

## Synthesis and Polymerization of 7,7-Bromo-8,8-dicyanoquinodimethane

Satoshi Ichikawa, Takahiro Uno, Masataka Kubo, Takahito Itoh\* (✉)

Department of Chemistry for Materials, Faculty of Engineering, Mie University, Kamihama-cho, Tsu-shi, Mie 514-8507, Japan

E-mail: [itoh@chem.mie-u.ac.jp](mailto:itoh@chem.mie-u.ac.jp); Fax Number: +81-59-231-9410

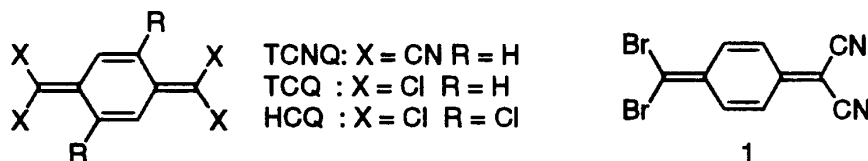
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### Summary

7,7-Dibromo-8,8-dicyanoquinodimethane (**1**) was synthesized successfully as orange needles. Its homopolymerization and copolymerization with styrene were investigated. **1** polymerized with AIBN and triethylamine, but not with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . **1** copolymerized with styrene in a random fashion and  $Q$  and  $e$  values were estimated to be 336 and +1.45, indicating a highly conjugative, electron-accepting monomer.

### Introduction

Introduction of electron-withdrawing substituents such as cyano, ester and acyl groups and/or electron-donating ones such as phenyl and alkylthio groups on exocyclic carbons of a very reactive unsubstituted quinodimethane, which polymerized spontaneously at room temperature, led to substituted quinodimethanes isolable as crystals at room temperature. We have studied a series of these isolable substituted quinodimethanes and related compounds in their polymerization behavior [1]. From a viewpoint of further study of polymerization behavior of substituted quinodimethanes, we were interested in synthesis and polymerization of isolable and polymerizable substituted quinodimethanes with a novel substitution mode. Previously as quinodimethanes with a novel substitution mode, we made attempts to prepare substituted quinodimethanes with different substituents at 7 and 8 positions such as 7,7-bis(alkoxycarbonyl)-8,8-dicyanoquinodimethanes, but failed [2]. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) is well known to be a very stable, isolable, not homopolymerizable compound. Chloro-substituted quinodimethanes such as 7,7,8,8-tetrachloroquinodimethane (TCQ) and 2,5,7,7,8,8-hexachloroquinodimethane (HCQ) were reported to be isolable as yellow needle crystals at temperatures lower than 0 °C and also highly homopolymerizable [3,4]. Therefore, 7,7-dihalo-8,8-dicyanoquinodimethane is expected to be one candidate of isolable, polymerizable substituted quinodimethanes with a novel substitution mode.



In this work were described a synthesis of 7,7-dibromo-8,8-dicyanoquinodimethane (**1**) as one of 7,7-dihalo-8,8-dicyanoquinodimethanes and its polymerization behavior.

## Experimental

Melting points were obtained with a Yanaco MP-53 melting point apparatus. Elemental analyses were performed on a Yanaco CHN Corder MT-3. Number-average molecular weights,  $M_n$ , of homopolymers and copolymers were estimated on a gel permeation chromatography (GPC) Tosoh HLC-803D with a series of Tosoh TSK-gel G2000H, G2500H, G3500H, and G4000H columns, calibrated with polystyrene standards as reference, with tetrahydrofuran (THF) as an eluent.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR and IR spectra were taken on a JEOL JNM-EX 270 FT NMR spectrometer using chloroform-*d* with tetramethylsilane as an internal standard and on a JASCO IR-700 spectrometer, respectively.

Reduction potentials were measured on a Yanaco Cyclic Voltammetric Analyzer VMA-010 at room temperature at a scanning rate of 100 mV/s using dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L) as a supporting electrolyte, with Ag/AgCl, glassy carbon, and platinum wire used as reference, working, and counter electrodes, respectively.

### Monomer Synthesis

*4-(Dibromomethylene)cyclohexanone (2)*. Triphenylphosphine (30.4 g, 116 mmol) and carbon tetrabromide (19.2 g, 58 mmol) were dissolved in 100 mL of dry benzene, the resulting solution stirred for 30 min at room temperature. Into the solution was added 1,4-cyclohexanedione (5 g, 44.6 mmol), refluxed for 15 h, and the reaction mixture filtered off. The filtrate was concentrated to about 10 mL and passed through a silica-gel column using dichloromethane as an eluent. The second elution band was collected, placed under reduced pressure to remove solvent and give 5.81 g (49% yield) of **2** as white crystals: mp 61-62 °C; IR (KBr):  $\nu_{\text{C-H}}$  2910,  $\nu_{\text{C=O}}$  1680,  $\nu_{\text{C=C}}$  1554,  $\nu_{\text{C-Br}}$  795  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.76 (t,  $J = 13.9$  Hz, 4H), 2.47 (t,  $J = 13.9$  Hz, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  210.0 (C=O), 139.7 (>C=), 85.7 (=CBr<sub>2</sub>), 38.2 (CH<sub>2</sub>), 30.9 (CH<sub>2</sub>). Anal. Calcd for C<sub>7</sub>H<sub>8</sub>Br<sub>2</sub>O: C, 31.38; H, 3.01; Br, 59.64; O, 5.97. Found: C, 31.41; H, 3.05; Br, 59.41; O, 6.13.

*1-(Dibromomethylene)-4-(dicyanomethylene)cyclohexane (3)*. **2** (2.67 g, 9.97 mmol) and malononitrile (0.66 g, 10 mmol) were refluxed in the presence of 0.18 g of  $\beta$ -alanine and 0.53 mL of acetic acid in 140 mL of benzene using a Dean-Stark water separator for 15 h. The reaction mixture was placed under reduced pressure to remove solvent and give pale brown solids, washed with diethyl ether, and then recrystallized from chloroform to give 3 g (95% yield) of **3** as white needles: mp 207-208 °C; IR (KBr):  $\nu_{\text{C-H}}$  2934,  $\nu_{\text{CN}}$  2210,  $\nu_{\text{C=C}}$  1566,  $\nu_{\text{C-Br}}$  788  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR: ( $\text{CDCl}_3$ ):  $\delta$  2.83 (t,  $J = 12.5$  Hz, 4H), 2.67 (t,  $J = 12.5$  Hz, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  185.0 (>C=), 140.6 (>C=), 111.9 (CN), 84.6 (=CBr<sub>2</sub>), 82.0 (=C(CN)<sub>2</sub>), 31.5 (CH<sub>2</sub>), 30.6 (CH<sub>2</sub>). Anal. Calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>Br<sub>2</sub>: C, 38.01; H, 2.55; N, 8.87; Br, 50.57. Found: C, 38.12; H, 2.85; N, 8.75; Br, 50.28.

*7,7-Dibromo-8,8-dicyanoquinodimethanes (1)*. **3** (0.3 g, 0.95 mmol) was dissolved in 540 mL of benzene, 3 g of activated manganese dioxide added, and refluxed for 40

min. The filtrate was placed under reduced pressure to remove solvent and give orange solids, which were recrystallized from hexane to give 29 mg (10% yield) of **la** as orange needles: mp 155 °C (polymerization); IR (KBr):  $\nu_{\text{C-H}}$  3020,  $\nu_{\text{CN}}$  2194,  $\nu_{\text{C=C}}$  1573, 1411,  $\nu_{\text{C-Br}}$  825  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.45 (d,  $J = 9.9$  Hz, 2H), 7.21 (d,  $J = 9.9$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  154.7 ( $>\text{C}=\text{}$ ), 137.0 ( $>\text{C}=\text{}$ ), 133.8 (CH), 125.0 (CH), 116.2 (CN), 113.6 ( $=\text{C}(\text{CN})_2$ ), 77.9 ( $=\text{CBr}_2$ ). Anal. Calcd for  $\text{C}_{10}\text{H}_4\text{N}_2\text{Br}_2$ : C, 38.50; H, 1.29; N, 8.98; Br, 51.23. Found: C, 38.44; H, 1.32; N, 8.88; Br, 51.36.

*1-(Dibromomethylene)-4-(dicyanomethylene)cyclohexene (1')*. Oxidation reaction of **3** for 30 min in chloroform in a procedure similar to that for **1** gave **1'** in 31% yield as yellow needles: mp 192-194 °C; IR (KBr):  $\nu_{\text{C-H}}$  2920,  $\nu_{\text{CN}}$  2198,  $\nu_{\text{C=C}}$  1536,  $\nu_{\text{C-Br}}$  796  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.19 (d,  $J = 9.9$  Hz, 1H), 6.86 (d,  $J = 9.9$  Hz, 1H), 2.89 (m, 2H), 2.79 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  166.8 ( $>\text{C}=\text{}$ ), 136.1 ( $>\text{C}=\text{}$ ), 125.0 (CH), 112.4 (CN), 111.6 (CN), 100.3 ( $=\text{C}(\text{CN})_2$ ), 81.8 ( $=\text{CBr}_2$ ), 28.9 ( $\text{CH}_2$ ), 28.1 ( $\text{CH}_2$ ). Anal. Calcd for  $\text{C}_{10}\text{H}_6\text{N}_2\text{Br}_2$ : C, 38.25; H, 1.93; N, 8.92; Br, 50.90. Found: C, 38.31; H, 1.96; N, 8.95; Br, 50.78.

#### Other Materials

7,8-Bis(ethoxycarbonyl)-7,8-dicyanoquinodimethane was prepared according to the method reported previously [5,6]. TCNQ and 2,2'-azobis(isobutyronitrile) (AIBN) were recrystallized from acetonitrile and methanol, respectively. Styrene (St), benzene and toluene were purified by conventional methods. Dichloromethane and chloroform were distilled over calcium hydride, and triethylamine over potassium hydroxide, respectively. Boron trifluoride etherate ( $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) was distilled under reduced pressure under nitrogen. Tetrabutylammonium perchlorate was dried under reduced pressure at 110 °C for 12 h.

#### Polymerization Procedure

For a radical polymerization, given amounts of **1**, styrene as a comonomer if necessary, AIBN as a radical initiator, and benzene as a solvent were placed in a glass ampoule, and degassed by a freeze-thaw method (repeated three times). The ampoule was sealed and placed in a bath thermostated at 60 °C for a given time of polymerization, and then opened. The reaction mixture was poured into an excess of hexane to precipitate products, which were purified by three or more cycles of a redissolution and reprecipitation. Chloroform and hexane were used as a solvent and a precipitant, respectively. The product obtained was dried under reduced pressure at room temperature until a constant weight was reached.

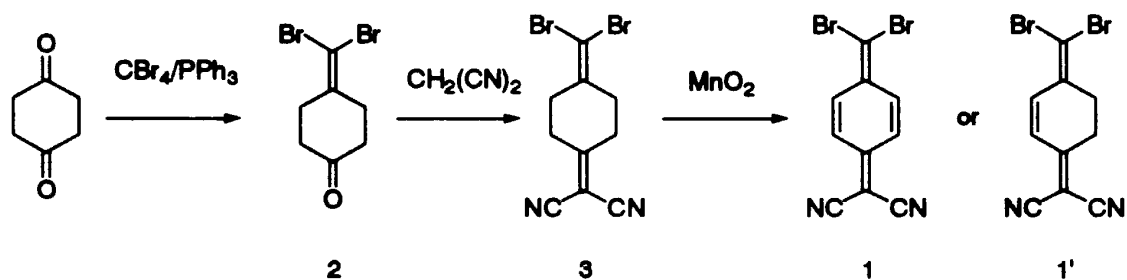
For an ionic polymerization, polymerization was carried out with a apparatus reported previously [6]. A given amount of **1** was placed in the apparatus, which was filled with nitrogen. Into it was introduced a given amount of solvent such as dichloromethane or toluene by a syringe. After the resulting solution was degassed by a freeze-thaw method (repeated twice), the apparatus was filled with nitrogen. It was sealed and set in a bath thermostated at 0 °C and a fixed amount of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  or triethylamine was injected by a syringe. After a given time of reaction, the reaction mixture was poured into an excess hexane to deposit a polymeric product. The rest of

procedure was carried out similarly to the above-mentioned radical polymerization.

## Results and Discussion

### Monomer Synthesis and Electron-Accepting Property

7,7-Bromo-8,8-dicyanoquinodimethanes (**1**) was obtained successfully by a synthetic route shown in Scheme 1.



**Scheme 1. Synthetic route of monomer**

The Wittig reaction of 1,4-cyclohexanedione with carbon tetrabromide/triphenylphosphine afforded **2** in 49% yield. The Knoevenagel condensation of **2** with malononitrile gave **3** in 95% yield. Oxidation reaction of **3** with an activated manganese in benzene yielded a desired monomer **1** in 10% yield as orange needles, but in chloroform **1'** was obtained in 31% yield as yellow needles.

Electron-accepting property of **1** was estimated as a value of first reduction potentials by a cyclic voltammetry using Ag/AgCl as a reference electrode. The value of **1** was estimated to be -0.12 V, and for comparison those of TCNQ and 7,8-bis(ethoxycarbonyl)-7,8-dicyanoquinodimethane were measured to be +0.16 V and -0.22 V, respectively. **1** was an intermediate in electron-accepting property between TCNQ and 7,8-bis(ethoxycarbonyl)-7,8-dicyanoquinodimethane as expected from difference in electron-accepting property among cyano ( $\sigma_m = 0.56$ ), bromo, ( $\sigma_m = 0.39$ ), and ethyl ester ( $\sigma_m = 0.37$ ) groups [7]. Therefore, this order could be explained well by an inductive effect.

### Polymerization

**1** polymerized on dissolving in basic polar solvents such as acetonitrile, acetone, THF, ethyl acetate and dimethyl sulfoxide (DMSO), but stable in nonpolar or less polar solvents such as benzene, toluene, chloroform and dichloromethane. Solvents of polymerizations were limited to only nonbasic, nonpolar or less polar solvents.

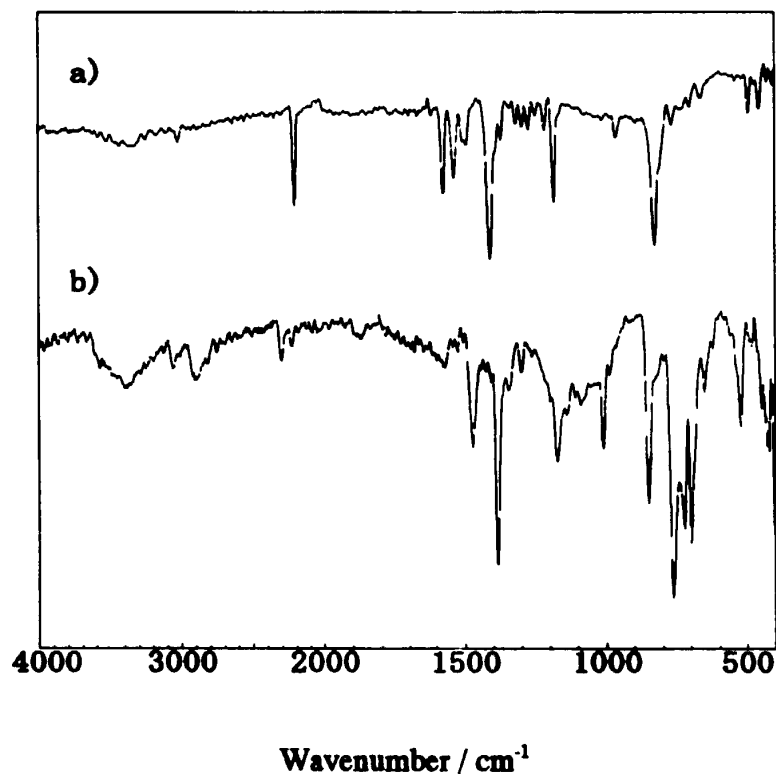
Homopolymerization of **1** was attempted with a radical initiator AIBN in benzene at 60 °C, and a base triethylamine in toluene and a cationic initiator boron trifluoride etherate in dichloromethane at 0 °C. Results of the polymerization were summarized in Table 1. All polymerizations proceeded heterogeneously. The radical initiator and the base were highly effective in the polymerization of **1**, but the cationic initiator

was not. These polymerization behaviors of **1** were similar to those of homopolymerizable substituted quinodimethanes such as 7,8-diacyl-7,8-dicyanoquinodimethanes, 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethanes and 7,7,8-tris(alkoxycarbonyl)-8-cyanoquinodimethanes [6,8-10]. All polymers were obtained as white solids, which were insoluble in benzene, toluene, chloroform and dichloromethane, and partially soluble in THF, DMSO and *N,N*-dimethylformamide.  $M_n$ s of THF-soluble parts of obtained polymers were estimated to be 500-2500, corresponding to the degree of polymerization of 2-8.  $M_n$ s of THF-insoluble parts is considered to be much higher as described below.

**Table 1 Homopolymerization of 1**

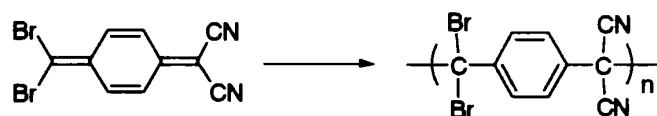
<b>1</b> /mg	Initiator [I]	[ <b>1</b> ]/[I]	Solvent mL	Temp °C	Time /h	Yield /%
30	AIBN	20	Benzene, 6	60	2	77
20	Et <sub>3</sub> N	10	Toluene, 10	0	4	95
20	BF <sub>3</sub> ·Et <sub>2</sub> O	10	CH <sub>2</sub> Cl <sub>2</sub> , 10	0	4	0

IR spectra of **1** and a polymer obtained by a radical polymerization were shown in parts a) and b) of Fig. 1, respectively. An absorption peak at 1573 cm<sup>-1</sup> due to a conjugated carbon-carbon double bond of **1** disappeared in the polymer, and the polymer exhibited absorption peaks at 2218 cm<sup>-1</sup> due to a nitrile group, 1473 and 1385 cm<sup>-1</sup> due to a carbon-carbon double bond of an aromatic ring, 849 cm<sup>-1</sup> due to a carbon-bromide bond, and 762 cm<sup>-1</sup> due to an out-of-plane deformation of a *para*-substituted benzene, characteristic of a two-adjacent-hydrogen system, respectively.



**Fig. 1 IR spectra of a) 1 and b) polymer of 1 obtained by radical polymerization (KBr).**

The polymer obtained with triethylamine showed a IR spectrum similar to one obtained with AIBN. And also, IR spectrum of the THF-soluble part of the polymer was almost same to THF-insoluble one. Elemental analysis values of the polymers were in good agreement with calculated ones of **1**. Further characterizations except for a IR spectrum and an elemental analysis were not performed because of insolubility of the polymer obtained. Polymerizations of quinodimethanes are known to occur at exocyclic methylene groups or disubstituted methylene ones with reversion of a ring to a stable aromatic structure [1,11]. It is considered, therefore, that polymers obtained with AIBN and triethylamine have following structures:



There should be two kinds of monomer unit placements in polymerization of **1** owing to a chemical structure with different exocyclic substituted methylene groups, i. e., head-to-tail or head-to-head and tail-to-tail placements. Unfortunately, a mode of monomer unit placements in the polymer could not be determined because of its insolubility.

Copolymerizations of **1** with styrene (St) in the presence of AIBN were carried out in benzene at 60 °C. Polymerizations proceeded homogeneously at high St composition in feed (runs 1 and 2), but did heterogeneously at low St composition in feed (runs 3, 4 and 5), probably due to an increased **1** unit content in the copolymers. All polymers were obtained as white solids, which were soluble in chloroform, THF and DMSO, but insoluble in hexane, diethyl ether and methanol.  $M_n$ s of copolymers were estimated to be  $1.3\text{-}20 \times 10^3$ . Results of the copolymerizations were summarized in Table 2 and the copolymerization composition curves were shown in Fig. 2, together with those of the TCQ-St and the HCQ-St systems [4] for comparison. Copolymerizations of **1** with St was found to be really in a random fashion because of the copolymerization composition curves. Monomer reactivity ratios of the copolymerization of **1** with St were calculated, according to integrated copolymerization equation and intersection methods, to be  $r_1(\mathbf{1}) = 14.0$  and  $r_2(\text{St}) = 0.0005$  at 60 °C. Alfrey-Price's  $Q$  and  $e$  values of **1** were calculated on the basis of the monomer reactivity ratios to be 336 and +1.45, respectively, indicating that **1** is highly conjugative and electron-accepting. The monomer reactivity ratios of copolymerizations of TCQ and of HCQ with St were reported to be  $r_1(\text{TCQ}) = 85$  and

**Table 2** Copolymerization<sup>1)</sup> of **1** with St in Benzene

Run no.	Monomer Feed			Time /h	Yield /%	Anal.		Copolym. 1/mol%	$M_n /10^3$
	1/mmol	St/mmol	1/mol%			C%	N%		
1	0.090	19.1	0.5	2	2	54.29	6.27	44.5	20.0
2	0.075	1.44	5.0	2	8	45.28	7.87	70.1	7.0
3	0.075	0.68	10.0	2	18	43.39	8.19	76.9	6.0
4	0.075	0.43	14.8	2	44	42.37	8.31	79.4	2.9
5	0.075	0.20	27.7	1	40	41.59	8.37	81.5	1.3

1) AIBN, 0.6 mg. Benzene, 10 mL.

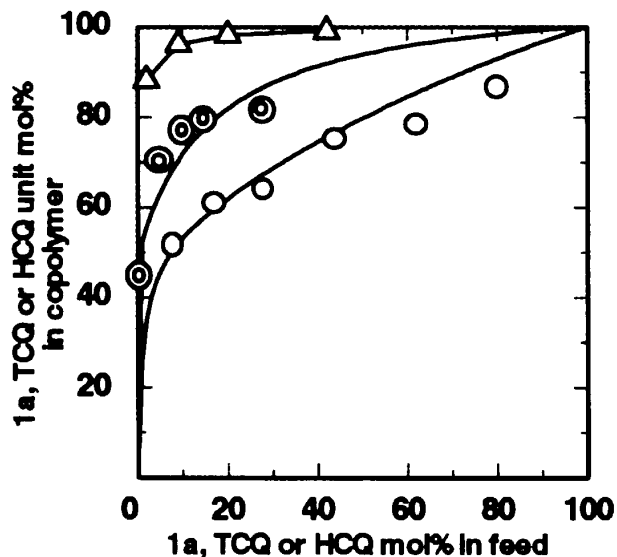


Fig. 2 Copolymerization composition curves for the (⊙) 1-St, (Δ) TCQ-St, and (○) HCQ-St systems, respectively

$r_2(\text{St}) = 0$  at 22 °C for the TCQ-St system and  $r_1(\text{HCQ}) = 3.0$  and  $r_2(\text{St}) = 0.02$  at 50 °C for the HCQ-St system, respectively [4]. The relative reactivity of **1**, TCQ and HCQ towards a polymeric radical with a St terminal unit was estimated from the comparison with  $1/r_2$  values to be TCQ ( $1/0$ ) > **1** ( $1/0.0005$ ) > HCQ ( $1/0.02$ ), indicating that **1** is an intermediate in reactivity between TCQ and HCQ.

In conclusions, **1** was successfully synthesized as orange needle crystals though the yield was low. **1** was homopolymerizable with AIBN and triethylamine, but not with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . **1** copolymerized with St in a random fashion and it was concluded to be a highly conjugative, electron-accepting monomer.

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