

## Functional Polymers. VII.\* Ethyl 4-Vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate

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**ABSTRACT:** Ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate was prepared by a five step synthesis from 4-ethylbenzoic acid in an overall yield of 20%. The acid chloride of 4-ethylbenzoic acid was condensed with benzene to 4-ethylbenzophenone. The most critical step in the synthesis was the Knoevenagel condensation of 4-ethylbenzophenone with ethyl cyanoacetate which was accomplished with ammonium acetate as the catalyst. Ethyl 4-ethyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate was readily brominated with *N*-bromosuccinimide and the bromination product, ethyl 4-(1-bromoethyl)- $\alpha$ -cyano- $\beta$ -phenylcinnamate was dehydrobrominated. Ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate consists of a mixture of *cis* and *trans* isomers of nearly equal amounts as indicated in  $^1\text{H}$  nuclear magnetic resonance and  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy. This new monomer was homopolymerized and copolymerized with styrene and methyl methacrylate with radical initiators.

**KEY WORDS** Ethyl 4-Vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate / Polymeric UV Absorbers / Knoevenagel Condensation / *N*-Bromosuccinimide Bromination / Poly(ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate) / Methyl Methacrylate / Styrene / Copolymers /

Photo-chemical reactions which occur in polymers on exposure to solar radiation cause damage to the physical and mechanical properties and to the appearance of polymers. When used outdoors, polymers are usually protected by adding ultraviolet (UV) stabilizers which can absorb most of the damaging radiation and reemit it in a form not harmful to the polymer. Low-molecular-weight UV absorbing compounds are used for the photo stabilization of polymers<sup>1,2</sup> with the most effective compounds being salicylates, 2,4-dihydroxybenzophenones, 2-hydroxyphenylbenzotriazoles or other more exotic, noncolor forming compounds.<sup>3,4</sup>

More recently, interest in polymeric UV stabilizers has been directed towards the synthesis of vinyl substituted monomers which have groups capable of UV absorption.<sup>3,4</sup> The successful synthesis of 3-vinyl,<sup>5</sup> 4-vinyl,<sup>6</sup> and 5-vinylsalicylic acid derivatives<sup>7</sup> has been reported.

The synthesis of 2,4-dihydroxy-4'-vinylbenzo-

phenone, a powerful UV absorber, was accomplished in about a 14% overall yield from 4-ethylbenzoic acid.<sup>8,9</sup> The last three steps consisted of bromination of 2,4-diacetoxy-4'-ethylbenzophenone with *N*-bromosuccinimide followed by dehydrobromination and hydrolysis to 2,4-dihydroxy-4'-vinylbenzophenone.

Esters of  $\alpha$ -cyano- $\beta$ -phenylcinnamic acid have also been used in the past as UV stabilizers,<sup>10,11</sup> especially when UV absorbers with free phenolic groups were undesirable. Certain polymers, especially polyacetals, are sensitive to high concentrations of phenol containing UV stabilizers. At temperatures above 200°C where polyacetals are fabricated, ethyl  $\alpha$ -cyano- $\beta$ -phenylcinnamate or the methyl ester have been found to have significant volatility and significant losses in stabilizer capacity. Consequently, attempts were made to decrease the volatility of  $\alpha$ -cyano- $\beta$ -phenylcinnamates without diminishing their effectiveness by increasing their molecular weights<sup>12</sup> by preparing bisesters of glycols and  $\alpha$ -cyano- $\beta$ -phenylcinnamic acid; the useful-

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ness of the diester of 1—10 decanediol in polyformaldehyde was demonstrated.<sup>12</sup> No polymers containing derivatives of  $\alpha$ -cyano- $\beta$ -phenylcinnamic acid have yet been reported.

In this paper, we describe the successful synthesis of ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate, its polymerization and copolymerization.

## EXPERIMENTAL

### Materials

4-Ethylbenzoic acid (Aldrich Chemical Co.) was used as obtained without further purification.

Thionyl chloride (Fisher Scientific Co.) was distilled at atmospheric pressure (bp 76°C) immediately before use.

Ethyl cyanoacetate (Eastman Organic Chemicals) was distilled under reduced pressure [bp 67—68°C (1 mmHg)].

*N*-Bromosuccinimide (NBS) (Eastman Kodak Co.) was dried overnight at 0.1 mmHg and room temperature over phosphorus pentoxide.

Tributylamine (Aldrich Chemical Co.) was heated to 100°C with potassium hydroxide and fractionally distilled under reduced pressure (bp 101°C (17 mmHg)).

Picric acid (Eastman Kodak Co.) was dried overnight at 0.1 mmHg and room temperature over calcium chloride.

Methyl methacrylate, styrene, and *N,N*-dimethylacetamide (DMAc) (all Aldrich Chemical Co.) were dried over calcium hydride for 24 hours and fractionally distilled under reduced pressure immediately before use.

Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co.) was recrystallized three times from dry methanol and dried for 24 hours at 0.01 mmHg and room temperature.

Benzene (Fisher Scientific Co.) was washed with sulfuric acid, aqueous sodium hydroxide and water, dried with phosphorus pentoxide and distilled at atmospheric pressure.

Carbon tetrachloride (Fisher Scientific Co.) was distilled at atmospheric pressure; chloroform (Fisher Scientific Co.) spectral grade was directly used.

### Measurements

Infrared spectra were recorded on a Perkin-Elmer

Model 727 spectrophotometer. Liquid samples were measured between sodium chloride plates and polymer samples were measured as KBr pellets. Peak assignments were made to the nearest 5 cm<sup>-1</sup>.

<sup>1</sup>H nuclear magnetic resonance (NMR) spectra were determined on a 60 MHz Varian A-60 spectrometer.

<sup>13</sup>C NMR spectra were measured on a Varian CFT-20 spectrometer under complete proton decoupling. These measurements were carried out in CDCl<sub>3</sub> at room temperature with tetramethylsilane (TMS) as the internal standard.

The ultraviolet spectra were measured in a chloroform solution with a Beckman-Acta MVI spectrophotometer at a scanning rate of 20 nm per second. The molar extinction coefficients represented an average value of measurement for four solutions. The solutions were prepared by diluting a sample (approximately 0.03 gm) in 10 ml of chloroform, diluting 2 or 3 ml of this solution to 25 ml, and again diluting 2 or 3 ml of this solution to 25 ml. The ultraviolet spectra were taken on solutions having concentrations of about 10<sup>-5</sup> M.

Elemental analyses were performed by the Microanalysis Laboratory, Office of Research Service, University of Massachusetts, Amherst, MA.

### Preparations

*4-Ethylbenzoyl Chloride.* The acid chloride was prepared from 4-ethylbenzoic acid (75 g, 0.50 mol), and thionyl chloride (178 g, 1.50 mol) in benzene (300 ml) and gave 81 g (96%) of colorless 4-ethylbenzoyl chloride [bp 125°C (20 mmHg)].

*4-Ethylbenzophenone.* 4-Ethylbenzoyl chloride (81 g, 0.48 mol) with benzene (530 g, 6.75 mol) and aluminum chloride (77 g, 0.58 mol) yielded after appropriate workup 4-ethylbenzophenone in 95 g (94%) yield [bp 120°C (0.035 mmHg)<sup>13</sup>].

The infrared spectrum (neat) showed an absorption at 1640 cm<sup>-1</sup> (C=O stretching). The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showed  $\delta$  1.18 (CH<sub>2</sub>CH<sub>3</sub>, 3H, triplet), 2.58 (CH<sub>2</sub>CH<sub>3</sub>, 2H, quartet), and 6.85—7.47 ppm (aromatic protons, 9H).

*4-(1-Bromoethyl)benzophenone.* This compound was prepared from 4-ethylbenzophenone (20 g, 95 mmol), NBS (18.6 g, 105 mmol) and carbon tetrachloride (86 ml). The progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. The <sup>1</sup>H

NMR spectrum of the reaction mixture showed  $\delta$  1.18 ( $\text{CH}_2\text{CH}_3$  of the starting material), 1.90 ( $\text{CHBr-CH}_3$  of the product), 2.58 ( $\text{CH}_2\text{CH}_3$  of the starting material), and 4.93 ppm ( $\text{CHBr-CH}_3$  of the product). The yield of crude viscous 4-(1-bromoethyl)benzophenone was 27.5 g (100%) which solidified on standing. The crude product was identified and used in the following reaction without purification.

The infrared spectrum (neat) showed an absorption at  $1640\text{ cm}^{-1}$  ( $\text{C=O}$  stretching). The  $^1\text{H}$  NMR spectrum ( $\text{CCl}_4$ ) showed  $\delta$  1.90 ( $\text{CHBr-CH}_3$ , 3H, doublet), 4.93 ( $\text{CHBr-CH}_3$ , H, quartet), and 7.03—7.45 ppm (aromatic protons, 9H).

4-Vinylbenzophenone was synthesized from crude 4-(1-bromoethyl)benzophenone (24 g, 83 mmol), tributylamine (72 ml, 302 mmol), DMAc (120 ml) and a trace of picric acid as a polymerization inhibitor. The progress of the reaction was followed by  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectrum of the reaction mixture showed  $\delta$  4.93 ( $\text{CHBr-CH}_3$  of the starting material) and 5.29—7.02 ppm ( $\text{CH=CH}_2$  of the product). After the solvent was removed by distillation in a rotary evaporator under reduced pressure, the product was distilled through a Claisen head fitted with a 10 cm Vigreux column [bp  $145\text{--}146^\circ\text{C}$  (0.002 mmHg)] and gave 9.1 g (53%) of a brown, viscous, 4-vinylbenzophenone.<sup>14</sup>

The infrared spectrum (neat) showed absorptions at  $1640\text{ cm}^{-1}$  ( $\text{C=O}$  stretching) and 980 and 905  $\text{cm}^{-1}$  (vinyl C-H out-of-plane bending). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) showed  $\delta$  5.29—7.02 (vinyl protons, 3H) and 7.40—7.88 ppm (aromatic protons, 9H).

*Ethyl 4-Ethyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate.* 4-Ethylbenzophenone (42 g, 0.20 mol), ethyl cyanoacetate (28 g, 0.25 mol), acetic acid (9.6 g, 0.16 mol), and benzene (40 ml) were placed in a 250 ml 3-neck round-bottom flask which was fitted with a 25 ml modified Dean-Stark constant water separator<sup>15</sup> filled with benzene. This mixture was vigorously refluxed and ammonium acetate (12 g, 0.16 mol) was added in 1.5 g portions at 3—4 hour intervals.<sup>16</sup> The progress of the reaction was monitored by thin layer chromatography, using a silica gel sheet as the adsorbent and a mixture of carbon tetrachloride-chloroform (2:1 volume ratio) as solvents.

After four days of heating under reflux, the

reaction mixture was cooled and added to 200 ml of water. An oil separated which was extracted with 50 ml of benzene, and the aqueous phase was washed with an additional 50 ml of benzene. The combined organic phases were then washed twice with 200 ml of 5% aqueous sodium bicarbonate, water, dried with magnesium sulfate, and filtered. Removal of the solvent on a rotary evaporator gave a crude viscous product which was distilled under reduced pressure [bp  $160^\circ\text{C}$  (0.002 mmHg)] and gave 46 g (75%) of pure, slightly yellow, viscous ethyl 4-ethyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate.

The infrared spectrum (neat) showed absorptions at  $2220\text{ cm}^{-1}$  ( $\text{C}\equiv\text{N}$  stretching) and  $1700\text{ cm}^{-1}$  ( $\text{C=O}$  stretching). The  $^1\text{H}$  NMR spectrum ( $\text{CCl}_4$ ) showed  $\delta$  1.05 ( $\text{OCH}_2\text{CH}_3$ , 3H, triplet), 1.23 ( $\text{CH}_2\text{CH}_3$ , 3H, triplet), 2.61 ( $\text{CH}_2\text{CH}_3$ , 2H, quartet), 3.97 ( $\text{OCH}_2\text{CH}_3$ , 2H, quartet), and 6.78—7.22 ppm (aromatic protons, 9H).

*Anal.* Calcd for  $(\text{C}_{20}\text{H}_{19})_2\text{N}$ : C, 78.66%, H, 6.27%, N, 4.59%. Found: C, 78.39%, H, 6.22%, N, 4.56%.

*Ethyl 4-(1-Bromoethyl)- $\alpha$ -cyano- $\beta$ -phenylcinnamate.* A 500 ml 3-neck round-bottom flask was charged with ethyl 4-ethyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate (40 g, 0.13 mol), carbon tetrachloride (170 ml) and NBS (25.7 g, 0.14 mol). The flask was fitted with a reflux condenser, flushed with nitrogen, and heated to reflux under a flow of nitrogen. After three hours, only a trace of yellow NBS remained, and the reaction mixture was allowed to cool to room temperature. The slightly yellow solution was filtered to remove succinimide which was washed twice with 50 ml of carbon tetrachloride. The combined organic phases were washed twice with 250 ml of water, dried with magnesium sulfate, and filtered. The solvent was removed under reduced pressure, leaving 50 g (100%) of slightly yellow, viscous ethyl 4-(1-bromoethyl)- $\alpha$ -cyano- $\beta$ -phenylcinnamate.

The infrared spectrum (neat) showed absorptions at  $2220\text{ cm}^{-1}$  ( $\text{C}\equiv\text{N}$  stretching) and  $1700\text{ cm}^{-1}$  ( $\text{C=O}$  stretching). The  $^1\text{H}$  NMR spectrum ( $\text{CCl}_4$ ) showed  $\delta$  1.09 ( $\text{OCH}_2\text{CH}_3$ , 3H, triplet), 2.00 ( $\text{CHBrCH}_3$ , 3H, doublet), 4.06 ( $\text{OCH}_2\text{CH}_3$ , 2H, quartet), 5.10 ( $\text{CHBrCH}_3$ , H, quartet), and 6.93—7.43 ppm (aromatic protons, 9H).

*Anal.* Calcd for  $\text{C}_{20}\text{H}_{18}\text{O}_2\text{NBr}$ : C, 62.51%, H, 4.72%, N, 3.65%, Br, 20.79%. Found: C, 62.51%,

H, 4.89%, N, 3.66%, Br, 20.61%.

*Ethyl 4-Vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate.* A 500 ml 3-neck round-bottom flask was charged with crude ethyl 4-(1-bromoethyl)- $\alpha$ -cyano- $\beta$ -phenylcinnamate (25 g, 65 mmol), tri-butylamine (62 ml, 260 mmol), DMAc (125 ml), and a trace of picric acid as polymerization inhibitor. The flask was fitted with a reflux condenser, flushed with nitrogen, and then immersed in an oil bath at 145°C under a flow of nitrogen. The color of the reaction mixture changed from light brown to dark brown as the reaction proceeded.

The progress of reaction was monitored by  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectrum of the reaction mixture showed 5.10 (CHBrCH<sub>3</sub> of the starting material) and 5.20–7.06 ppm (CH=CH<sub>2</sub> of the product). Dehydrobromination was complete in 1.5 hours.

The contents of the flask were added to a mixture of benzene–water (150 ml : 350 ml). The organic phase was separated and the aqueous phase was washed with 50 ml of benzene. The combined organic phases were washed twice with 250 ml of 1 *N* hydrochloric acid, 2.5% aqueous sodium bicarbonate, and water, dried with magnesium sulfate containing a trace of picric acid, and filtered. After removal of the solvent by a rotary evaporator under reduced pressure, the contents of the flask were placed in a Kugelrohr,<sup>17</sup> held at 140°C and 0.002 mmHg for 30 minutes to remove any volatile compounds. 6.7 g of a slightly yellow viscous material was distilled at 200–202°C (0.002 mmHg). The distillate was chromatographed on basic and acidic alumina, using benzene as the eluent, and gave 6.4 g (32%) of pure, slightly yellow, viscous ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate.

The infrared spectrum (neat) showed absorptions at 2215 cm<sup>-1</sup> (C $\equiv$ N stretching); 1700 cm<sup>-1</sup> (C=O stretching), and 905 cm<sup>-1</sup>, 990 cm<sup>-1</sup> (vinyl C–H out-of-plane bending). The  $^1\text{H}$  NMR spectrum (CCl<sub>4</sub>) showed  $\delta$  1.18 (OCH<sub>2</sub>CH<sub>3</sub>, 3H, triplet), 4.13 (OCH<sub>2</sub>CH<sub>3</sub>, 2H, quartet), 5.29–6.74 (vinyl protons, 3H), and 7.03–7.51 ppm (aromatic protons, 9H).

*Anal.* Calcd for C<sub>20</sub>H<sub>17</sub>O<sub>2</sub>N: C, 79.18%, H, 5.65%, N, 4.62%. Found: C, 79.48%, H, 5.81, N, 4.38%.

*Identification of Residue from Distillation of Ethyl 4-Vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate.* The residue ob-

tained from the distillation of ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate was dissolved in 30 ml of acetone and reprecipitated by the addition of this solution to 300 ml of diethyl ether. The resulting brown solid was collected by filtration, washed with diethyl ether, and dried for several days at room temperature under 20 mmHg.

The infrared spectrum (KBr) showed absorptions at 2215 cm<sup>-1</sup> (C=N stretching) and 1700 cm<sup>-1</sup> (C=O stretching). The  $^1\text{H}$  NMR spectrum (CDCl<sub>3</sub>) showed  $\delta$  0.66–2.66 (CH–CH<sub>2</sub>– and OCH<sub>2</sub>CH<sub>3</sub>, 6H), 3.72–4.42 (OCH<sub>2</sub>CH<sub>3</sub>, 2H), and 6.17–7.82 ppm (aromatic protons, 9H).

*Anal.* Calcd for (C<sub>20</sub>H<sub>17</sub>O<sub>2</sub>N)<sub>n</sub>: C, 69.18%, H, 5.65%, N, 4.62%. Found: C, 79.29%, H, 5.87%, N, 4.78%.

*Reaction of 4-Vinylbenzophenone with Ethyl Cyanoacetate.* In a 50 ml round-bottom flask equipped with a reflux condenser were placed 4-vinylbenzophenone (2.0 g, 9.6 mmol), ethyl cyanoacetate (1.3 g, 11.5 mmol), acetic acid (0.46 g, 7.7 mmol), benzene (2 ml), and a trace of picric acid as a polymerization inhibitor. The reaction mixture was vigorously refluxed and ammonium acetate (0.41 g, 5.3 mmol) was added in 0.1 g portions at 4–17 hour intervals.<sup>16</sup> The progress of reaction was checked by thin-layer chromatography (TLC), using a silica gel sheet as an adsorbent and a mixture of carbon tetrachloride–chloroform (2:1 volume ratio) as a solvent.

After heating for 2 days under reflux, the reaction mixture was cooled and added to 50 ml of water, resulting in an emulsion. After standing, the organic phase was separated and the aqueous phase was washed twice with 50 ml of benzene. The combined organic phases were then washed twice with 100 ml of 5% aqueous sodium bicarbonate, 5% aqueous sodium chloride and water, dried with magnesium sulfate, and filtered. After removing the solvent on a rotary evaporator under reduced pressure, TLC measurement of the reaction product showed the presence of ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate in 20–30% yield and also the starting material, 4-vinylbenzophenone.

#### Polymerizations

*Polymerization of Ethyl 4-Vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate.* A polymerization tube was charged with ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate

(0.99 g, 3.26 mmol), benzene (1.14 ml) and AIBN (0.9 mg,  $6.6 \times 10^{-3}$  mmol, 0.2 mol percent) and flushed with nitrogen. The tube was then degassed by three freeze-thaw cycles under 0.01 mmHg, sealed, and placed in a bath at 60°C. After five days the tube was opened, the viscous solution was diluted with 20 ml of benzene, and the polymer was precipitated by adding the solution to 200 ml of diethyl ether. The yellow powdery polymer was collected by filtration, washed with diethyl ether, and dried for one day at room temperature and 0.01 mmHg, and gave 0.42 g (43%) of poly(ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate). The inherent viscosity of the polymer (0.5% in benzene, 30°C.) was 0.18 dl g<sup>-1</sup>. The infrared spectrum (KBr) showed absorptions expected for this polymer at 2215 cm<sup>-1</sup> (C $\equiv$ N stretching) and 1700 cm<sup>-1</sup> (C=O stretching). The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showed  $\delta$  0.80–2.35 (–O–CH<sub>2</sub>–CH<sub>3</sub>, 3H), 0.80–2.50 (–CH–CH<sub>2</sub>–, 3H), 3.70–4.40 (–O–CH<sub>2</sub>–CH<sub>3</sub>, 2H), and 6.00–8.00 ppm (aromatic protons, 9H).

*Anal.* Calcd for (C<sub>20</sub>H<sub>17</sub>O<sub>2</sub>N)<sub>n</sub>: C, 79.18%, H, 5.65%, N, 4.62%. Found: C, 79.44%, H, 5.57%, N, 4.46%.

*Copolymerization of Ethyl 4-Vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate with Styrene.* A polymerization tube was charged with ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate (0.68 g, 2.24 mmol), styrene (1.34 g, 12.9 mmol), benzene (2.3 ml) and AIBN (4.3 mg,  $3.16 \times 10^{-2}$  mmol, 0.2 mol percent), and flushed with nitrogen. The tube was degassed, sealed at 0.01 mmHg, and placed in a bath of 60°C. After five days the tube was opened, the viscous solution was diluted with 20 ml of acetone, and the polymer was precipitated by adding the solution to 300 ml of methanol. The white powdery polymer was collected by filtration, washed with methanol, and dried for one day under 0.01 mmHg at room temperature; the yield of polymer was 0.98 g (48%). The inherent viscosity of the polymer (0.5% in benzene, 30°C) was 0.21 dl g<sup>-1</sup>. The infrared spectrum (KBr) showed absorptions at 2215 cm<sup>-1</sup> (C $\equiv$ N stretching) and 1700 cm<sup>-1</sup> (C=O stretching). According to the <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) the copolymer consisted of about 80 mol% of styrene units and about 20 mol% of ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate units.

*Copolymerization of Ethyl 4-Vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate with Methyl Methacrylate.* A

polymerization tube was charged with ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate (0.69 g, 2.29 mmol), methyl methacrylate (1.33 g, 13.3 mmol), benzene (2.28 ml) and AIBN (4.4 mg,  $3.23 \times 10^{-2}$  mmol, 0.2 mol percent). The tube was flushed with nitrogen, degassed, sealed at 0.01 mmHg, and placed in a bath at 60°C. After five days, the tube was opened, the viscous solution was diluted with 20 ml of benzene, and the polymer was precipitated by adding the solution to 300 ml of methanol. The white powdery polymer was collected by filtration, washed with methanol, and dried for one day at room temperature and 0.01 mmHg; yield of polymer was 1.8 g (90%). The inherent viscosity of the polymer (0.5% in benzene, 30°C.) was 0.32 dl g<sup>-1</sup>. The infrared spectrum (KBr) showed absorption at 2215 cm<sup>-1</sup> (C $\equiv$ N stretching) and 1700 cm<sup>-1</sup> (C=O stretching). According to elemental analysis and <sup>1</sup>H NMR spectrum the copolymer has a composition of 87 mol% of methyl methacrylate and 13 mol% of ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate.

## RESULTS AND DISCUSSION

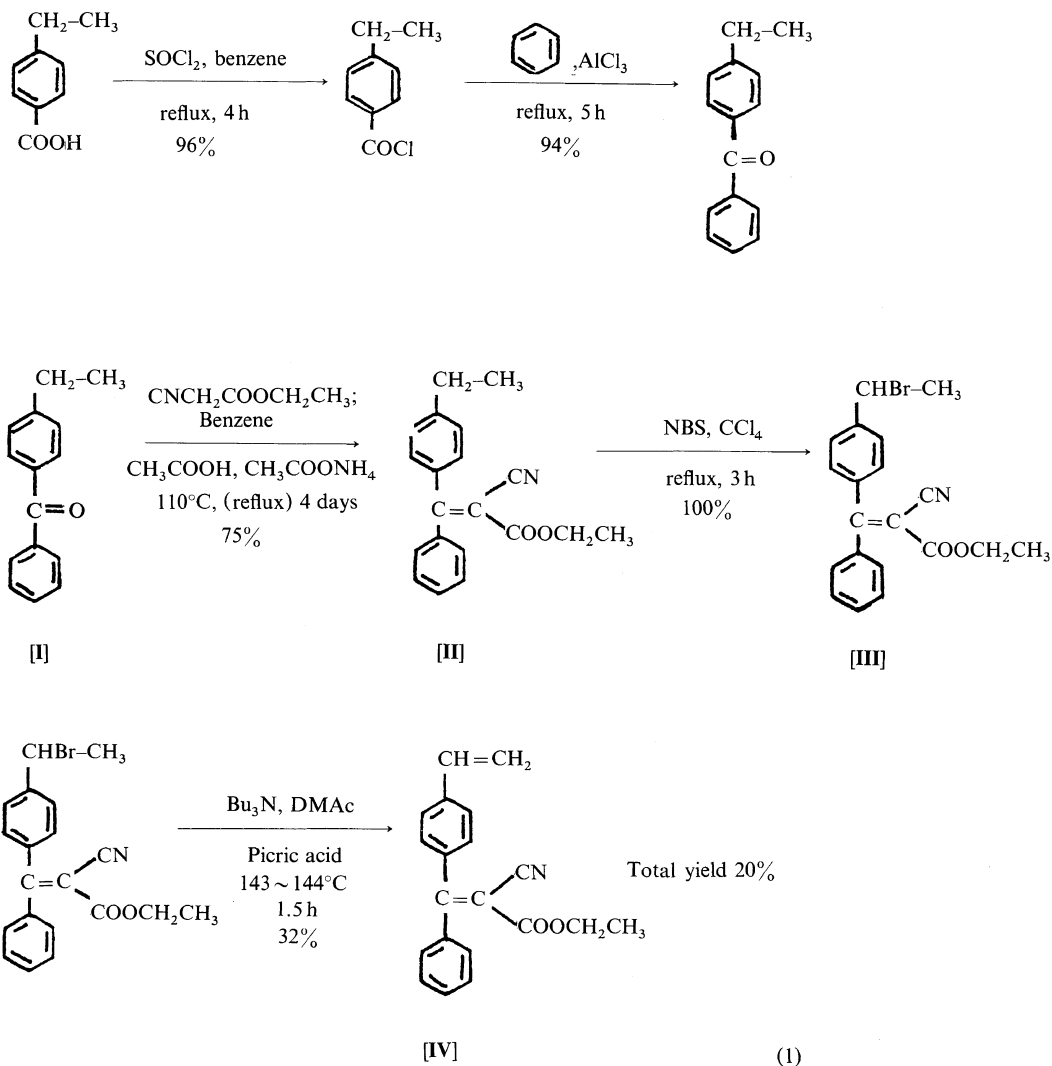
Ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate (**IV**) was synthesized in five reaction steps and an overall yield of 20% from 4-ethylbenzoic acid as indicated in the Reaction Scheme.

4-Ethylbenzoyl chloride was prepared in 96% yield by heating 4-ethylbenzoic acid under reflux in benzene with SOCl<sub>2</sub>. The acid chloride was then allowed to react with benzene and AlCl<sub>3</sub> under the Friedel–Crafts acylation condition and gave 4-ethylbenzophenone (**I**) in 94% yield.

4-Ethylbenzophenone (**I**) was the key intermediate in the preparation of (**IV**). The Knoevenagel reaction of (**I**) with cyanoacetate gave ethyl 4-ethyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate (**II**) in a very good yield. The success of the Knoevenagel reaction depends on the careful optimization of reaction conditions, as can be seen in Table I. When ammonium acetate, which is the most effective catalyst for the Knoevenagel reaction, was added, in one portion, the yield of the reaction product was almost nil. On the other hand, when the reaction mixture was heated too long, side reactions occurred and the yield of the desirable product was diminished.

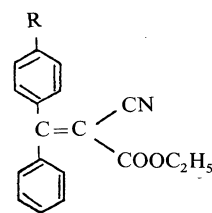
After a long and careful study, it was finally

## Synthesis route



found that the most effective way to carry out the Knoevenagel reaction was at  $110^\circ\text{C}$ . (the reflux temperature of the reaction mixture) using ammonium acetate-acetic acid as the catalyst in a ratio of 4-ethylbenzophenone-ethyl cyanoacetate-acetic acid-benzene mixtures of 1:1.2:0.8:2.3. Ammonium acetate was added in eight portions at 3-4 hour intervals, as convenient, and a total reaction time of three days was found desirable; the

progress of the reaction was followed by thin-layer chromatography. Under the best conditions, (II) was obtained in 75% yield although a 45% yield was typical when the reaction conditions were not optimal. As expected, (II) was obtained as an oil since the Knoevenagel reaction of an unsymmetric benzophenones or ketones with cyanoacetate is known to give a mixture of *cis* and *trans* compounds which are the two expected geometric isomers of



**Table I.** Optimization of Knoevenagel condensation of 4-substituted benzophenones and ethyl cyanoacetate<sup>a</sup>

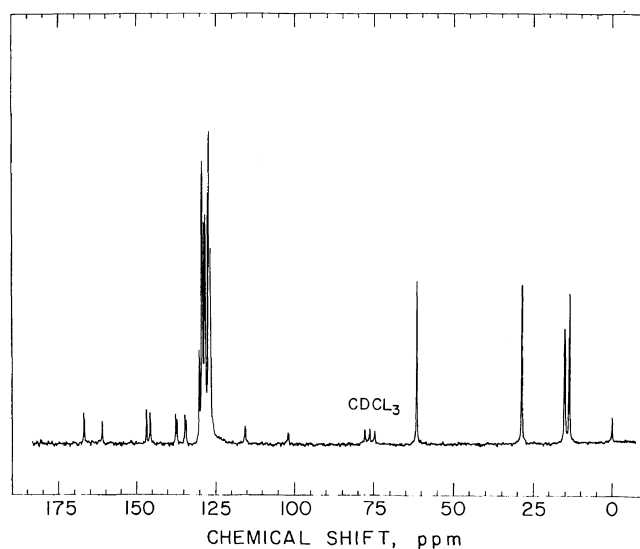
4-Substituted benzophenone		Ammonium acetate		Reaction time h	Reaction yield %	
Substituent R	Amount g	Amount g	Molar ratio <sup>b</sup>			Number of additions
H	91	18	0.47	7	72	
H	91	20	0.52	14	80 <sup>c</sup>	
Ethyl	20	6.7	0.91	5	45	
Ethyl	42	12	0.78	8	75	
Vinyl	8.0	1.4	0.47	1	22.5	<30 <sup>d</sup>
Vinyl	2.0	0.41	0.55	4	46	<30 <sup>d</sup>
1-Bromoethyl	4.2	0.57	0.50	4	71	— <sup>d</sup>

<sup>a</sup> Molar ratio of 4-substituted benzophenone–ethyl cyanoacetate–acetic acid–benzene feed was 1.0:1.2:0.8:2.3.

<sup>b</sup> Molar ratio to 4-substituted benzophenone.

<sup>c</sup> Data from reference 16.

<sup>d</sup> Reaction mixture contained about 2 mol% of picric acid. The yield was judged from TLC; some polymer was also formed.



**Figure 1.** <sup>13</sup>C NMR spectrum of ethyl 4-ethyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate: solvent, CDCl<sub>3</sub>, 6000 transients.

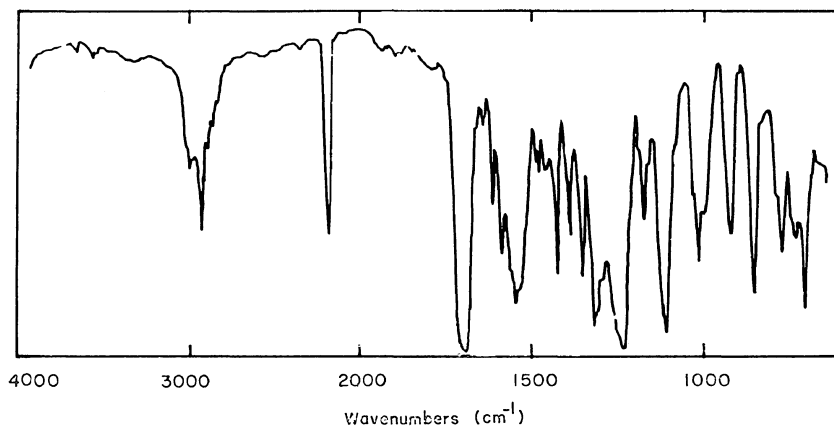


Figure 2. IR spectrum (liquid) between NaCl plates of ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate.

this reaction. The  $^{13}\text{C}$  NMR spectrum indeed revealed two peaks with a chemical shift difference of approximately 1 ppm (Figure 1); the infrared (IR) spectrum (Figure 2) was also consistent with the proposed structure.

The Knoevenagel reaction was initially studied with benzophenone and ethylcyanoacetate; at a 0.5 molar scale, 72% yields could be consistently obtained under the reaction conditions ultimately used for the preparation of (II).

In order to study the most effective means for preparing (IV), the conditions for the Knoevenagel reaction with ethyl cyanoacetate were also studied using not only 4-ethylbenzophenone but also 4-(1-bromoethyl)benzophenone and 4-vinylbenzophenone.

The reaction of 4-(1-bromoethyl)benzophenone with ethyl cyanoacetate for three days gave a mixture consisting of a number of products judged by TLC which include the starting product 4-(1-bromoethyl)benzophenone and also the desired reaction product (III). This observation was made on the basis of the  $^1\text{H}$  NMR spectrum which clearly indicated the presence of a vinyl compound, possibly the desired (IV) in very small amounts. It would be reasonable to expect dehydrobromination of 4-(1-bromoethyl) compounds through the action of ammonium acetate under our reaction conditions, and either 4-(1-bromoethyl)benzophenone or (III) may possibly have been dehydrobrominated to 4-vinylbenzophenone or (IV), respectively. 4-Vinylbenzophenone could either polymerize or condense with ethyl cyanoacetate to (IV).

The reaction of 4-vinylbenzophenone with ethyl cyanoacetate was studied under various conditions since this route provides the most direct way to the formation of (IV). It is expected that under these conditions some polymeric materials would be obtained. In fact, poly(4-vinylbenzophenone) and poly(IV) are possibly formed as well as the copolymers of 4-vinylbenzophenone and (IV). Under our reaction conditions, no (IV) was obtained from either 4-vinylbenzophenone and ethyl cyanoacetate in high yield, although TLC revealed that our reaction mixture contained (IV), poly(IV), and starting materials (4-vinylbenzophenone). From TLC estimates, the Knoevenagel product (IV) yield was 20–30%; however, it could not be conveniently separated from the starting material.

Knoevenagel reactions with 4-vinylbenzophenones were carried out in the presence of 2–5 mol% of radical inhibitors such as picric acid, or with picric acid, with 0.0025 mol% of Galvinoxyl radical or with hydroquinone, although hydroquinone is a very poor carbon radical inhibitor and seems to have produced the largest amount of polymer.

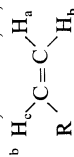
Bromination of (II) with NBS was accomplished to give a 100% yield of (III) which is a high boiling viscous yellowish oil which cannot be distilled in the Kugelrohr<sup>17</sup> without some decomposition. It was consequently not possible to obtain correct elemental analysis of the distilled product since there was always the occurrence of some dehydrobromination. Distillation had to be carried out above 200°C, and at such temperatures, thermal dehy-

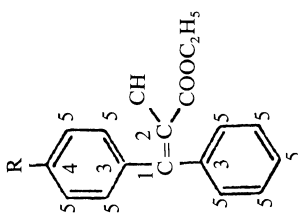


Table II. <sup>1</sup>H NMR chemical shifts of 4-substituted derivatives of benzophenone (BP) and ethyl α-cyano-β-phenylcinnamate (CPC)<sup>a</sup>

Compound	OCH <sub>2</sub> CH <sub>3</sub>	φCH <sub>2</sub> CH <sub>3</sub>	φCHBrCH <sub>3</sub>	φCH <sub>2</sub> CH <sub>3</sub>	φCH <sub>2</sub> CH <sub>3</sub>	OCH <sub>2</sub> CH <sub>3</sub>	φCHBrCH <sub>3</sub>	Vinyl protons <sup>b</sup>			Aromatic protons
								H <sub>a</sub>	H <sub>b</sub>	H <sub>c</sub>	
BP-CH <sub>2</sub> CH <sub>3</sub>	—	1.18 (T)	—	2.58 (Q)	—	—	—	—	—	—	6.85—7.47
BP-CHBrCH <sub>3</sub>	—	—	1.90 (D)	—	—	—	4.93 (Q)	—	—	—	7.03—7.45
BP-CH=CH <sub>2</sub>	—	—	—	—	—	—	—	5.38	5.86	6.78	7.40—7.88
CPC-H	1.07 (T)	—	—	—	—	4.01 (Q)	—	—	—	—	6.83—7.18
CPC-CH <sub>2</sub> CH <sub>3</sub>	1.04 (T)	1.23 (T)	—	2.61 (Q)	3.96 (Q)	3.99 (Q)	—	—	—	—	6.78—7.22
	1.06 (T)										
CPC-CHBrCH <sub>3</sub>	1.08 (T)	—	2.01 (D)	—	4.05 (Q)	4.08 (Q)	5.10 (Q)	—	—	—	6.93—7.43
	1.10 (T)										
CPC-CH=CH <sub>2</sub>	1.13 (T)	—	—	—	4.10 (Q)	4.13 (Q)	—	5.29	5.76	6.74	7.03—7.51
	1.18 (T)										

<sup>a</sup> D, doublet; T, triplet; Q, quartet.





**Table III.** <sup>13</sup>C NMR chemical shifts of 4-substituted derivatives of ethyl α-cyano-β-phenylcinnamate <sup>a</sup>

Substituent R	CH <sub>3</sub> CH <sub>2</sub> O		CH <sub>3</sub> CH <sub>2</sub>		CH <sub>3</sub> CHBr		CH <sub>2</sub> =CH-		C≡N		C=O		Aromatic carbons		
	CH <sub>3</sub>	CH <sub>2</sub>	CH <sub>3</sub>	CH <sub>2</sub>	CH <sub>3</sub>	CH <sub>2</sub>	CH <sub>2</sub>	CH	1	2	1	2	3	4	5
H	13.70 (35)	62.14 (37)							116.90 (2)	168.97 (4)	162.69 (3)	104.19 (2)	138.34 (6)		
									104.31 (2)	138.69 (6)	128.21 (92)	128.53 (99)	129.28 (93)	130.25 (100)	
Ethyl	13.64 (47)	61.94 (51)	15.12 (36)	28.70 (50)					117.04 (5)	168.86 (9)	162.83 (7)	103.28 (2)	135.61 (7)	127.64 (62)	127.98 (91)
			15.30 (32)						103.51 (3)	148.25 (9)	148.25 (10)	128.40 (80)	129.28 (73)	129.61 (70)	131.25 (86)
									138.53 (7)	138.89 (9)					

1-Bromoethyl	13.64	62.14	26.52	47.91	116.62	167.96	162.51	104.33	138.03	145.46	126.67	127.01	128.24
	(66)	(68)	(74)	(42)	(7)	(8)	(10)	(4)	(15)	(11)	(75)	(93)	(95)
			26.95	48.10					138.43	146.46	128.54	129.21	129.65
			(7)	(40)					(21)	(15)	(90)	(100)	(87)
								138.67		130.15	130.34	130.59	
								(5)		(93)	(75)	(98)	
										131.42			
										(38)			
Vinyl	13.70	62.09			116.91	168.41	162.70	103.70	137.46	139.75	125.94	126.29	128.21
	(49)	(48)			(6)	(5)	(9)	(3)	(9)	(12)	(64)	(68)	(76)
			135.85	115.87					103.84	140.71	128.51	129.33	129.66
			(13)	(34)					(3)	(9)	(91)	(74)	(27)
			135.92	116.45							129.88	130.29	130.71
			(47)	(31)							(88)	(100)	(72)
										138.65	131.41		
										(9)	(35)		

<sup>a</sup> In ppm downfield from TMS in CDCl<sub>3</sub> (25%); 6000—26000 transients.

<sup>b</sup> Numbers in parenthesis indicate peak intensities.

drobromination becomes noticeable.

The  $^1\text{H}$  NMR spectrum, however, clearly showed that (III) had been formed exclusively. No 4-(1-dibromoethyl)- or 4-(2-bromoethyl) $\alpha$ -cyano- $\beta$ -phenylcinnamate could be detected in the bromination product of (II). The  $^1\text{H}$  NMR spectrum of (III) showed a triplet at 1.09 ppm, indicating the methyl protons of ethyl ester. At 2.00 ppm, the methyl protons of the 1-bromoethyl group were noticeable as a doublet; a quartet at 4.06 ppm was due to the methylene group of the ethyl ester group. The protons of the carbon atom in the 1-position (which is also substituted by the bromine atom) were located at 5.10 ppm (quartet), and the aromatic protons had shifts between 7.0 and 7.5 ppm (Table II).

Dehydrobromination of (III) to (IV) was accomplished with tributylamine in DMAc with a trace of picric acid added to prevent any possible polymerization of (IV). As in other dehydrobromination cases, the progress of this dehydrobromination reaction was readily followed by  $^1\text{H}$  NMR spectroscopy. The disappearance of the 5.1 ppm chemical shift in the spectrum of the proton of the (1-bromoethyl) group in (III) and the appearance of the  $-\text{CH}=\text{CH}_2$  (vinyl) protons between 5.2 and 7.1 ppm could be readily followed as the reaction proceeded.

The dehydrobromination product, (IV), a slightly yellow viscous oil, was distilled at  $200^\circ\text{C}$ , and 0.002 mmHg. The  $^1\text{H}$  NMR spectrum of (IV) showed aromatic protons to be occupying about the same position as that in compounds (III) or (II), with a small shift to lower field. The protons of the vinyl group could be clearly distinguished from the protons of the 1-bromoethyl group of the starting material (III).

Experience in the past has shown that vinyl compounds of the styrene type, especially those with high boiling points which readily undergo polymerization, must be stabilized by a radical inhibitor in order to purify these compounds by distillation at higher temperatures without significant thermal polymerization.<sup>9</sup> As a consequence, about 2 mol% of picric acid was always added when distilling (IV). Nevertheless, distillation residues from the purification of (IV) were always observed. In order to identify these residues as poly(IV), the distillation residues were dissolved in acetone and

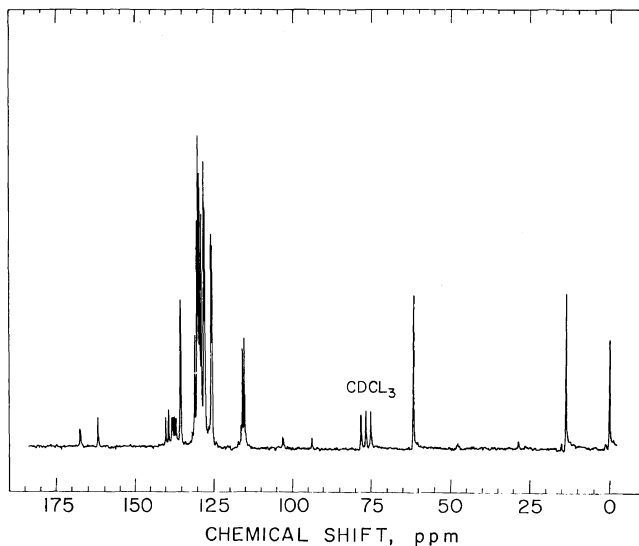
the material precipitated into diethyl ether. A light brown solid was isolated whose elemental analysis showed that the purified distillation residue was indeed an oligomer of (IV); infrared and NMR spectrum were in agreement with this structure.

It should be pointed out the low yields of (IV) from the Knoevenagel reactions of 4-vinylbenzophenone with ethyl cyanoacetate could be caused not only by incomplete reactions but may result from thermal polymerization of (IV) to oligomers since distillation even under good vacuum has to be carried out at relatively high temperatures. In addition (III) could be thermally dehydrobrominated to (IV) under the distillation conditions. This sequence of reactions can be observed even in the presence of the normally very effective radical polymerization inhibitor picric acid which was added to codistill with (IV).

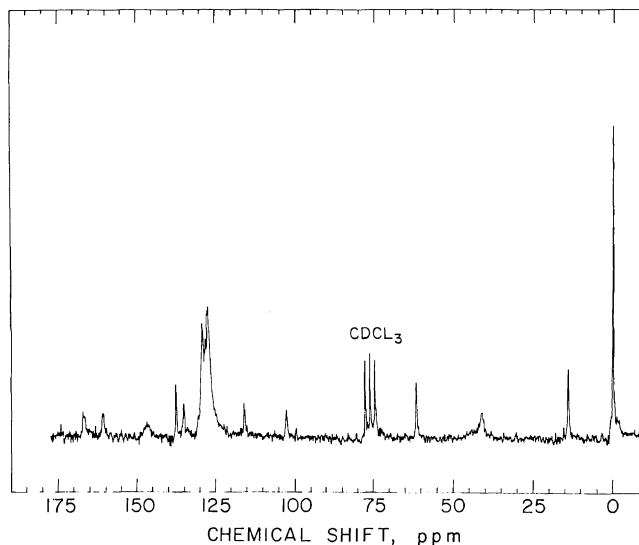
The  $^{13}\text{C}$  NMR chemical shift data for all four substituted derivatives of ethyl  $\alpha$ -cyano- $\beta$ -phenylcinnamate are shown in Table III. It can be seen that the carbon atom of the methyl group of the ethyl ester function is at 137 ppm, and the carbon atom of the methylene group at 62 ppm. The carbon atom of the methyl group of the 1-bromoethyl group is at 26 to 27 ppm and the carbon atom of the  $\text{CHBr}$  group at 48 ppm. The methylene group of the vinyl group is at 136 ppm and the  $\text{CH}$  group at 116 ppm. The other chemical shift data can also be clearly recognized and identified. Compounds (II), (III), and (IV) are mixtures of *cis* and *trans* isomers and have a number of carbon atoms which are sensitive to the  $^{13}\text{C}$  NMR resonance chemical shifts of the *cis* and *trans* isomers. The chemical shift difference between the *cis* and *trans* isomers is approximately 1 ppm. The detailed chemical shifts of compounds (II), (III), and (IV) are given in Table III and the  $^{13}\text{C}$  NMR spectrum of (IV) is shown in Figure 3. The objective of this work has not been the identification of geometric isomers (II), (III), and (IV) nor the separation of isomers.

A comparison of the NMR peak intensities indicate that the two isomers are formed in nearly equal amounts under the Knoevenagel reaction conditions. No attempts were made to develop reaction conditions under which the Knoevenagel reaction was stereospecific and forms only one or the other geometric isomer.

Ethyl-4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate (IV)



**Figure 3.**  $^{13}\text{C}$  NMR spectrum of ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate: solvent,  $\text{CDCl}_3$ ; 26,000 transients.



**Figure 4.**  $^{13}\text{C}$  NMR spectrum of poly(ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate: solvent,  $\text{CDCl}_3$ ; 26,000 transients.

was homopolymerized in a 50% benzene solution with AIBN (0.2 mol%) as the initiator. The polymer was obtained in nearly 50% yield as a yellow powder soluble in aromatic hydrocarbons but insoluble in ether. The inherent viscosity was only  $0.2 \text{ dl g}^{-1}$ . Elemental analysis, IR,  $^1\text{H}$  and  $^{13}\text{C}$

NMR spectrum confirmed the structure of poly(IV) (Figure 4).

Low-molecular-weight  $\alpha$ -cyano- $\beta$ -phenylcinnamate derivatives, (IV), poly(IV), and 85:15 percent copolymers of methyl methacrylate or styrene and (IV) showed absorption maxima

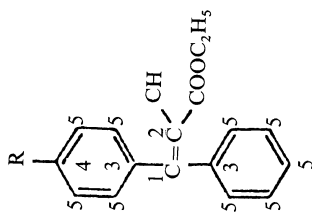


Table IV.  $^{13}\text{C}$  NMR chemical shifts of homopolymer and copolymers of ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate<sup>a</sup>

Polymers	$\text{CH}_3\text{CH}_2\text{O}-$		$\text{CH}_3$	$-\text{CH}_2-\text{C}-$	$-\text{OCH}_3$	$-\text{CH}_2-\text{C}-$	$-\text{CH}_2\text{CH}-$	$-\text{CN}$	$-\text{COOCH}_2-$	$-\text{COOCH}_3$	$\phi-\text{C}=\text{C}-$		Aromatic protons				
	$\text{CH}_3$	$\text{CH}_2$									1	2	1	2	3	4	5
Homopolymer of (IV)	13.74	62.03					40.49	116.07	168.14		162.06	103.39	136.10	147.29	125.60		
	13.91						42.07	116.93	168.95		162.64	103.69	138.60	148.63	131.47		
Copolymer (Styrene) 20 mol% (IV)	13.77	61.98					39.18	116.93	168.57		No	99.61	135.43	144.09	125.25		
							44.04		168.92		clear	104.95	139.00	145.66	131.27		
Copolymer (MMA) 13 mol% (IV)	13.74	62.12	16.71	51.75			44.69	116.71	168.36	174.64	162.75	103.62	136.38	146	127.59		
	14.29		20.01				46.48			178.28			138.86	149	131.36		
							52.49										
						55.32											

<sup>a</sup> In ppm downfield from TMS in  $\text{CDCl}_3$  (25%); 6000–26000 transients.

**Table V.** Ultraviolet spectral data<sup>a</sup> for ethyl  $\alpha$ -cyano- $\beta$ -phenylcinnamate, ethyl 4-ethyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate, ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate, poly(ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate) [poly(IV)], poly[(IV)-*co*-methylmethacrylate] (15:85), poly[(IV)-*co*-styrene] (15:85)<sup>b</sup>

Concn	$\lambda$	$A$	$\Sigma_M^c$	Averaged $\Sigma_M$
M	nm		l mol <sup>-1</sup> cm <sup>-1</sup>	
(a) Ethyl $\alpha$ -cyano- $\beta$ -phenylcinnamate				
$7.47 \times 10^{-5}$	306	0.956	12,800	12,730
$1.12 \times 10^{-5}$	306	1.423	12,700	
$1.25 \times 10^{-5}$	306	1.604	12,830	
$2.08 \times 10^{-4}$	306	2.614	12,570	
(b) Ethyl 4-ethyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate				
$2.96 \times 10^{-5}$	315	0.4065	13,720	13,680
$5.92 \times 10^{-5}$	315	0.807	13,620	
$2.40 \times 10^{-5}$	315	0.329	13,700	
$4.80 \times 10^{-5}$	315	0.655	13,650	
(c) Poly(ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate) [poly(IV)]				
$4.43 \times 10^{-5}$	310	0.555	12,530	12,400
$1.11 \times 10^{-5}$	309	1.378	12,410	
$6.43 \times 10^{-5}$	309	0.795	12,360	
$9.64 \times 10^{-5}$	309	1.187	12,310	
(d) Poly[(IV)- <i>co</i> -methyl methacrylate] (15:85)				
$2.80 \times 10^{-5}$	310	0.421	15,000	15,050
$4.70 \times 10^{-5}$	309	0.703	14,960	
$3.00 \times 10^{-5}$	309	0.453	15,100	
$4.93 \times 10^{-5}$	310	0.746	15,130	
(e) Poly[(IV)- <i>co</i> -styrene] (15:85)				
$5.53 \times 10^{-5}$	312	0.829	14,990	14,940
$7.74 \times 10^{-5}$	313	1.156	14,940	
$5.12 \times 10^{-5}$	313	0.763	14,900	
$8.54 \times 10^{-5}$	313	1.275	14,930	

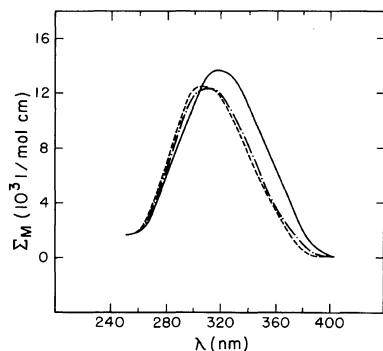
<sup>a</sup> Measurements in  $10^{-5}$  molar chloroform solutions.<sup>b</sup> Calculated for 100% poly(IV).<sup>c</sup> Molar extinction coefficient.

that were very similar and were between 306 and 315 nm with extinction coefficients of 12,000 to 15,000 l mol<sup>-1</sup> cm<sup>-1</sup> (Table V, Figures 5 and 6).

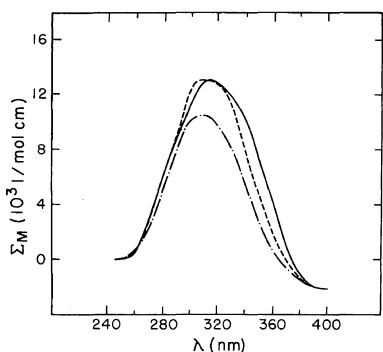
Ethyl-4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate (IV) could also be copolymerized with styrene and methyl methacrylate at a feed ratio of 15 mol% of (IV) in styrene and with 0.2 mol% of AIBN in 50% benzene solution. A viscous solution was obtained and poured into methanol. The resulting white powder was isolated in a 48% yield. According to elemental analysis and NMR spectrum, this polymer was a copolymer containing 20 mol% of (IV) units

in copolystyrene. The copolymerization of (IV) (15 mol%) with methyl methacrylate under similar polymerization conditions gave a viscous solution from which a white powdery polymer was precipitated in 90% yield. The inherent viscosity of this polymer was 0.3 dl g<sup>-1</sup> and infrared and NMR spectra confirmed its structure. Elemental analysis and <sup>1</sup>H NMR spectrum showed that the polymer contained 13 mol% of (IV) units. The <sup>13</sup>C NMR chemical shift data of the homopolymer and the two copolymers are shown in Table V.

In conclusion, it has been shown that (IV) can be



**Figure 5.** Ultraviolet spectra of derivatives of ethyl  $\alpha$ -cyano- $\beta$ -phenylcinnamate:  $\cdots$ , 4-H;  $-\cdot-$ , 4-ethyl;  $-\cdot-$ , 4-vinyl (IV);  $-$ , poly(IV).



**Figure 6.** Ultraviolet spectra of polymers and copolymers of ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate (IV):  $-$ , poly(IV);  $\cdots$ , poly[(IV)-*co*-styrene](15:85);  $-\cdot-$ , poly[(IV)-*co*-methyl methacrylate] (15:85).

obtained readily from (II) via bromination of the ethyl group with NBS and dehydrobromination without the formation of byproducts. In all reactions leading to (IV), the other parts of the molecule are surprisingly unaffected, especially the central tetrasubstituted ethylene double bond of the  $\alpha$ -cyano- $\beta$ -phenylcinnamate system which has two phenyl, one cyano and one carboethoxy group as substituents and does not become involved in bromination, dehydrobromination or the subsequent polymerization and copolymerization of (IV). Finally, it was demonstrated that (IV) can be homopolymerized or copolymerized with styrene and methyl methacrylate.

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