

distribution will be considered.

In conclusion, we have demonstrated the pronounced effect of laser repetition rate on the molecular weight distribution of photopolymerized methyl methacrylate. The narrow peaks found in the GPC chromatogram of poly(methyl methacrylate) generated by firing the laser at a repetition rate of 40 Hz (25 ms between successive pulses) have been initially described by a simple kinetic model based upon a series of Poisson distribution functions. Complete details of the computer simulation of the molecular weight distributions as a function of pulsing frequency as well as several refinements to our current approach, will be published in a full paper. This paper serves to provide a basis for describing the crucial effect of laser parameters on the polymerization of monofunctional monomers. Extension of this work to encompass multifunctional monomers is in progress.

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Preparation and Polymerization Behavior of 2,4-Dicyanostyrene and 2,4,6-Tricyanostyrene

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ABSTRACT: 2,4-Dicyanostyrene (DCS) was successfully prepared in 18% yield via a series of six reactions and 2,4,6-tricyanostyrene (TCS) was barely in 0.15% yield via five reaction steps. It was found that DCS and TCS are polymerizable with radical and anionic initiators. DCS and TCS are copolymerizable in a random and an alternating fashion, respectively, with styrene (St) in the presence of 2,2'-azobis(isobutyronitrile) (AIBN) in acetonitrile to afford the monomer reactivity ratios $r_1(\text{DCS}) = 1.85 \pm 0.03$ and $r_2(\text{St}) = 0.08 \pm 0.03$ for the DCS-St system at 60 °C and $r_1(\text{TCS}) = 0.02 \pm 0.02$ and $r_2(\text{St}) = 0.04 \pm 0.01$ for the TCS-St system at 60 °C. By using these values, the Alfrey-Price's Q and e values were determined to be $Q = 4.10$ and $e = +0.58$ for DCS and $Q = 2.83$ and $e = +1.86$ for TCS. When DCS or TCS was mixed with *p*-(dimethylamino)styrene (DMASt), the former system was colored pale yellow and did not undergo further reaction, while the latter one was colored red and underwent spontaneous reaction to give polymeric product containing homopolymers of TCS and DMASt, suggesting that anionic polymerization of TCS and cationic one of DMASt occur at the same time.

Introduction

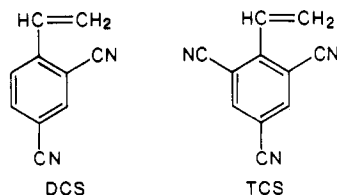
Only a few compounds have been reported of the electron-accepting group substituted styrenes carrying more than two strongly electron-withdrawing groups on the benzene nucleus, such as 2,4,6-trinitrostyrene (TNS),¹⁻³ 2,4,6-tris(trifluoromethyl)styrene (TFS),⁴ and 2,5-, 3,5-, and 3,4-bis(trifluoromethyl)styrenes.⁵ Although the cyano ($\sigma_p = 0.674$)⁶ group is strongly electron withdrawing and its character is just intermediate between that of nitro ($\sigma_p = 0.778$)⁶ and trifluoromethyl ($\sigma_p = 0.532$)⁶ groups, polycyano-substituted styrenes have not yet been found in any literature, but *o*-, *m*-, and *p*-monocyanostyrenes⁷⁻⁹ were

reported. In addition, because the cyano group appears to be almost insensitive to free radical species compared with the nitro group, it was expected that polycyano-substituted styrenes would be readily polymerizable with a free radical initiator while TNS is not so polymerizable.^{1,2}

In this work, 2,4-dicyanostyrene (DCS) and 2,4,6-tricyanostyrene (TCS) were first prepared as new polycyano-substituted styrenes, and their polymerization behaviors were studied.

Experimental Section

***p*-Bromoethylbenzene (1).**¹⁰ *p*-Bromoacetophenone (83.7 g, 0.42 mol) was reduced with zinc amalgam¹¹ which was prepared



from 170 g (2.60 mol) of mossy zinc and 17 g (0.063 mol) of mercuric chloride¹² to obtain 59.2 g (in 76% yield) of colorless oily *p*-bromoethylbenzene (1), boiling at 87–88 °C under pressure of 18 mmHg (lit.¹⁰ bp 188–189 °C): ¹H NMR (CCl₄) δ 1.20 (t, *J* = 7.5 Hz, 3 H), 2.57 (q, *J* = 7.5 Hz, 2 H), 6.97 (d, *J* = 7.5 Hz, 2 H), 7.33 (d, *J* = 7.5 Hz, 2 H).

***p*-Ethylbenzonitrile (2).**¹³ The compound 1 (59.2 g, 0.32 mol) was reacted with 34.4 g (0.38 mol) of copper(I) cyanide in 50 mL of *N,N*-dimethylformamide (DMF) under refluxing for 6 h to obtain 38.0 g (in 88% yield) of colorless oily *p*-ethylbenzonitrile (2) boiling at 84–86 °C under pressure of 5 mmHg: IR (NaCl) ν(CN) 2240 cm⁻¹; ¹H NMR (CCl₄) δ 1.25 (t, *J* = 7.5 Hz, 3 H), 2.70 (q, *J* = 7.5 Hz, 2 H), 7.23 (d, *J* = 7.5 Hz, 2 H), 7.73 (d, *J* = 7.5 Hz, 2 H).

3-Bromo-4-ethylbenzonitrile (3). The compound 2 (14.1 g, 0.11 mol) was reacted with 19.8 g (0.12 mol) bromine in the presence of 46.9 g (0.35 mol) of finely powdered anhydrous aluminum chloride to give 18.5 g (in 81.5% yield) of colorless oily 3-bromo-4-ethylbenzonitrile (3), boiling at 83–85 °C under pressure of 1.5 mmHg, which crystallized on standing for a long time: mp 43.5–45.0 °C: IR (NaCl) ν(CN) 2220, σ(CH) 880, 835 cm⁻¹; ¹H NMR (CCl₄) δ 1.23 (t, *J* = 7.5 Hz, 3 H), 2.77 (q, *J* = 7.5 Hz, 2 H), 7.2–7.7 (m, 3 H). Anal. Calcd for C₉H₉BrN: H, 3.84; C, 51.46; N, 6.67; Br, 38.03. Found: H, 3.67; C, 51.07; N, 6.45; Br, 38.81.

2,4-Dicyano-1-ethylbenzene (4). The compound 3 was reacted with copper(I) cyanide in DMF under refluxing for 6 h to give crystalline material which was recrystallized from hexane to obtain white needles: mp 72.5–73.5 °C; IR (KBr) ν(CN) 2230, σ(CH) 890, 840 cm⁻¹; ¹H NMR (CCl₄) δ 1.37 (t, *J* = 7.5 Hz, 3 H), 2.95 (q, *J* = 7.5 Hz, 2 H), 7.3–7.9 (m, 3 H). Anal. Calcd for C₁₀H₈N₂: H, 5.16; C, 76.90; N, 17.94. Found: H, 5.02; C, 76.51; N, 17.86.

1-(1-Bromoethyl)-2,4-dicyanobenzene (5). The compound 4 (10.0 g, 0.064 mol) was brominated with 12.1 g (0.038 mol) of *N*-bromosuccinimide (NBS) in the presence of 0.05 g of AIBN in 80 mL of carbon tetrachloride under refluxing for 24 h to give a brown solid which was recrystallized from isopropyl ether to obtain 11.2 g (in 70.4% yield) of pale orange needles of 5: mp 90–91 °C; IR (KBr) ν(CN) 2225, σ(CH) 900, 860 cm⁻¹; ¹H NMR (CCl₄) δ 2.09 (d, *J* = 7.5 Hz, 3 H), 5.48 (q, *J* = 7.5 Hz, 1 H), 7.58–8.20 (m, 3 H). Anal. Calcd for C₁₀H₇N₂Br: H, 3.00; C, 51.09; N, 11.92; Br, 33.99. Found: H, 3.08; C, 51.43; N, 12.05; Br, 33.44.

2,4-Dicyanostyrene (DCS). Compound 5 (3.9 g, 16.6 mmol), 5.4 g (53.8 mmol) of triethylamine, and 5 mg of 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL) as a radical polymerization inhibitor were dissolved in 20 mL of acetonitrile and the solution was refluxed with stirring under nitrogen for 9 h. The reaction mixture was placed under reduced pressure to give a brown solid, which was dissolved in 30 mL of chloroform. The resulting solution was washed with two 10-mL portions of water and two 10-mL portions of 5% sodium hydroxide solution and dried over anhydrous magnesium sulfate. It was placed under reduced pressure to evaporate the solution until its volume amounted to about 5 mL. The concentrate was passed through a column of 2-cm diameter and 20-cm length packed with silica gel, using chloroform as eluent. The first elution band was collected and placed under reduced pressure to obtain 1.8 g of white solid, which was recrystallized from dry ethanol to give 1.7 g (in 67.5% yield) of white needles of DCS, which is soluble in benzene, toluene, acetone, chloroform, tetrahydrofuran (THF), and acetonitrile and sparingly soluble in isopropyl ether and hexane: mp 155–156 °C; UV (CH₃CN) 267 nm (ε 1.55 × 10⁴); IR (KBr) ν(C=C) 1595, σ(CH) 900, 845 cm⁻¹; ¹H NMR (CDCl₃) δ 5.79 (d, *J* = 11.4 Hz, 1 H), 6.14 (d, *J* = 17.44 Hz, 1 H), 7.14 (dd, *J* = 17.4 and 11.4 Hz, 1 H), 7.80 (s, 2 H), 7.93 (s, 1 H). Anal. Calcd for C₁₀H₆N₂: H, 3.92; C, 77.91; N, 18.17. Found: H, 4.00; C, 77.85; N, 18.15.

2,6-Dibromo-4-cyanotoluene (7). *p*-Tolunitrile (6) (25 g, 0.26

mol) was brominated with 85.2 g (0.53 mol) of bromine in the presence of 90.7 g (0.68 mol) of finely divided anhydrous aluminum chloride 70–80 °C for 7 h. The reaction mixture was poured into 500 mL of ice water containing 100 mL of concentrated hydrochloric acid. The mixture was extracted with four 200-mL portions of toluene. The combined extract was washed and evaporated to obtain a liquid residue which was fractionally distilled under pressure of 0.5 mmHg to obtain 30.5 g of the fraction boiling at 80–100 °C and 28.1 g of the fraction boiling above 100 °C. The latter fraction was recrystallized three times from isopropyl ether to give 17.1 g (in 29.2% yield) of pale brown needles of 7: mp 95–98 °C; IR (KBr) ν(CN) 2240, ν(C=C) 1530, 1450 cm⁻¹; ¹H NMR (CDCl₃) δ 2.63 (s, 3 H), 7.80 (s, 2 H).

2,4,6-Tricyanotoluene (8). Compound 7 (20.0 g, 0.073 mol) was reacted with 15.5 g (0.173 mol) of copper(I) cyanide in 100 mL of DMF under refluxing for 12 h. The reaction mixture was slowly poured into 500 mL of water to deposit dark green solid which was suspended in the solution composed of 60 g of ferric chloride hexahydrate, 15 mL of concentrated hydrochloric acid, and 100 mL of water. The resulting suspension was kept warm at 100 °C with stirring for 6 h and extracted with two 200-mL portions of toluene. The combined extract was washed with two 50-mL portions of 5% hydrochloric acid, two 50-mL portions of 10% sodium hydroxide solution, and two 100-mL portions of water and then dried over anhydrous magnesium sulfate. It was placed under reduced pressure to obtain 2.5 g of yellow solid, which was recrystallized from a mixture of dichloromethane and hexane to give 2.4 g (in 19.2% yield) of pale yellow needles of 8: mp 132–133 °C; IR (KBr) ν(CN) 2240, ν(C=C) 1465, σ(CH) 925 cm⁻¹; ¹H NMR (CDCl₃) δ 2.87 (s, 3 H), 78.11 (s, 2 H). Anal. Calcd for C₁₀H₅N₃: H, 3.02; C, 71.84; N, 25.14. Found: H, 2.67; C, 72.72; N, 24.61.

2,4,6-Tricyano-1-ethylbenzene (9). The solution of 1.0 g (6.0 mmol) of 8 and 2.8 g (24.1 mmol) of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in 50 mL of THF was added dropwise into the solution of 24 mmol of lithium diisopropylamide (LDA) in 100 mL of THF cooled to -78 °C with stirring. The resulting dark red solution was kept cold at -78 °C with stirring for 1 h, and 8.7 g (61.0 mmol) of methyl iodide was added. Furthermore, it was kept cold at -78 °C with stirring for an additional 1 h and, then, warmed slowly to room temperature. It was placed under reduced pressure to remove solvents, and the residual brown solid was dissolved in 100 mL of dichloromethane. The solution was washed with two 50-mL portions of 5% hydrochloric acid and two 50-mL portions of water and then dried over anhydrous magnesium sulfate. It was placed under reduced pressure to remove solvents and the residue was chromatographed over silica gel by using dichloromethane as eluent to separate a yellow portion, which was evaporated to give 0.58 g (in 53.5% yield) of yellow solid of 9: mp 123–125 °C; IR (KBr) ν(CN) 2240, ν(C=C) 1455, σ(CH) 925 cm⁻¹; ¹H NMR (CDCl₃) δ 1.41 (t, *J* = 7.5 Hz, 3 H), 3.20 (q, *J* = 7.5 Hz, 2 H), 8.13 (s, 2 H). Anal. Calcd for C₁₁H₇N₃: H, 3.89; C, 72.92; N, 23.19. Found: H, 2.89; C, 72.45; N, 22.65.

1-(1-Bromoethyl)-2,4,6-tricyanobenzene (10). Compound 9 (1.0 g, 5.5 mmol), 1.0 g (5.8 mmol) of NBS, 5 mg of AIBN, and 40 mL of carbon tetrachloride were placed in a 100-mL flask. While the mixture was refluxed with stirring for 12 days, additional portions composed of 5 mg of AIBN and 0.5 g of NBS were added every day. The hot mixture was filtered to remove solid material such as succinimide. The filtrate was placed under reduced pressure to obtain brown viscous residue, which was dissolved in 30 mL of chloroform, and the resulting solution was washed with three 50-mL portions of water and dried over anhydrous magnesium sulfate. It was placed under reduced pressure to yield pale brown viscous material, which was recrystallized from isopropyl ether to give 0.65 g (in 45% yield) of colorless crystal of 10: mp 125–127 °C; IR (KBr) ν(CN) 2240, ν(C=C) 1465, σ(CH) 930 cm⁻¹; ¹H NMR (CDCl₃) δ 2.29 (d, *J* = 7.5 Hz, 3 H), 5.65 (q, *J* = 7.5 Hz, 1 H), 8.17 (s, 2 H). Anal. Calcd for C₁₁H₆N₃Br: H, 2.33; C, 50.80; N, 16.14; Br, 30.73. Found: H, 2.31; C, 50.56; N, 16.25; Br, 30.88.

2,4,6-Tricyanostyrene (TCS). Compound 10 (0.3 g, 1.2 mmol), 0.2 g (2.0 mmol) of triethylamine, and 1 mg of TEMPOL were dissolved in 10 mL of acetonitrile and the solution was refluxed with stirring under nitrogen for 5 h. The reaction mixture was placed under reduced pressure to obtain dark yellow solid,

which was dissolved in 20 mL of chloroform. The resulting solution was washed successively with two 10-mL portions of water, two 10-mL portions of 5% sodium hydroxide solution, and 10 mL of water and, then, dried over anhydrous magnesium sulfate. It was placed under reduced pressure to remove solvents. The remaining yellow solid was dissolved in 1 mL of benzene. The resulting solution was passed through a column of 2-cm diameter and 20-cm length packed with silica gel, using isopropyl ether as eluent. The first elution band separated was placed under reduced pressure to obtain 32 mg of pale yellow solid, which was recrystallized from dry ethanol to give 22.1 mg (in 10.7% yield) of pale yellow needles of TCS, which is soluble in benzene, toluene, chloroform, THF, and acetonitrile and sparingly soluble in ethanol and hexane: mp 143–144 °C; UV (CH₃CN) 237 (ϵ 3.06 \times 10⁴), 267 nm (ϵ 1.35 \times 10⁴); IR (KBr) ν (CN) 2240, ν (C=C) 1630, 1595, 1455, ν (CH) 975, 955, 925, 780 cm⁻¹; ¹H NMR (CDCl₃) δ 6.14 (d, J = 11.4 Hz, 1 H), 6.49 (d, J = 17.4 Hz, 1 H), 7.12 (dd, J = 17.4 and 11.4 Hz, 1 H), 8.14 (s, 2 H). Anal. Calcd for C₁₁H₅N₃: H, 2.81; C, 73.74; N, 23.45. Found: H, 2.89; C, 74.05; N, 23.08.

Other Reagents. *p*-(Dimethylamino)styrene (DMASt), prepared according to the procedure of Strassburg et al.,¹⁴ was stirred over calcium hydride for 3 h and distilled at 91 °C under pressure of 3 mmHg. Styrene (St) was washed with 2% sodium hydroxide solution and water, dried over barium oxide for 5 h and then over calcium hydride, and distilled at 52 °C under pressure of 30 mmHg. Triethylamine and diisopropylamine were refluxed over calcium hydride for 5 h and distilled at 88.5 and 82 °C, respectively. THF was refluxed over lithium aluminum hydride for 12 h and then distilled at 66 °C over benzophenone–metal sodium. Benzene, acetonitrile, and carbon tetrachloride were purified from commercial products according to conventional methods. AIBN was recrystallized from ethanol. Butyllithium (Aldrich Co.) was used without further purification. Tetrabutylammonium perchlorate was dried at 150 °C under pressure of 0.01 mmHg for 16 h. Methyl iodide was distilled at 42.5 °C under dark conditions. Isophthalonitrile (DCB) was recrystallized from benzene. 1,3,5-Tricyanobenzene (TCB) was prepared according to the method of Bailey et al.¹⁵ and recrystallized from ethanol.

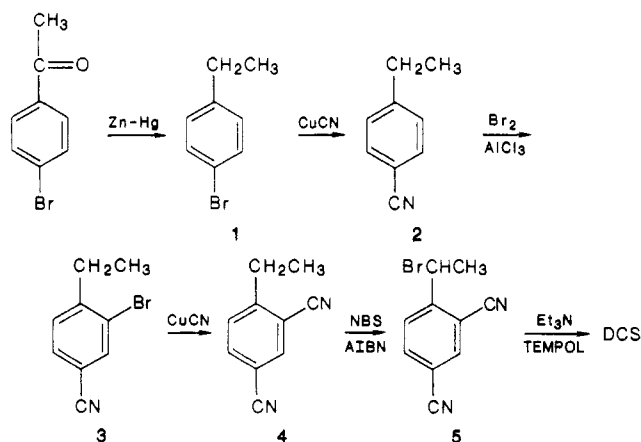
Polymerization Procedure. In the case of radical polymerization with AIBN, given amounts of DCS or TCS as monomer, acetonitrile or benzene as solvent, and AIBN were placed in an ampule, which was degassed by the freeze–thaw method (repeatedly three times) and sealed. The ampule was set in a bath thermostated at 60 °C for the time of polymerization and then opened. The reaction mixture was poured into an excess methanol to precipitate the polymer. For purification, the polymer obtained was dissolved again in a small amount of acetonitrile and the resulting solution was poured into excess methanol to precipitate the polymer, which was dried under reduced pressure.

In the case of polymerization with butyllithium, the apparatus reported in the previous paper¹⁶ was employed. Given amounts of DCS or TCS as monomer and THF as solvent were placed in the apparatus which was degassed by the freeze–thaw method (repeatedly three times) and then filled with argon. Into the apparatus immersed in an ice–water bath, a given amount of butyllithium in THF was injected by means of a syringe. After 24 h, the reaction mixture was poured into excess hexane to deposit the polymer. The rest of the procedure was similar to above mentioned one for the polymerization with AIBN except for using THF and hexane instead of acetonitrile and methanol as solvent and precipitant for purification.

In the case of copolymerizations of the DCS–St, TCS–St, and DCS–DMASt systems, given amounts of DCS or TCS as monomer, St or DMASt as comonomer, acetonitrile as solvent, and 0.5 mol % AIBN to the total monomer were placed in an ampule, which was degassed by the freeze–thaw method and sealed. The ampule was set in a bath thermostated at 60 °C for the time of polymerization and then opened. The reaction mixture was poured into an excess methanol to precipitate the copolymer. The rest of the procedure was similar to above-mentioned one for the radical polymerization.

In the case of the reaction of the TCS–DMASt system without initiator, 28.6 mg of TCS and 55.1 mg of DMASt were placed in an ampule, which was degassed by the freeze–thaw method and sealed. The ampule was kept at room temperature for 98 h and then opened. The reaction mixture was divided into four fractions

Scheme I



by the dissolution–precipitation process as follows: The reaction mixture was dissolved in 5 mL of THF and the resulting solution was poured into 100 mL of isopropyl ether to give a suspension, which was separated into supernatant and precipitate by centrifugation. The isopropyl ether solution as supernatant was placed under reduced pressure to remove solvents. Viscous material (36 mg) as fraction I was obtained. The precipitate (26 mg) was dissolved again in 5 mL of THF and the resulting solution was poured into 100 mL of methanol to give the second suspension. The methanol solution as supernatant was placed under reduced pressure to remove solvents. Solid residue (4.5 mg) as fraction II was obtained. The precipitate (21.5 mg) was dissolved in 10 mL of THF and the resulting solution was poured into 100 mL of methanol to give 8.1 mg of a precipitate as fraction IV. The filtrate was evaporated under reduced pressure to give 13.3 mg of pale yellow solid material as fraction III.

Characterization. Voltammetric measurement was carried out at room temperature by using a Yanagimoto new cyclic voltammetric analyzer VMA-010 instrument. Dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L) as solvent, a glassy carbon as working electrode, and a platinum wire as third electrode were used.

Copolymer composition was established by elemental analysis. The number-average molecular weight, M_n , of the polymers and the copolymers was determined without correction by gel permeation chromatography (GPC) using standard polystyrene as reference and THF as eluent. Solution viscosity was determined at 30 °C by using the Ostwald viscometer and acetone for the polymer of DCS and THF for the copolymer of the DCS–St system as solvent. In ¹H NMR measurement solvents employed were acetone-*d*₆ for the polymers of DCS and TCS and chloroform-*d* for the fractions of the reaction product of TCS with DMASt.

Results and Discussion

Preparation of DCS. DCS was successfully prepared via a series of six reactions as shown in the Scheme I.

p-Bromoacetophenone was subjected to the Clemmensen reduction to give 1 in 76% yield. The compound 1 underwent the Rosenmund–von Brawn reaction to yield 2 in 88% yield. The compound 2 was brominated with Friedel–Crafts catalyst to obtain 3 in 81.5% yield. The compound 3 was again subjected to the Rosenmund–von Brawn reaction to give 4 in 76% yield, which was brominated with NBS in the presence of AIBN to give 5 in 70% yield. Finally, the compound 5 was subjected to dehydrobromination with triethylamine in the presence of a small amount of TEMPOL as a free radical scavenger in refluxing acetonitrile to give DCS in 67.5% yield without polymer of DCS. The overall yield of DCS was 18%. When dehydrobromination of 5 was carried out without any free radical scavenger, only the polymer of DCS was obtained instead of the monomer. When picric acid, 4-*tert*-butylcatechol, and hydroquinone were used instead

Table I
First Reduction Potential, E_1 , and Electron Affinity, EA, of 2,4,6-Tricyanostyrene (TCS), 2,4-Dicyanostyrene (DCS), 1,3,5-Tricyanobenzene (TCB), and 1,3-Dicyanobenzene (DCB)

compound	E_1 , ^b V	EA, ^c eV	compound	E_1 , ^b V	EA, ^c eV
TCS	-1.29	1.78	DCS	-1.65	1.42
TCB	-1.50	1.57	DCB	-1.88	1.19

^a Solvent: dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L). Reference electrode: Ag/AgLc.
^b Relative error: ± 0.01 V. ^c Calculated by using the equation $EA = -E_{1/2} + 3.09$ V.³⁰

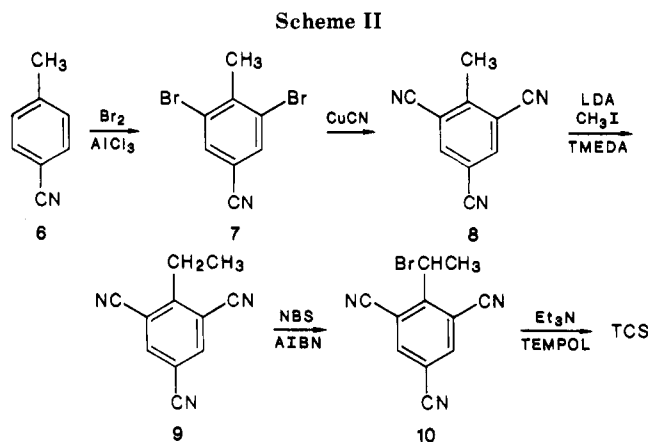
of TEMPOL the yield of monomeric DCS was as low as 20–40%, and the polymer of DCS was formed in above 50% yield.

Preparation of TCS. Preparation of TCS was carried out even in a low total yield via a series of five reaction steps as shown in the Scheme II. *p*-Tolunitrile (6) was brominated in the presence of anhydrous aluminum chloride at room temperature to give a mixture of 2-bromo-4-cyanotoluene, 2,6-dibromo-4-cyanotoluene (7), and 2,3,6-tribromo-4-cyanotoluene. It was fractionally distilled under the reduced pressure of 0.5 mmHg to give the fraction boiling at 80–100 °C, mainly composed of 2-bromo-4-cyanotoluene, and the fraction boiling above 100 °C, composed of 7 and 2,3,6-tribromo-4-cyanotoluene. The latter fraction was recrystallized three times from isopropyl ether to give 7 in 29% yield, which was subjected to the Rosenmund–von Braun reaction to give 8 in 19% yield. This reaction was carried out under various experimental conditions such as reaction time, reaction temperature, and amount of copper(I) cyanide, but the yield of 8 unfortunately could not be beyond 20%.

Instead of 6, 2 underwent the bromination in the presence of Lewis acid to give 3-bromo-4-ethylbenzonitrile, 2,5-dibromo-4-ethylbenzonitrile, and 2,3,5-tribromo-4-ethylbenzonitrile. The intended compound, 3,5-dibromo-4-ethylbenzonitrile, could not be obtained.

According to the method of Mao and Boekelheide,¹⁷ 8 underwent the methylation to obtain 9 in 54% yield. Free radical bromination of 9 gave 10 in 45% yield. It was found that this bromination of 9 (45% yield for the reaction time of 12 days) takes place much more reluctantly compared to that of 4 (67.5% yield for the reaction time of 1 day), probably due to serious steric hindrance effect of two ortho cyano groups.

Dehydrobromination of 10 was carried out in a process similar to DCS. When it was performed under the same conditions as DCS (for 8 h), 10 reacted nearly quantitatively but monomeric TCS was barely obtained in 5% yield. The polymer of TCS with the molecular weight of 2500 (by GPC) was produced abundantly, probably suggesting that anionic polymerization of TCS can be induced



with triethylamine. When the reaction time was reduced to 5 h, about a half amount of 10 remained unreacted and polymer of TCS had not yet formed at that time. Therefore, the reaction product in about a half extent of reaction was chromatographed with a silica gel column using isopropyl ether as eluent to separate monomeric TCS and unreacted 10. The overall yield of TCS was barely 0.15%.

Electron-Accepting Character of DCS, TCS, DCB, and TCB. First reduction potential, E_1 , for DCS, TCS, DCB, and TCB and their electron affinity values, EA, are summarized in Table I. TCS and TCB were found to be more electron accepting than DCS and DCB, respectively, the electron-accepting character apparently depending on the number of cyano groups. TCS and DCS are more electron accepting than TCB and DCB, respectively, implying an electron-withdrawing character of the vinyl group even though its Hammett's substituent or Taft's polar substituent constant, σ^* , has not been reported yet. This character is reasonably assumed also by comparing the Taft's substituent constants between 1-propenyl ($\sigma^* = 0.360$)¹⁸ and *n*-propyl groups ($\sigma^* = -0.15$).¹⁸

Polymerization of DCS and TCS. It was found that DCS and TCS are polymerizable with initiators, AIBN, butyllithium, and triethylamine, as summarized in Table II. Their polymers were obtained as white powder. The polymer of DCS is soluble in acetonitrile, acetone, and DMF and insoluble in benzene, chloroform, ethyl acetate, methanol, and THF. The polymer of TCS also exhibits a similar solubility behavior except for THF, in which it is soluble.

In IR measurements, DCS and TCS exhibit an absorption at 1595 cm^{-1} due to the stretching vibration of the carbon–carbon double bond and their polymers do not. In ¹H NMR spectra, DCS and TCS show the peaks in the region δ 6.0–7.3 assigned to the protons of vinyl group and their polymers have a broad absorption in the region δ 2.7–2.0 due to methylene and methine protons. It is

Table II
Polymerizations of 2,4-Dicyanostyrene (DCS) and 2,4,6-Tricyanostyrene (TCS)

run	[M], ^a mg	[I] ^b	[M]/[I]	solvent, mL	temp, °C	time, h	conv, %	η_{sp}/C , ^c dL/g	$\bar{M}_n/10^4$ ^d
DCS									
1	191.6	AIBN	128	CH ₃ CN, 8	60	24	55.7	0.31	
2	31.4	BuLi	12	toluene, 5	0	24	4.2	0.1	
3	30.4	Et ₃ N	10	toluene, 5	0	24	2.5	0.1	
TCS									
4	45.7	AIBN	42	benzene, 1	60	17	57.3		1.03
5	25.1	BuLi	12	toluene, 4	0	20	1.8		0.1
6	30.4	Et ₃ N	10	toluene, 5	0	24	1.5		0.1

^a Monomer feed. ^b Initiator. ^c The solution viscosity was measured with acetone as solvent at 30 °C. ^d Determined by GPC with THF as eluent.

Table III
Copolymerizations^a of 2,4-Dicyanostyrene (DCS) and 2,4,6-Tricyanostyrene (TCS) with Styrene (St) in Acetonitrile at 60 °C

run	monomer feed			time, h	conv, %	copolymer and its composition					
	comonomer, mg	St, mg	comonomer, mol %			elem. anal.			comonomer, mol %	$\eta_{sp}/C,^b$ dL/g	$\bar{M}_n/10^4^c$
						H, %	C, %	N, %			
DCS Comonomer											
1	76.9	480.0	9.75	2.0	9.61	5.40	84.08	10.52	48.3		
2	100.0	272.7	19.9	2.0	11.0	5.78	82.53	11.34	52.9	0.22	
3	65.4	133.5	24.9	3.0	10.8	5.63	82.60	11.77	55.4		
4	136.9	221.8	29.4	1.8	9.79	5.27	82.04	12.69	61.0	0.22	
5	150.0	154.5	39.6	3.0	19.4	5.08	81.73	13.19	64.2		
6	143.0	117.3	42.5	1.8	12.6	4.99	80.99	14.13	70.3	0.24	
7	189.0	86.3	59.7	1.5	10.3	4.89	79.59	15.51	79.8		
8	235.6	62.9	71.7	1.3	8.07	4.81	79.16	16.03	83.5		
TCS Comonomer											
9	53.6	308.3	9.2	4.0	1.0	5.12	81.92	12.96	41.8		1.03
10	54.8	141.3	18.4	2.5	5.6	4.80	81.48	13.72	45.0		5.2
11	87.9	83.6	37.9	4.0	16.7	4.19	81.03	14.78	49.8		6.0
12	109.4	72.7	46.7	7.0	6.0	4.57	80.87	14.56	48.8		2.3
13	145.7	54.2	61.0	8.0	7.3	4.95	80.29	14.76	50.0		2.5

^a Initiator, AIBN 0.5 mol % to total monomer amount; acetonitrile as solvent, 5 mL for the DCS-St system and 3 mL for the TCS-St system. ^b The solution viscosity was measured by using THF as solvent at 30 °C. ^c Determined by GPC with THF as eluent.

concluded, therefore, that DCS and TCS polymerize through a conventional vinyl polymerization.

According to a well-known Tsuruta's classification¹⁹ of monomers and initiators in anionic polymerization, DCS and TCS are considered to be members of the class of the most susceptible monomers, i.e., nitroethylene, methyl α -cyanoacrylate, vinylidene cyanide, etc., because they are polymerizable with a weak base such as triethylamine.

Many attempts to polymerize TNS with radical and other initiators failed¹ but TNS was spontaneously copolymerized alternately with 2- and 4-vinylpyridines (2VP and 4VP) and DMASt.² Its anionic polymerization, with tertiary amines only, such as triethylamine and vinylpyridines, took place successfully.³ The lack of the polymerizability with radical initiator for TNS was proposed to be associated with the facts that 1,3,5-trinitrobenzene is an efficient retarder or inhibitor of vinyl radical polymerization²⁰ and that the retarding effect of aromatic nitro compounds is related to the number of nitro groups.^{21,22} The anionic polymerizability of TNS with tertiary amines such as triethylamine and pyridine³ relates to the fact that TNS is electron accepting enough to interact with those weak bases.

It was reported that TFS is not polymerizable with a radical initiator,⁴ while 2,5-, 3,5-, and 3,4-bis(trifluoromethyl)styrenes are polymerizable.⁵ It was suggested that the lack of the polymerizability for TFS arises from steric hindrance by two ortho trifluoromethyl groups.⁴ Taft's steric substituent constants, E_s , of trifluoromethyl, nitro, and cyano groups are reported²³ to be -2.4, -1.01, and -0.50, respectively. The trifluoromethyl group with the lowest value exhibits a steric hindrance effect which is sufficient to prevent polymerization, while the cyano group with the highest value has too small an effect to prevent polymerization. With regard to TNS, the steric effect cannot be discussed at the moment because TNS is polymerizable only with weak bases such as triethylamine and pyridine³ but not polymerizable with other strong base¹ such as sodium alkoxide and also radical initiators.¹

Copolymerizations of DCS and TCS with St. Table III summarizes the results of the copolymerizations of DCS and TCS with St and Figure 1 shows their composition diagram. These results were calculated according to the intersection²⁴ and the Kelen-Tüdös methods²⁵ to obtain the monomer reactivity ratios $r_1(\text{DCS}) = 1.85 \pm 0.3$ and $r_2(\text{St}) = 0.08 \pm 0.03$ at 60 °C for the copolymerization of

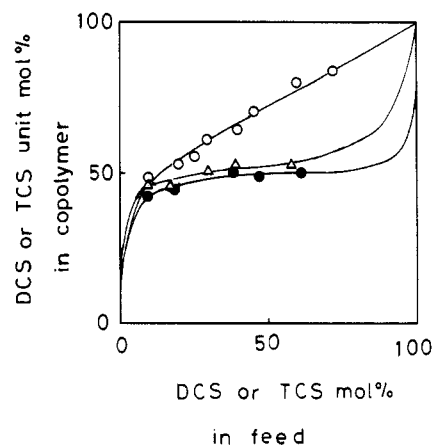


Figure 1. Composition diagrams for the copolymerization of the DCS-St (○), TCS-St (●), and DCS-DMASt (△) systems in acetonitrile at 60 °C.

DCS with St and $r_1(\text{TCS}) = 0.02 \pm 0.02$ and $r_2(\text{St}) = 0.04 \pm 0.01$ at 60 °C for the copolymerization of TCS with St. Alfrey-Price's Q and e values of the DCS and TCS were determined by using these values to be $Q = 4.10$ and $e = +0.58$ for DCS and $Q = 2.83$ and $e = +1.86$ for TCS, indicating that both DCS and TCS are highly conjugative as well as electron accepting. The copolymerization of *p*-cyanostyrene (MCS) with St in the presence of benzoyl peroxide at 60 °C in bulk was reported to give its monomer reactivity ratios, $r_1(\text{MCS}) = 1.16 \pm 0.13$ and $r_2(\text{St}) = 0.28 \pm 0.025$.²⁶ The products, r_1r_2 , of the monomer reactivity ratios for the copolymerizations of MCS, DCS, and TCS with St are 0.325, 0.148, and 0.0008, respectively. Thus, the alternating tendency of these copolymerizations increases in the order of MCS, DCS, and TCS, corresponding well to an electron-accepting character of these cyano-substituted styrenes, the more cyano groups the more electron accepting.

Copolymerizations of DCS and TCS with DMASt. Spontaneous copolymerization of TNS with 4VP was found by Yang and Gaoni² and Butler and Sivaramakrishnan³ even though the polymerization mechanism appears to remain still somewhat equivocal. It was expected on the analogy between nitro and cyano groups that DCS and TCS would be able to polymerize spontaneously with an electron-donating monomer. In this work, DMASt ($e = -1.37$)²⁷ was employed as an electron-donating monomer

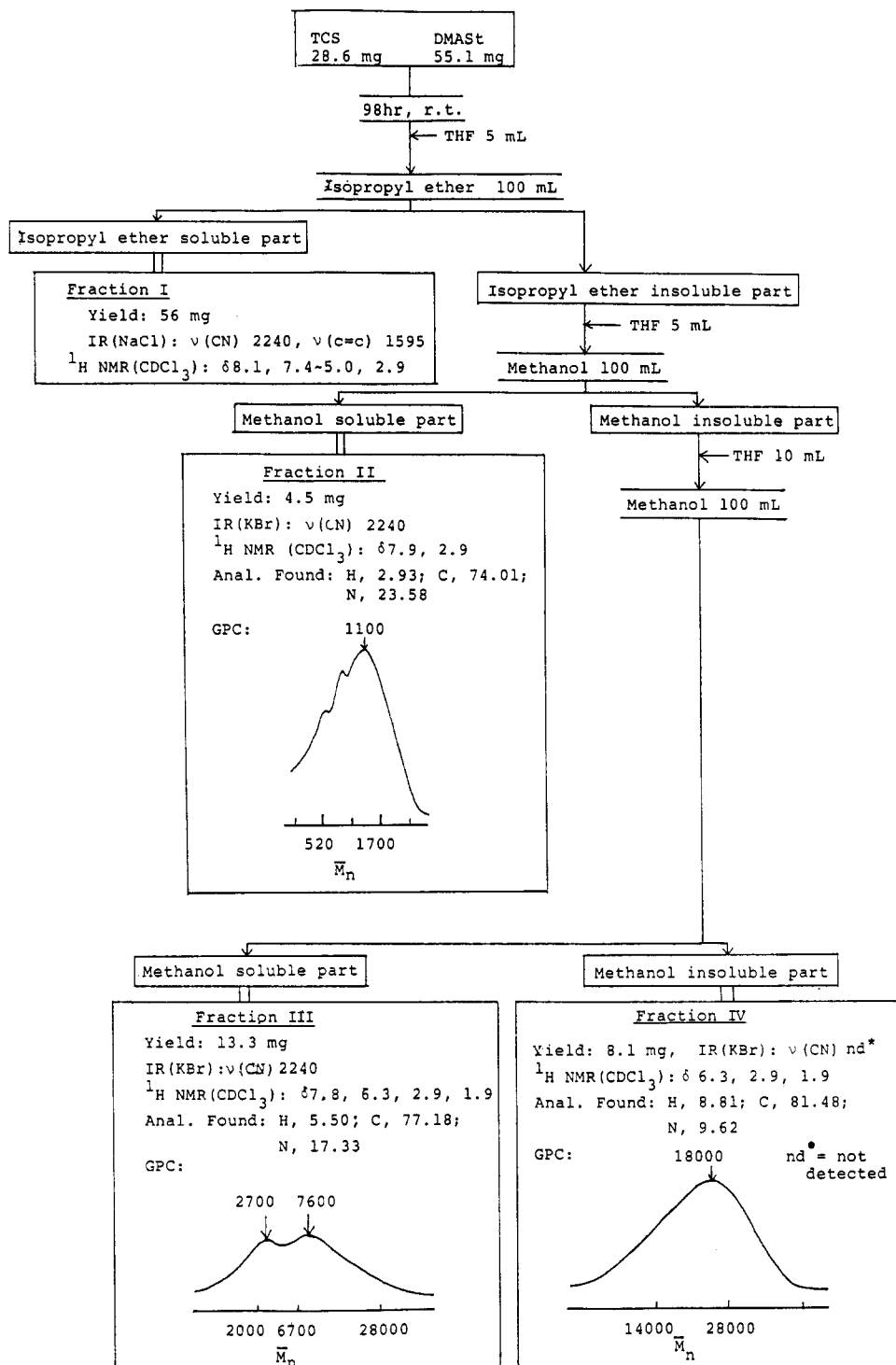


Figure 2. Fractionation scheme of the reaction product between TCS and DMASt and their characterizations.

because it is much more electron donating than St and 4VP ($e = -0.28$).²⁷

When the DCS was mixed with DMASt in acetonitrile, a pale yellow color developed and no further reaction took place. When a radical initiator was added, their copolymerization took place successfully to obtain the polymer with a molecular weight above fifty thousands. Table IV summarizes the results of the copolymerization of DCS with DMASt. The copolymer is soluble in acetone, acetonitrile, DMF, DMSO, and THF and insoluble in chloroform, ethyl acetate, and methanol. These results were calculated according to the intersection²⁴ and the integrated equation²⁴ methods to obtain the monomer reactivity ratios as follows: $r_1(\text{DCS}) = 0.12 \pm 0.02$, $r_2(\text{DMASt}) = 0.03 \pm 0.02$ at 60 °C. The product, $r_1 r_2$, of the

monomer reactivity ratio is as small as 0.0036, attributable to the fact that the electron-donating character of DMASt is much stronger than that of St.

When TCS was mixed with DMASt, a red color developed. The mixture was kept at room temperature for 98 h and then it was separated into four fractions, I to IV, by the dissolution-precipitation process (see Experimental Section). Figure 2 shows an outline of the fractionation procedure and some properties of the fractions.

For fraction I, its $^1\text{H NMR}$ spectrum shows three kinds of sharp peaks δ 8.1 (singlet), 7.4-5.0 (multiplet), and 2.9 (singlet). The first peak is assigned to the phenyl protons of the TCS unit, the second is to protons of vinyl groups of TCS and DMASt units and phenyl protons of the (dimethylamino)phenyl group of the DMASt unit, and the

Table IV
Copolymerization^a of 2,4-Dicyanostyrene (DCS) with *p*-(Dimethylamino)styrene (DMASt) in Acetonitrile at 60 °C

run	monomer feed			time, h	conv, %	copolymer and its composition				
	DCS, mg	DMASt, mg	DCS, mol %			elem. anal.				DCS, mol %
				H, %	C, %	N, %				
1	50.5	452.5	9.6	2.0	2.3	6.97	79.48	13.55	45.4	
2	54.4	249.5	17.2	3.5	12.0	6.95	75.54	13.51	45.0	
3	156.0	344.4	30.2	3.3	17.8	6.58	79.46	13.96	50.0	
4	139.2	207.1	39.1	3.3	22.5	6.79	79.88	14.15	52.4	6.4
5	166.4	1115.0	58.0	3.0	26.0	6.80	81.05	14.15	52.4	8.0

^a Initiator, AIBN 0.5 mol % to total monomer amount; acetonitrile as solvent, 5 mL. ^b Determined by GPC with THF as eluent.

third is to methyl protons of the dimethylamino group of the DMASt unit. This spectrum can be composed by superposing individual ones of TCS and DMASt monomers. The IR spectrum shows both absorptions of cyano and vinyl groups. It is conceivable, therefore, that fraction I is a mixture of unreacted TCS and DMASt monomers.

For fraction II, its ¹H NMR spectrum shows two broad peaks in the δ 7.9 and 2.9 regions, and it is in good agreement with that of the polymer of TCS with a radical initiator. Its IR spectrum exhibits an absorption at 2240 cm⁻¹, assigned to the stretching vibration of cyano group. In elemental analysis, the found values of fraction II are in good agreement with the calculated ones for the polymer of TCS (H, 2.81; C, 73.74; N, 23.45). Its GPC chart shows an unimodal peak corresponding to the molecular weight of 1100. It is concluded, therefore, that fraction II is composed of an oligomer of TCS with a degree of polymerization, \overline{DP} , of 6.

For fraction IV, its ¹H NMR spectrum exhibits three broad peaks in the δ 6.3, 2.85, and 1.9 regions, and its profile appears similar to the corresponding one of the polymer of DMASt with a radical initiator. Its IR spectrum carries no absorption at 2240 cm⁻¹, due to the stretching vibration of cyano group. In elemental analysis, the found values coincide well with the calculated ones for the polymer of DMASt (H, 8.92; C, 81.57; N, 9.51). Its GPC chart has an unimodal peak corresponding to a molecular weight of 18000. It is concluded, therefore, that fraction IV is a polymer of DMASt with \overline{DP} of 122.

For fraction III, its ¹H NMR spectrum shows several broad peaks in the δ 7.8, 6.3, 2.9, and 1.9 regions. The peaks in the δ 7.8 and 6.3 regions are assigned to respective phenyl protons of TCS and DMASt units. Its IR spectrum has an absorption at 2240 cm⁻¹, due to the stretching vibration of the cyano group. In elemental analysis, the found values correspond to the calculated ones either for the copolymer composed of 51 mol % TCS unit and 49 mol % DMASt or for the mixture of polymers of TCS and DMASt with the same unit composition. Its GPC chart exhibits bimodal peaks, corresponding to the molecular weight of 2700 and 7600. It is obvious, therefore, that fraction III is an oligomeric material composed of TCS and DMASt units, but detailed information cannot be obtained at the moment as to whether its structure is a real copolymer or a mixture of homopolymers.

It can be pointed out that when TCS was mixed with DMASt, spontaneous polymerization took place to give a mixture of polymers of TCS (fraction II) and DMASt (fraction IV), indicating interestingly that anionic polymerization of TCS and cationic polymerization of DMASt occur at the same time.

It was reported by Yang and Gaoni² and Butler and Sivaramakrishnan³ that, when TNS was mixed with 4VP or DMASt, spontaneous polymerizations took place to give copolymers composed of both monomer units. It was found out by Stille and Chung^{28,29} that when vinylidene

cyanide was mixed with vinyl ethers, two kinds of polymers of respective monomers were obtained at the same time, and they proposed a reaction mechanism that vinylidene cyanide and vinyl ethers are subjected to charge-transfer complex formation and further electron-transfer reaction to give radical cation and radical anion, the former being able to initiate the cationic polymerization of vinyl ethers and the latter being able to initiate the anionic polymerization of vinylidene cyanide. Although no definite information has been obtained on the structure of fraction III, composed of both monomer units, it is conceivable that TCS and DMASt simultaneously react via a mechanism similar to that of Stille and Chung to give the mixture of the respective polymers.

In summary, TCS is highly polymerizable by radical initiation, different from the related 2,4,6-trisubstituted styrenes, TNS and TFS, and it is able to undergo anionic polymerization with weak base initiator such as triethylamine due to its high electron-accepting character. When it is mixed with DMASt carrying with tertiary amine group, anionic polymerization of TCS and cationic polymerization of DMASt take place at the same time to give the mixture containing the homopolymers of TCS and DMASt.

Registry No. 1, 1585-07-5; 2, 25309-65-3; 3, 104614-57-5; 4, 104614-58-6; 5, 104614-59-7; 6, 104-85-8; 7, 116596-20-4; 8, 116596-21-5; 9, 116596-22-6; 10, 116596-23-7; DCS, 104696-83-5; TCS, 116596-24-8; St, 100-42-5; DMASt, 2039-80-7; DCS (homopolymer), 104696-84-6; TCS (homopolymer), 116596-25-9; (DCS)(St) (copolymer), 104696-85-7; (St)(TCS) (copolymer), 116596-26-0; (DMASt)(DCS) (copolymer), 116596-27-1; DMASt (homopolymer), 24936-45-6; 4-BrC₆H₄COCH₃, 99-90-1.

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Reaction of α -(Trifluoromethyl)styrene with Anionic Initiators

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ABSTRACT: α -(Trifluoromethyl)styrene ($Q = 0.43$, $e = 0.90$) does not undergo radical homopolymerization. Anionic polymerization fails to produce appreciable amounts of polymer even in bulk at -78 °C in spite of its high e value. The resistance to anionic polymerization is primarily due to side reactions involving addition-elimination sequences (S_N2') when initiators are nucleophilic enough to add to the β -carbon of TFMST. Weaker anionic initiators such as pyridine and potassium *tert*-butoxide that effectively induce polymerization of methyl α -(trifluoromethyl)acrylate ($Q = 0.74$, $e = 2.5$) do not react with TFMST. Reactions of TFMST with several anionic initiators are described in detail.

Introduction

Methyl α -(trifluoromethyl)acrylate (MTFMA) is reluctant to undergo radical homopolymerization.^{1,2} Alfrey-Price Q and e parameters for this fluoromonomer have been determined by Ito et al.³ ($Q = 0.74$, $e = 2.5$) based on copolymerization analysis and the "mercury method"⁴ and also by Iwatsuki et al.² ($Q = 0.8$, $e = 2.9$) using the Lüssi's method.⁵ The high e value suggests that MTFMA should readily undergo anionic polymerization. However, anionic initiators such as *n*-butyllithium (*n*-BuLi) or phenylmagnesium bromide (PhMgBr) typically employed for polymerization of methyl methacrylate (MMA) failed to produce high molecular weight polymers in good yield.¹ A similar anomalous behavior of ethyl α -(trifluoromethyl)acrylate in anionic polymerization has been noted by Narita et al.⁶ Much weaker initiators such as pyridine^{1,7} and organic and inorganic salts⁷ successfully polymerize MTFMA to high molecular weight polymers. On the basis of GC/MS analysis of *n*-BuLi-MTFMA reaction products along with the literature survey, Ito and Schwalm suggested that *n*-BuLi reacts with the β -carbon of MTFMA followed by spontaneous elimination of LiF to form $CF_2=$, which then reacts with additional *n*-BuLi (addition-elimination sequence).⁷

Ueda and Ito extended the investigation of the effect of α -CF₃ group on the reactivity of vinyl monomers to α -(trifluoromethyl)styrene (TFMST).⁸ TFMST fails to undergo radical homopolymerization even in bulk at low temperatures and does not self-propagate ($r_{TFMST} = 0$) in copolymerization with styrene (ST).⁸ As is the case with MTFMA mentioned above, the Q and e parameters were determined by combining the copolymerization analysis with the mercury method⁸ since Q and e values cannot be obtained only from the reactivity ratios when one of the ratios is 0. In spite of the favorable Q (0.43) and e (0.90) parameters and the fact that the mercury method has indicated that TFMST adds to a cyclohexyl radical 1.5 times and 7.5 times faster than MMA and ST, respectively, TFMST does not homopolymerize under radical condi-

Table I
Attempted Anionic Polymerization of TFMST at -78 °C

initiator (mol %)	THF/TFMST (mL/mL)	time (day)	initiation mode
KO- <i>t</i> -Bu/18-crown-6 (2.0)	2	5	<i>a</i>
KO- <i>t</i> -Bu/18-crown-6 (2.0)	0	4	<i>b</i>
PhMgBr (2.2)	2	3.6	<i>b</i>
PhMgBr (2.4)	0	5	<i>a</i>
EtMgBr (5.0)	0	6	<i>a</i>
<i>n</i> -BuLi (1.5)	1	3	<i>b</i>
<i>n</i> -BuLi (5.0)	0	7	<i>b</i>

^a Mixed at room temperature and cooled to -78 °C. ^b Mixed at -78 °C.

tions presumably due to the large steric hindrance and very low ceiling temperature.

Since TFMST ($e = 0.90$) is more electron-deficient than MMA ($e = 0.40$) and as electron-poor as methacrylonitrile ($e = 0.81$), we attempted anionic polymerization of TFMST with several initiators, which are discussed in this paper. Reactions of acrylic monomers with anionic initiators are quite complex due to the participation of the ester functionality. Therefore, TFMST should provide a good opportunity to study pathways of the reaction between α -CF₃-substituted vinyl monomers with anionic initiators without such complications as in the MTFMA case. Although there have been published several papers on the reaction of α -(fluoroalkyl)ethylenes with nucleophiles, systematic studies in relation to anionic polymerization have not been reported. In this paper are discussed primary pathways in the reaction of TFMST with various anionic initiators.

Results and Discussion

As summarized in Table I, anionic polymerizations of TFMST failed under several conditions despite its low electron density on the β -carbon ($e = 0.90$). Either bulk anionic polymerizations with a high initiator concentration at -78 °C or mixing TFMST with anionic initiators at room temperature followed by cooling to -78 °C did not