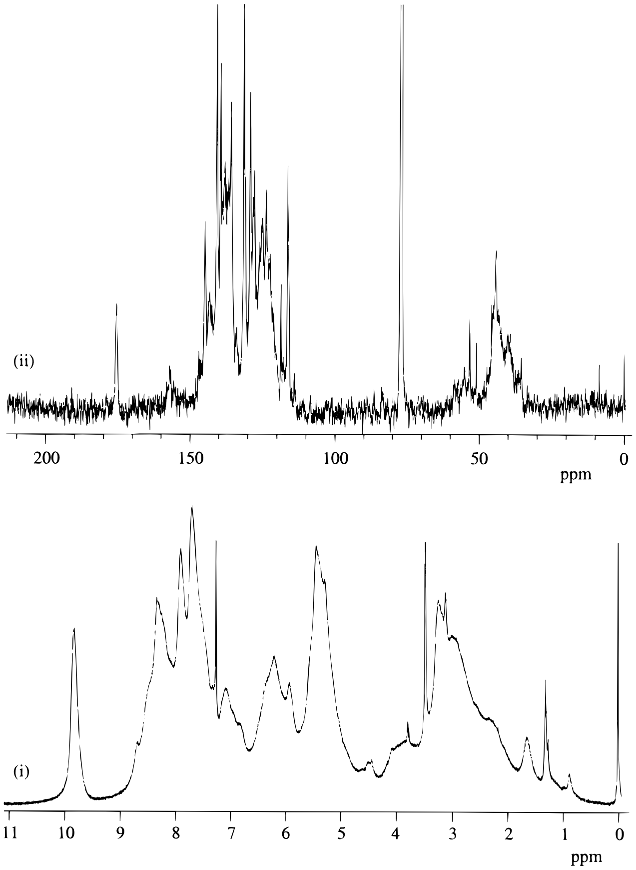

Figure 1. NMR spectra of polyazulene: (i) ^{1}H-NMR spectrum (500 MHz, $CDCl_3$); (ii) ^{13}C-NMR spectrum (125 MHz, $CDCl_3$).

Scheme 1

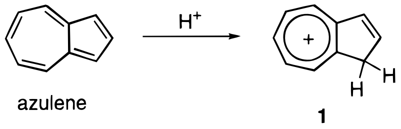

Table 1. Polymerization of Azulene

time (h)	temp (°C)	solvent[a]	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	60	CF_3COOH	5	*d*	*d*
6	60	CF_3COOH	24	1800	4.01
16	60	CF_3COOH	53	*d*	*d*
24	60	CF_3COOH	67	3300	8.30
48	60	CF_3COOH	72	3400	8.45
24	25	CF_3COOH	36	*d*	*d*
24	45	CF_3COOH	60	2800	6.52
24	80	CF_3COOH	69	3500	7.95
24	100	CF_3COOH	89	3600	8.02
24	60	CH_3COOH	0		
24	60	CH_3SO_3H	0		
24	60	CF_3SO_3H	0		

[a] 1 mol/L. [b] Methanol-insoluble part. [c] Estimated by GPC (THF, based on PSt standards). [d] Not determined.

The polymerization was carried out under various conditions. The results are summarized in Table 1. The yield increased as the polymerization temperature rose, and M_n increased as the polymerization time increased. It is interesting that polyazulene could not be obtained when acids other than trifluoroacetic acid were used as solvents. This result indicates that the appropriate strength of acidity is necessary for the cationic polymerization of azulene. Thus, we can propose the possible polymerization mechanism illustrated in Scheme 2. Azulene that is present in the solution of **1** at equilibrium, was alkylated by **1**. The resulting heptafulvene structure should be protonated rather easily compared to azulene to form the cycloheptatrienyl cation. When

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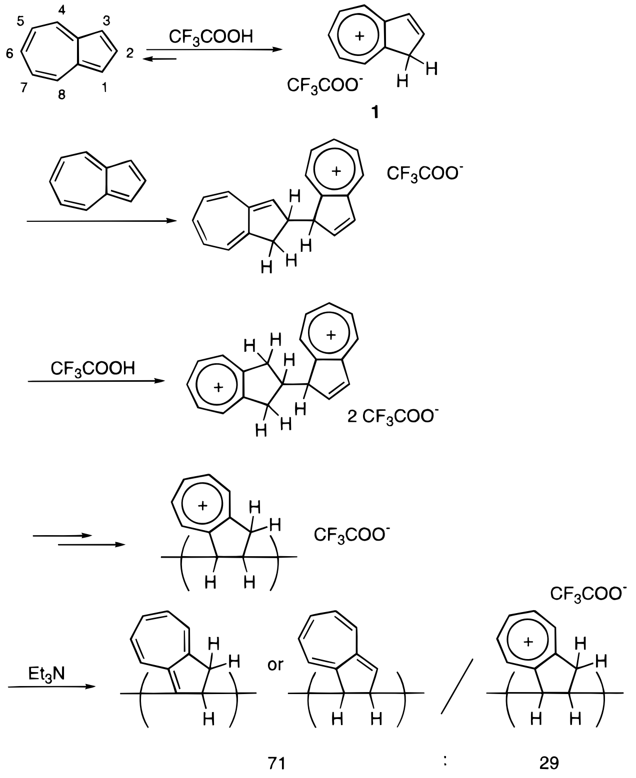
Scheme 2



the acidity of the solvent is too high, the concentration of azulene is so low that the polymerization does not proceed. When the acidity of the solvent is lower than that of trifluoroacetic acid, the protonation does not occur. After treatment with triethylamine, polyazulene bearing the heptafulvene structure was obtained, while the elemental analysis clearly showed that a part of the cycloheptatrienyl trifluoroacetate unit remained. Indeed, the remaining cycloheptatrienyl cation moiety can be observed in the ^{1}H-NMR (9.7 ppm) and ^{13}C-NMR (150−180 ppm) spectra.

The position of **1** where azulene attacked was estimated by the semiempirical molecular orbital calculation method using the program MOPAC with the PM3 Hamiltonian.[6] Since the LUMO of **1** was calculated to be delocalized at the positions 2, 5, 6, 7, and 8, the following calculations were made for these positions. First, the heats of formation of the adducts of azulene and **1** were calculated. The calculations were made for all possible diastereomers and conformers, as shown in Table 2. The adducts at the 2-position are >5 kcal/mol more stable than the other adducts. Further, activation energies when the above described conformers would be formed were estimated, as shown in Table 3. To simplify the calculations, isobutene was used as a model compound of azulene. The activation energies to form 2-position adducts are >1 kcal/mol lower than those to form other adducts. These results clearly indicate that nucleophilic attack of azulene to **1** at the 2-position is more favored than those at other positions both thermodynamically and kinetically.

Aromatization of polyazulene was attempted by DDQ oxidation.[7] A black powder, which was insoluble in any organic solvents, was obtained. Elemental analysis of this material, however, showed that it was not a simple dehydropolyazulene. (See Experimental Section.) It seemed that the oxidative aromatization proceeded quantitatively although a complex with DDQ was obtained. The structure of this material was not clear at this time. The content of DDQ in this material was estimated to be >50 mol % from elemental analysis.

Table 2. Heat of Formation (kcal/mol) of Adduct of Azulene and 1

		conformation[c]		
position[a]	diastereomer[b]	anti	gauche(+)	gauche(−)
2	R*-R*	289.18	289.32	290.53
2	R*-S*	289.99	289.59	290.23
5	R*-R*	294.15	295.52	295.54
5	R*-S*	295.03	295.52	295.77
6	R*-R*	293.42	295.63	295.64
6	R*-S*	293.29	295.09	295.71
7	R*-R*	293.99	295.37	295.34
7	R*-S*	293.87	295.33	295.25
8	R*-R*	294.17	296.39	295.78
8	R*-S*	293.97	295.97	295.85

[a] The position of **1** where azulene attacks. [b] Relative stereoregularity at the 1-position on azulene is indicated first, and relative stereoregularity at the position where azulene adds on **1** is indicated second. [c] Relationship of hydrogens around newly formed bonds.

Table 3. Activation Energy (kcal/mol) of the Addition of Isobutene to 1

	conformation[b]		
position[a]	anti	gauche(+)	gauche(−)
2	16.02	15.68	16.33
5	16.97	17.29	17.03
6	17.22	17.28	17.29
7	17.30	17.66	17.31
8	17.28	18.13	17.53

[a] The position of **1** where azulene attacks. [b] Related to the conformations denoted in Table 2.

Conductivities of thus obtained materials were measured as one of the basic properties. Although the conductivity of the polyazulene was 5.38×10^{-8} S/cm, it increased to 8.16×10^{-3} S/cm after the molded pellet of polyazulene was exposed to an iodine atmosphere at room temperature. The pellet became insoluble in any solvent. This remarkable increase of conductivity indicates the occurrence of oxidative aromatization to dehydropolyazulene followed by doping of iodine. The conductivity of dehydropolyazulene was 5.52×10^{-7} S/cm, and 6.11×10^{-5} S/cm after doping by iodine. The relatively lower conductivity observed for dehydropolyazulene may be due to the contamination of DDQ and/or related compounds.

In conclusion, true polyazulene can be simply obtained by heating azulene in trifluoroacetic acid. Since conductive but insoluble dehydropolyazulene can be easily prepared from polyazulene by oxidative aromatization, soluble polyazulene is expected as a superior precursor of dehydropolyazulene.[8] Further, we wish to point out the unusual cationic polymerization condition mentioned above. Cationic polymerization has been carried out in a neutral media in the presence of a small amount of cationically activated molecule. In this polymerization system, however, most of the monomer was activated, and the small amount of monomer that is present in the polymerization system as an equilibrium reacted with the cation. This novel cationic polymerization system is expected to be utilized on various highly reactive monomers.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX-500 spectrometer. IR spectra were recorded on a JEOL JIR-AQS20M spectrometer. Gel permeation chromatography (GPC) analyses were carried out to estimate molecular weights using a HITACHI L-6000 equipped with three Shodex KF-804L columns, a HITACHI L-4000 UV detector, and a HITACHI L-3300 RI detector, eluted with THF (1 mL/min, 40 °C). Calibration was carried out using polystyrene standards. Molecular orbital calculations were made on an Apple Power Macintosh 7200 (90 MHz) using the program MOPAC version 6.0 using key word PRECISE. The conductivity was measured on a ADVANTST R8340/8340A high-resistance meter.

Materials. Azulene was purchased from Aldrich and used directly. Trifluoroacetic acid was dried over phosphorus pentoxide and used after distillation. Other chemicals were reagent grade and used without further purification.

Polymerization of Azulene: General Procedure. A colorless solution of 42.1 mg (0.33 mmol) of azulene in 0.90 mL of trifluoroacetic acid was heated at 60 °C for 24 h in a sealed tube. The color of the solution turned to dark green immediately, and a dark red solution was obtained at the end of the polymerization. The reaction mixture was poured into 15 mL of methanol containing 1 mL of triethylamine. The precipitate was filtered out, washed thoroughly by methanol, and dried *in vacuo* to give 28.2 mg (67%) of polyazulene as a dark brown powder. IR (KBr): 1657, 1182, 1139, 733 cm^{-1}. Anal. Calcd for $(C_{10}H_8)_{0.71}(C_{12}H_9F_3O_2)_{0.29}$: C, 78.81; H, 5.18; N, 0.00. Found: C, 78.71; H, 4.89; N, 0.00.

DDQ-Oxidation of Polyazulene. A solution of 19.0 mg of polyazulene (0.15 mmol unit) and 67.3 mg (0.30 mmol) of DDQ in 9 mL of chlorobenzene was refluxed for 12 h. The black product was precipitated during the reaction. The precipitate was filtered out, washed thoroughly by dichloromethane, and dried *in vacuo* to give a black powder. Anal. Calcd for $(C_{10}H_6)_{0.71}(C_{12}H_9F_3O_2)_{0.29}(C_8Cl_2N_2O_2)_{1.00}$: C, 57.69; H, 1.79; N, 7.24. Found: C, 53.29; H, 1.99; N, 5.99.

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