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Cycloaddition and Polymerization Reactions of Methyl α -Cyanoacrylate with Electron-Rich Olefins

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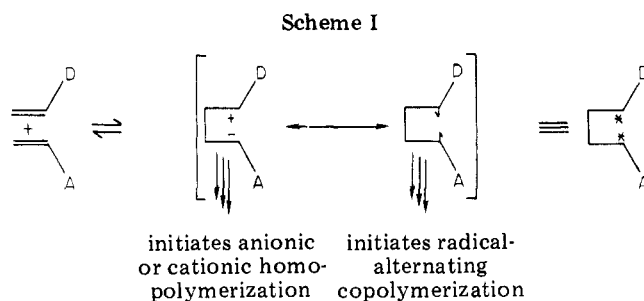
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Methyl α -cyanoacrylate reacts with isobutyl vinyl ether to form a zwitterionic tetramethylene intermediate which can cyclize in a [4 + 2] fashion to 2-isobutoxy-5-cyano-6-methoxy-3,4-dihydro-2H-pyran. This cycloadduct isomerizes to methyl 2-cyano-5-isobutoxypent-4-enoate at 70 °C. The zwitterionic intermediate can be trapped with methanol. When methyl α -cyanoacrylate reacts with *p*-methoxystyrene and styrene, the tetramethylene intermediates now display biradical character because of resonance stabilization. They initiate alternating 1:1 copolymerizations of the reaction components. Under appropriate conditions *p*-methoxystyrene and methyl α -cyanoacrylate also undergo two consecutive Diels-Alder reactions to a Wagner-Jauregg adduct. β -Bromostyrene is not reactive enough to form a tetramethylene at room temperature. At 110 °C a Diels-Alder reaction occurs, followed by hydrogen bromide elimination to form methyl 1-cyano-1,2-dihydronaphthalene-1-carboxylate.

The reactions of electron-rich olefins with electron-poor olefins form a remarkable variety of polymeric and small-molecule products.¹⁻⁶ Polymeric products include homopolymers of either or both monomers and alternating copolymers of both monomers. Small-molecule addition products include cyclobutanes, 1-butenes, 1,3-butadienes, cyclohexanes, etc. These reactions involve bond formation between the respective β -positions of the double bonds, generating a tetramethylene intermediate which behaves as a resonance hybrid of a zwitterion and singlet biradical.⁷⁻⁹ If derived from polymerizable olefins, the tetramethylene intermediate can then initiate cationic or anionic homopolymerization of, respectively, the electron-rich or electron-poor olefin or can initiate free-radical alternating copolymerization, depending on which character is predominant in the hybrid^{4,10} (Scheme I).

The small molecules formed by cyclization of the tetramethylenes, on the other hand, are not diagnostic for the nature of the tetramethylene intermediate. However, substituent and solvent effects as well as trapping experiments^{8,10} have been used to distinguish both mechanisms.

If further double bonds are present in either of the olefins, [4 + 2] cycloadditions will compete with the tetramethylene-type reactions. For example, in the presence of inhibitor, styrene reacts with maleic anhydride with participation of ring unsaturation to yield the "Wagner-Jauregg-type" 2:1 adduct¹¹ (two consecutive Diels-Alder reactions). The presence of an ester group in the elec-



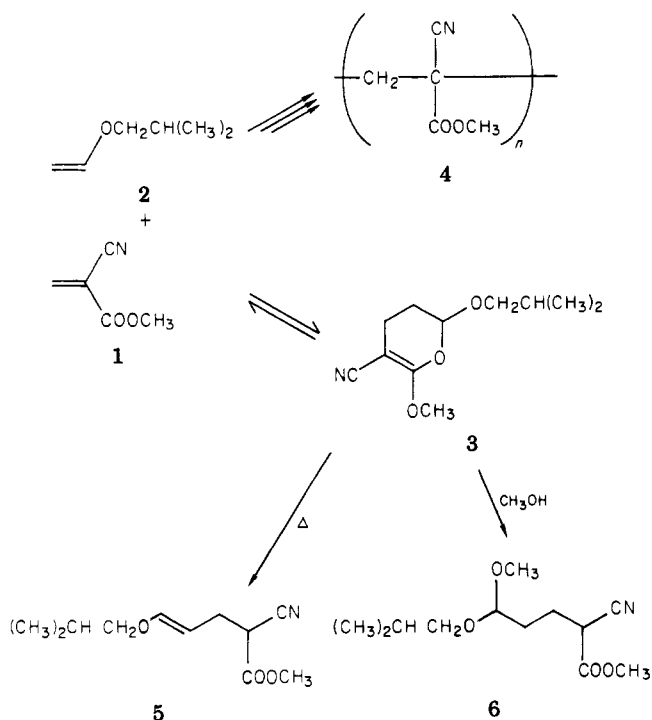
trophile can cause an inverse-electron-demand Diels-Alder reaction to occur. 6-Alkoxy-3,4-dihydro-2H-pyrans have been suggested in the dimerization and cycloaddition of acrylates.¹²⁻¹⁵ Recently, dihydropyrans were isolated in the reaction of carboxylic ester containing electron-poor olefins with electron-rich vinyl compounds.^{10,16}

Methyl α -cyanoacrylate is an extremely reactive monomer in anionic polymerization.¹⁷ In the presence of amines, Pepper reports that methyl α -cyanoacrylate polymerizes via a macrozwitterionic mechanism.¹⁸ It has also been widely studied in radically initiated homopolymerization and in copolymerizations with various vinyl compounds.¹⁹⁻²² Snider and Phillips report the formation of cyclobutane adduct and dihydropyran in the presence of alkenes when catalyzed by dimethylaluminum chloride.²³

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Scheme II



Continuing our study of the reactions of electron-rich with electron-poor olefins,^{3,4,5,10,16} we studied the behavior of methyl α -cyanoacrylate in the presence of a variety of electron-rich vinyl monomers.

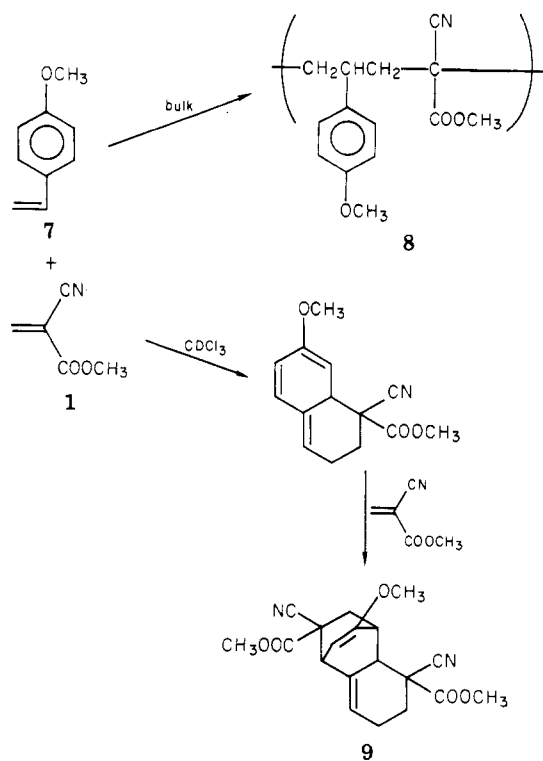
Results

Methyl α -cyanoacrylate is polymerized anionically with great ease by donor solvents. This fact limited the choice of reaction solvents and of working conditions.

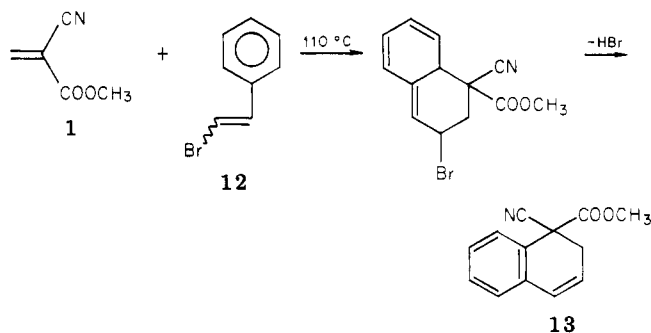
Isobutyl vinyl ether (2) reacted with methyl α -cyanoacrylate (1) in equimolar amounts at room temperature in bulk to give, after 24 h, 35% of cycloadduct 3 along with 56% of poly(methyl α -cyanoacrylate) (4). Addition of 2% acetic acid as inhibitor limits the polymer formation to 4%. In benzene, 86% of the cycloadduct 3 is obtained after 72 h and only a trace of poly(methyl α -cyanoacrylate). The cycloadduct 3 was identified as 2-isobutoxy-5-cyano-6-methoxy-3,4-dihydro-2H-pyran by spectroscopic methods (Scheme II). Pyran 3 itself is not a very stable compound. It isomerizes to the thermodynamically more stable isomer, methyl 2-cyano-5-isobutoxypent-4-enoate (5) when left at room temperature for 2 weeks or upon heating a benzene solution of 3 at 70 °C for 2 days. Distillation of 3 also gave the more stable isomer 5. Stirring 3 in methanol at room temperature for 2 days gave a 92% yield of the methanol adduct 6.

***p*-Methoxystyrene (7)** reacts spontaneously and exothermically with methyl α -cyanoacrylate (1) in bulk to give a 61% yield of a 1:1 alternating copolymer (8, Scheme III). A small amount of ether-soluble 1:2 Wagner-Jauregg-type adduct 9 was isolated. In 1,2-dichloroethane at 68 °C for 72 h, an equimolar mixture of *p*-methoxystyrene (7) and methyl α -cyanoacrylate yielded 82% of the 1:1 alternating copolymer 8 in addition to small amounts of 9. Deliberate free-radical-initiated copolymerization using azobis(isobutyronitrile) (AIBN) and UV light at 40 °C resulted in a 74% yield of the same copolymer 8. The cycloaddition reaction in deuterated chloroform solution at room tem-

Scheme III



Scheme IV



perature, was monitored by NMR spectroscopy. After 18 h, the spectrum showed the formation of the adduct 9, dimethyl 5,10-dicyano-3-methoxy-1,4,4a,5,6,7-hexahydro-1,4-ethanonaphthalene-5,10-dicarboxylate. The use of free-radical inhibitor, bis(4-hydroxy-3-*tert*-butyl-5-methylphenyl)sulfide, does not affect the formation of adduct 9. In benzene solution both copolymer 8 and 2:1 adduct 9 are formed.

Styrene (10) was copolymerized with methyl α -cyanoacrylate (1) by using AIBN and UV light in a benzene solution at 40 °C to give a 98% yield of the 1:1 alternating copolymer 11. Deliberate free-radical initiation is not necessary to produce copolymer 11; a 58% yield of 11 was produced spontaneously at room temperature in benzene.

β -Bromostyrene (12) did not react with 1 at room temperature. The reaction in bulk at 110 °C gave a yield of methyl 1-cyano-1,2-dihydronaphthalene-1-carboxylate (13). Diels-Alder-type addition, followed by dehydrobromination, is responsible for the formation of 13 (Scheme IV). No polymer was isolated in these reactions. All the results are summarized in Table I.

Discussion

In our previous work^{3,4,10} we have proposed the formation of a tetramethylene intermediate as a unifying concept

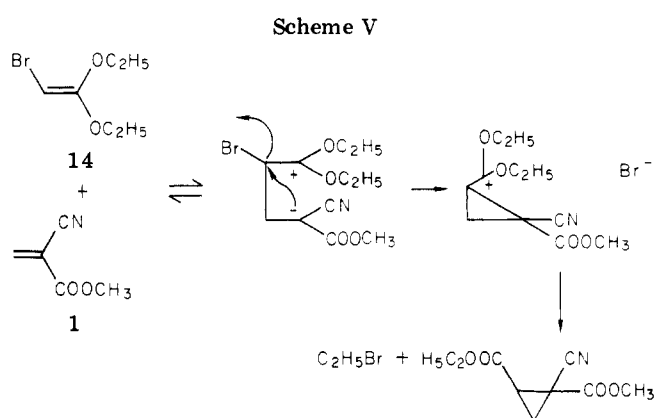
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Table I. Reactions of Methyl α -Cyanoacrylate

electron-rich olefin	feed, ^a mmol	initiator ^b	temp, °C	time, h	solvent ^c	yield, %		
						homo- polymer 4	co- polymer	cycloadduct
CH ₂ =CHOCH ₂ CH(CH ₃) ₂	8:8	none	28	24	none	56	0	35 (3)
CH ₂ =CHOCH ₂ CH(CH ₃) ₂	4:4	none	28	72	benzene	trace	0	86 (3)
<i>p</i> -CH ₃ OC ₆ H ₄ CH=CH ₂	2:2	none	28	24	none		61	small amount (9)
<i>p</i> -CH ₃ OC ₆ H ₄ CH=CH ₂	2:2	I	40	24	1,2-dichloro- ethane		74	
<i>p</i> -CH ₃ OC ₆ H ₄ CH=CH ₂	2:2	none	68	72	1,2-dichloro- ethane		82	small amount (9)
<i>p</i> -CH ₃ OC ₆ H ₄ CH=CH ₂	4:8	none	28	24	benzene	47		50 (9)
C ₆ H ₅ CH=CH ₂	2.7:2.7	I	40	24	benzene		98	
C ₆ H ₅ CH=CH ₂	7.5:7.5	none	28	72	benzene		58	
C ₆ H ₅ CH=CHBr	4:4	none	28	24	benzene	0	0	0
C ₆ H ₅ CH=CHBr	12:12	none	110	17	none	0	0	60 (13)

^a A feed ratio in millimoles of 4:8 means 4 mmol of electron-rich olefin and 8 mmol of methyl α -cyanoacrylate.

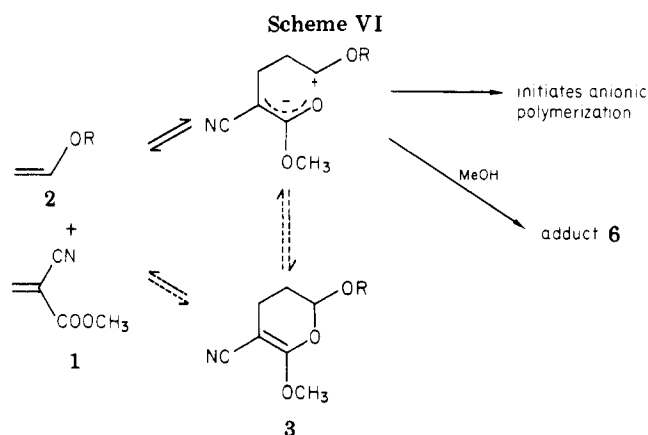
^b Initiator I: AIBN at 40 °C under photoirradiation for 24 h at 40 °C. ^c Solvent volume was 5 mL.



for the reactions of electron-rich with electron-poor olefins. Huisgen¹ notes that the substituents on the terminal centers jointly decide where a given tetramethylene species has to be located on the continuous scale between biradical and zwitterion. In this study the negative end of the tetramethylene is kept constant (cyanoester) while the positive end is being varied. It is of interest to compare the results obtained in this investigation with those established in earlier papers.

In the reaction of methyl α -cyanoacrylate and isobutyl vinyl ether a zwitterionic intermediate can be trapped by methanol. Anionic homopolymerization of the very sensitive cyanoacrylate is due either to the zwitterionic intermediate or to adventitious initiation. No spontaneous copolymerization was observed as described in a recent paper.²² The zwitterionic intermediate is in agreement with earlier work by Huisgen¹ and Hall and Ykman³ where it has been found that alkoxy substituents, strong electron-pair-donating groups, always favor zwitterion behavior. Also, in the reaction of methyl α -cyanoacrylate with a 1,1-diethoxy-2-bromoethylene (14) the zwitterion behavior was clearly demonstrated by internal trapping resulting in a cyclopropane derivative (Scheme V).²⁵

Contrastingly, in the reactions of *p*-methoxystyrene and styrene with methyl α -cyanoacrylate, the formation of 1:1 alternating copolymers clearly indicated the occurrence of biradical tetramethylene intermediates. *p*-Methoxyphenyl and phenyl substituents are clearly softer donors which are less effective as cation stabilizers. They can, however,



still resonance stabilize a biradical intermediate, as was also shown in the reactions of *p*-methoxystyrene with several trisubstituted ethylenes by Abdelkader and Hall.¹⁰ Only the extremely basic (dimethylamino)phenyl group as donor group leads to zwitterionic tetramethylenes.⁴

As far as the negative end of the tetramethylene intermediates is concerned, two ester groups show biradical behavior¹⁰ and two cyano groups show zwitterion behavior as was shown by Stille and Chung.²⁴ One cyano and one ester group is an intermediate case in which either zwitterion or biradical behavior can occur, as shown in this work.

β -Bromostyrene is not electron-rich enough to form a tetramethylene intermediate with methyl α -cyanoacrylate.

In these reactions [4 + 2] cycloadducts were also formed. In the case of *p*-methoxystyrene, two consecutive Diels-Alder reactions led to a 2:1 adduct, the so-called Wagner-Jauregg adduct. While structure 9 is the one expected from the known regioselectivity of the Diels-Alder reaction, the isomeric structure is not excluded by the NMR data. β -Bromostyrene and methyl α -cyanoacrylate from a Diels-Alder adduct; dehydrobromination leads to the dihydronaphthalene derivative 13.²⁶ In the case of isobutyl vinyl ether, the obtained dihydropyran 5 can originate either from a concerted Diels-Alder-type reaction or from a stepwise [4 + 2] cycloaddition (Scheme VI). The trapping of the zwitterion in methanol leading to adduct 6 would imply a stepwise mechanism. The normal addition product of methanol to the dihydropyran 3 would be a

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cyclic pyran with two methoxy groups on the 6-carbon. However, the dihydropyran formation is reversible and the formed starting materials could then combine to form the zwitterion which would be trapped. As yet, no information is available as to if these cycloadditions are independently competing concerted reactions or if they follow a stepwise mechanism involving a tetramethylene intermediate.

Experimental Section

Instrumentation. All boiling points and melting points are uncorrected. Melting points were determined on a Thomas-Hoover melting point apparatus. Infrared spectra were taken on a Perkin-Elmer 398 spectrophotometer, and nuclear magnetic resonance spectra were obtained on a Varian EM360 spectrometer. Mass spectra were obtained on a Varian 311A mass spectrometer. Elemental analyses were performed by a University of Arizona Analytical Center, Tucson, or Huffman Laboratories, Inc., Wheatridge, CO.

Solvents. Benzene was purified by refluxing over sodium metal, followed by fractional distillation, and was stored over molecular sieves under argon. 1,2-Dichloroethane was purified by drying over phosphorus pentoxide overnight, followed by fractional distillation and storing under argon over molecular sieves.

Materials. *p*-Methoxystyrene, styrene, isobutyl vinyl ether, and β -bromostyrene (Aldrich) were distilled from calcium hydride at appropriate pressures and stored in capped bottles under argon at -10°C .

Methyl α -cyanoacrylate (Eastman 9/10 FS adhesive) was distilled from phosphorus pentoxide and stored under argon at -10°C .

2-Isobutoxy-5-cyano-6-methoxy-3,4-dihydro-2H-pyran (3). A solution of 1.7 g (13 mmol) of methyl α -cyanoacrylate in 5 mL of dry benzene was mixed under argon with another solution of 1.32 g (13 mmol) of isobutyl vinyl ether in 5 mL of dry benzene. The mixture was stirred at room temperature for 72 h. The reaction mixture was then diluted with 30 mL of benzene. The precipitated poly(methyl α -cyanoacrylate) was filtered (trace) and washed with small amounts of benzene. The benzene solvent was evaporated under vacuum at room temperature to give 2.6 g (87%) of the pyran: IR (neat) 2200 (C \equiv N), 1680 (C=C) cm^{-1} ; NMR (CDCl₃) δ 5.2 (t, 1, O—CH—O), 3.82 (s, 3, OCH₃), 3.2–3.7 (m, 2, OCH₂), 1.5–2.6 (m, 5, ring and CH(CH₃)₂), 0.95 (d, 6, CH₃). Anal. Calcd for C₁₁H₁₇NO₃: C, 62.53; H, 8.11; N, 6.63. Found: C, 61.83; H, 7.99; N, 6.69.

Methyl 2-Cyano-5-isobutoxypent-4-enoate (5). Compound 3 isomerizes to 5 upon distillation under vacuum: IR (neat) 2240 (C \equiv N), 1750 (C=O), 1650 (C=C) cm^{-1} ; NMR (CDCl₃) δ 6.5 (d, $J = 14$ Hz, OCH=, trans), 6.16 (d, $J = 7$ Hz, OCH=, 4.9–4.2 (m, 1, CH₂CH=), 3.8 (s, 3, COOCH₃), 3.4 (t, 2, CH₂O), 2.8 (t, 1, CH(CN)(COOCH₃)), 2.1–1.5 (m, 1, CH(CH₃)₂), 0.95 (d, $J = 6$ Hz, 6, (CH₃)₂CH). Anal. Calcd for C₁₁H₁₇NO₃: C, 62.53; H, 8.11; N, 6.63. Found: C, 61.93; H, 8.03; N, 6.84. The product is a mixture of cis and trans isomers (70:30), respectively, by NMR.

Methyl 2-Cyano-5-methoxy-5-isobutoxypentanoate (6). A solution of 0.5 g (2.4 mmol) of 3 was stirred in 10 mL of methanol for 2 days at room temperature. The solvent was then evaporated under vacuum, and the colorless oil was collected and dried to give 6: 0.53 g (92%); IR (neat) 2250 (C \equiv N), 1750 (C=O) cm^{-1} ;

NMR (CDCl₃) δ 4.45 (t, $J = 5$ Hz, O—CH—O), 3.8 (s, 3, COOCH₃), 3.5–3.2 (s and m, 6, OCH₃, NCCHCOOCH₃, and OCH₂), 2.2–1.5 (m, 5, CH₂CH₂ and CH). Anal. Calcd for C₁₂H₂₁O₄N: C, 59.23; H, 8.70; N, 5.76. Found: C, 58.72; H, 8.96; N, 5.58.

Dimethyl 5,10-Dicyano-3-methoxy-1,4,4a,5,6,7-hexahydro-1,4-ethanonaphthalene-5,10-dicarboxylate (9). A solution of 0.27 g (2.0 mmol) of *p*-methoxystyrene in 5 mL of benzene was mixed with another solution of 0.22 g (2.0 mmol) of methyl α -cyanoacrylate in 5 mL of benzene. The mixture was stored at room temperature for 24 h. The precipitated poly(methyl α -cyanoacrylate) (0.1 g) was filtered and washed with benzene. Benzene solvent was then evaporated to give 9: 0.36 g (50%); mp 154–155 $^\circ\text{C}$; IR (KBr) 2240 (C \equiv N), 1730 (C=O), 1630 (C=C) cm^{-1} ; NMR (CDCl₃) δ 5.6 (br t, 1, =CHCH₂), 4.8 (dd, 1, =CHCH); 3.8 (s, 3, COOCH₃), 3.75 (s, 3, COOCH₃), 3.55 (s, 3, OCH₃), 2.9–2.0 (m, 9, CH₂CH₂, CH₂CH, and CH); mass spectrum (molecular ion), m/e 356, 325, 245, 134. Anal. Calcd for C₁₅H₂₀O₅N₂: C, 64.03; H, 5.66; N, 7.86. Found: C, 63.98; H, 5.76; N, 7.79.

Methyl 1-Cyano-1,2-dihydronaphthalene-1-carboxylate (13). β -Bromostyrene (2.19 g, 15 mmol) was mixed with 1.32 g (15 mmol) of methyl α -cyanoacrylate in bulk. The mixture was stirred at 110 $^\circ\text{C}$. After 17 h, the reaction mixture was allowed to cool to room temperature, diluted with 30 mL of benzene, and filtered. The solvent was then removed under vacuum. The product was distilled twice under reduced pressure to give 1.6 g (60%) of methyl 1-cyano-1,4-dihydronaphthalene-1-carboxylate [13; bp 100–105 $^\circ\text{C}$ (0.05 mmHg)], which crystallized on standing to very nice crystals: mp 52–54 $^\circ\text{C}$; IR (KBr) 2210 (C \equiv N); 1740 (C=O) cm^{-1} ; NMR (CDCl₃) δ 7.1–7.7 (m, 3, disubstituted phenyl), 6.6 (d, $J = 8$ Hz, 1, CH=CH), 5.8–6.2 (m, 1, CH=CHCH₂), 3.8 (s, 3, OCH₃), 2.9–3.2 (m, 2, CH=CHCH₂). mass spectrum (molecular ion), m/e 213, 186, 154. Anal. Calcd for C₁₃H₁₁NO₂: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.4; H, 5.2; N, 6.5.

Solution Copolymerization. A solution of 2.7 mmol of methyl α -cyanoacrylate in 5 mL of benzene was mixed under argon atmosphere with another solution of 2.7 mmol of styrene in 5 mL of benzene. AIBN (10 mg) was added to the mixture. The system was degassed by several freeze-thaw cycles under vacuum and then argon. Finally, the reaction tube was flushed with argon, capped, and irradiated with UV light for 24 h at 40 $^\circ\text{C}$. At the end of this period the polymer was precipitated in methanol, washed with methanol, and dried overnight at 70 $^\circ\text{C}$ under vacuum.

Bulk Copolymerization. Under a dry argon atmosphere, methyl α -cyanoacrylate was injected into a capped polymerization tube containing an equimolar amount of *p*-methoxystyrene at room temperature. Acetic acid (2%) was added in one run. After 24 h, the polymer was dissolved in chloroform, precipitated in methanol, and dried overnight at 70 $^\circ\text{C}$ under vacuum.

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Registry No. 1, 137-05-3; 2, 109-53-5; 3, 81245-85-4; 4, 25067-29-2; (E)-5, 81245-86-5; (Z)-5, 81245-87-6; 6, 81245-88-7; 7, 637-69-4; 8, 81246-01-7; 9, 81245-89-8; 10, 100-42-5; 11, 55231-18-0; 12, 103-64-0; 13, 81245-90-1.