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A general synthesis of 1,1 disubstituted electron deficient olefins and their polymer properties

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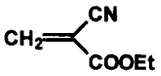
A general procedure was developed for the synthesis of 1,1 disubstituted electron deficient olefin monomers. The formation of the phenylselenide precursor, followed by hydrogen peroxide oxidation produced the monomers in good yields and purity. Acidic by-products of the oxidation reaction act as stabilizers to prevent polymerization of these base sensitive monomers. The dicyanoacrylate ester of butanediol, diethyl methylenemalonate, N,N diethyl 2-cyanoacrylamide, and 2′-octyl 2-cyanoacrylate were prepared by this method. These monomers were polymerized alone and copolymerized with ethyl 2-cyanoacrylate (ECA) in THF with pyridine as the initiator. Gel permeation chromatography and thermogravimetric analysis were utilized to study some of the polymer properties. The ECA homopolymer yielded the polymer with the highest degree of polymerization, while the diethyl methylenemalonate homopolymer possessed the highest decomposition temperature. © 1997 Elsevier Science Ltd.

(Keywords: cyanoacrylate; copolymer; phenylselenide oxidation)

INTRODUCTION

Alkyl cyanoacrylate instant adhesives are utilized in a wide variety of adhesive applications because of their rapid rate of polymerization and their effectiveness on a range of substrates under ambient conditions[1]. Ethyl 2-cyanoacrylate (ECA), **1**, is the most widely



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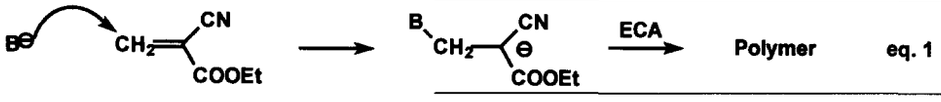
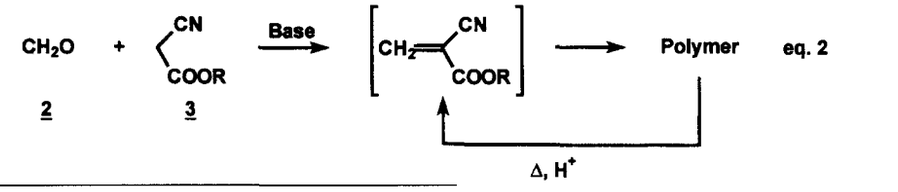
utilized alkyl cyanoacrylate instant adhesive monomer. Its chemical structure, a 1,1 disubstituted olefin with two electron withdrawing groups, is responsible for its ability to polymerize rapidly. ECA is an excellent Michael acceptor for polymer initiation by weak nucleophiles or bases, while the nitrile and carboethoxy groups stabilize the propagating anion during rapid polymerization, as shown in equation (1).



(1)

Alkyl cyanoacrylate adhesives have been modified extensively with additives that do not copolymerize with the alkyl cyanoacrylate monomer[2], and many studies have been performed on the copolymerization of alkyl cyanoacrylate monomers with other monomers using radical initiators[3]. However, little has been published on the nucleophile initiated copolymerization of alkyl cyanoacrylates with other 1,1 disubstituted, electron-deficient olefin monomers or the modification of adhesives with these monomers. In addition, only a limited amount of information has been published on difunctional cyanoacrylate monomers, which can be utilized to produce cross-linked alkyl cyanoacrylate polymers[4]. The reason for this might be the lack of a simple, general procedure for the synthesis of electron deficient monomers or difunctional cyanoacrylate monomers.

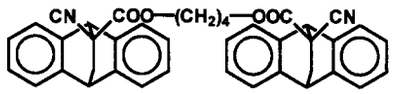
The conventional synthesis of ECA, **1**, involves the Knoevenagel reaction between formaldehyde, **2**, and ethyl 2-cyanoacetate, **3**[5]. Polymerization of **1** occurs *in situ*, but heating the polymer in the presence of acid effects a thermal reversion back to the ECA monomer, as shown in equation (2).



(2)

Thermolysis of the ECA polymer is relatively straightforward because of the low boiling point of ECA under vacuum distillation conditions, but the preparation of higher boiling alkyl cyanoacrylate monomers is more difficult. The higher distillation temperatures results in lower yields and purity because of the side-reactions and more extensive thermal decomposition that occur during thermal reversion and distillation. Additionally, this reaction sequence is not viable for the preparation of difunctional cyanoacrylate monomers. Thermal degradation of the polymer occurs prior to thermal reversion because of the extensive cross-linking.

Two syntheses of dicyanoacrylate monomers have been reported that do not require a base to form the desired difunctional monomer. The first reported synthesis of a difunctional cyanoacrylate, such as the dicyanoacrylate ester of butanediol (BDDCA), **4**, utilized a reverse Diels–Alder reaction of the difunctional cyanoacrylate dihydroanthracene precursor, **5**, in the



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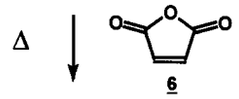

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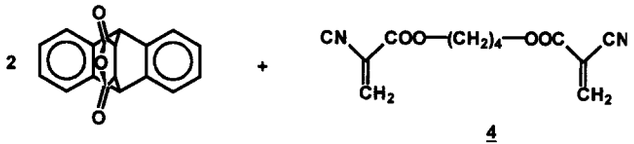

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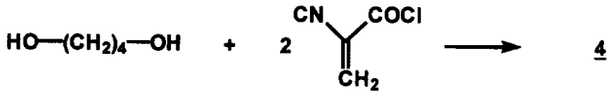
presence of maleic anhydride, **6**[4]. The second synthesis used an excess of 2-cyanoacryloyl chloride, **7**, to esterify a diol[6], such as 1,4 butanediol, but both methods yield by-products that



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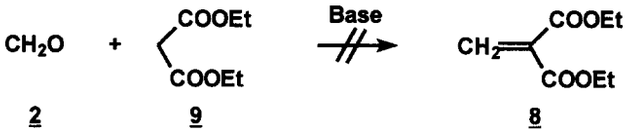
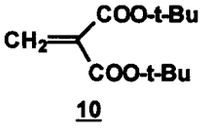
are difficult to separate from the difunctional monomer. A proper evaluation of their polymer properties and their use as cross-linkers with monofunctional alkyl cyanoacrylate monomers is difficult because of their limited purity.

The synthetic procedure for the preparation of ECA cannot be applied as a general method for other monofunctional 1,1 disubstituted electron deficient olefins. For example, attempts to prepare diethyl methylenemalonate (DEMM), **8**, from formaldehyde, **2**, and diethyl



2 **9** **8**

malonate, **9**, under the same reaction conditions as those employed for ECA does not yield the desired product, **8**. Di-t-butyl methylenemalonate, **10**, can be prepared under acidic conditions with a metal catalyst[7], but this procedure is not effective for ECA.



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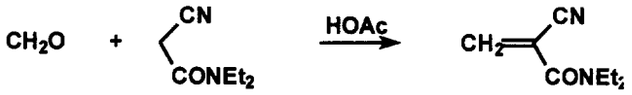
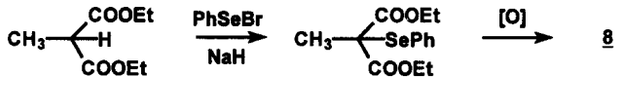
N,N diethyl 2-cyanoacrylamide, **11**, is also prepared under acidic conditions from N,N diethyl 2-cyanoacetamide, **12**, and paraformaidehyde[8], but, again, these reaction conditions are not very effective for the preparation of ECA.



12 **11**

DEMM, **8**, has been prepared by the reaction of diethyl methylmalonate, **13**, with phenylselenium bromide to form a phenylselenide precursor, **14**, in quantitative yield and good purity of the crude product. Oxidation of crude **14** with ozone or hydrogen peroxide produces



13 **14**

olefin **8** with only trace amounts of unidentified by-products. Distillation removes these impurities and **8** is isolated in high yield and purity[9].

This investigation describes the extension of this same synthetic methodology to the preparation of a difunctional cyanoacrylate monomer, a dialkyl cyanoacrylamide, and an alkyl cyanoacrylate monomer with a long alkyl ester group. Polymerization studies were also performed with each monomer alone and with ECA to form copolymers.

EXPERIMENTAL SECTION

Diethyl methylmalonate was obtained from Aldrich Chemical Co. and ethyl 2-cyanopropionate was obtained from TCI America. Both were used without further purification. Diphenyl diselenide was purchased from Aldrich or Janssen Chimica and was recrystallized from ethanol prior to use. THF was distilled from sodium-benzophenone immediately before use. Sodium hydride (95%) was purchased from Aldrich as a powder and was stored in a desiccator.

Reaction glassware was oven dried before use. All glassware for the preparation of BDDCA, DEMM, DECA and 2-OCA was immersed overnight in 0.5 M H_2SO_4, rinsed with deionized water, and oven dried. All transfers of dried solvents were performed with a syringe.

Proton NMR spectra were obtained on a Varian Gemini 300 MHz NMR spectrometer. Infrared (i.r.) analyses were done on an ATI Mattson Genesis Series FTi.r. TGA data was obtained under nitrogen on a TA Instrument 951 Thermogravimetric Analyser. GPC analyses were performed with a Waters 600E Controller and pumps, PL gel 5μ mixed bed columns, a Waters 410 RI detector, and Maxima software for analysis. The GPC solvent was THF and the flow rate was 1.0 ml min^{-1}. Narrow polymethylmethacrylate standards were utilized to calculate molecular weights.

Phenylselenium bromide

To a three-necked 250 ml flask, equipped with a nitrogen inlet, magnetic stirrer and rubber septum, was added diphenyl diselenide (20.9 g, 67 mmol) and THF (100 ml) under nitrogen. Bromine (9.8 g, 61 mmol) was added by syringe. The solution was stirred for 5 min and added to the reaction flask with the organic anion by syringe.

Diethyl methylmalonate phenylselenide (**14**)

To a four-necked 500 ml flask, equipped with a condenser, mechanical stirrer, thermometer and nitrogen inlet, was added sodium hydride (3.9 g, 153 mmol) and THF (250 ml) under nitrogen. Diethyl methylmalonate (20 g, 115 mmol) was added carefully over 10 min and the reaction mixture was stirred for 1 h at room temperature. Hydrogen gas evolved during the addition of diethyl methylmalonate. A solution of phenylselenium bromide, prepared by the above method, was added by syringe. The reaction mixture was stirred for 1 h and added to 250 ml each of ether and saturated aqueous $NaHCO_3$. The organic layer was washed twice with 250 ml of H_2O and once with 250 ml saturated aqueous NaCl. The organic layer was separated, dried ($MgSO_4$) and filtered. Solvent was removed under reduced pressure. Yield = 38.5 g (quant.); NMR δ ($CDCl_3$) 7.65 (d, 2H, Ph), 7.30 (m, 3H, Ph), 4.20 (q, 4H, J = 7 Hz, OCH_2), 1.30 (s, 3H, CH_3), 1.25 (t, 6H, J = 7 Hz, CH_3); i.r. (neat) 1726, 1250 cm^{-1}.

Diethyl methylenemalonate (DEMM, **8**)

To a 500 ml flask, equipped with a condenser, mechanical stirrer, thermometer and addition funnel, was added the crude diethyl methylmalonate phenylselenide (38.5 g, 115 mmol) and methylene chloride (300 ml). Hydrogen peroxide, 30% (47 g, 418 mmol) was dissolved in water (30 ml) and added to the reaction flask over 15 min. The reaction temperature was kept at 20–30°C with an ice bath. After the addition was complete, the reaction mixture was stirred for 1 h at room temperature. The organic layer was separated and washed once with 100 ml of H_2O. The organic layer was separated, dried (anhydrous silicic acid), and filtered. Solvent was removed under reduced pressure. The crude product was distilled under a vacuum. Yield = 13.0 g (66%), B.P. = 52°C per 0.4 Torr; NMR δ ($CDCl_3$) 6.50 (s, 2H,=CH_2), 4.30(q, 4H, J = 7 Hz, OCH_2), 1.33 (t, 6H, J = 7 Hz, CH_3); i.r. (neat) 1730, 1625, 1237 cm^{-1}.

N,N Diethyl 2-cyanopropionamide (DECP, **16**)

To a 1000 ml four-necked flask, equipped with a condenser, mechanical stirrer, thermometer, nitrogen inlet and addition funnel, was added 2.0 M trimethyl aluminium in hexane (228 ml, 456 mmol) and toluene (500 ml) under nitrogen. The solution was cooled with an ice/salt bath to 0–5°C. Diethylamine (32.2 g, 440 mmol) was added over 30 min. The rate of addition was controlled to keep the reaction temperature less than 10°C. After the addition was complete, the solution was stirred for 20 min with cooling and for 45 min at room temperature. Ethyl 2-cyanopropionate (50.8 g, 400 mmol) was dissolved in toluene (50 ml) and added to the reaction flask over 15 min. The solution was heated to 75–80°C. After heating for 16 h, the reaction was complete, as shown by i.r. analysis. The solution was cooled to 5-10°C in an ice bath and 0.67 M HCl (800 ml) was added very slowly to quench the reaction. After the HCl addition was complete, the reaction mixture was stirred for 45 min at room temperature. The organic layer was separated, and the aqueous layer was washed twice with 100 ml of ethyl acetate. The organic layers were combined and washed once with 500 ml of saturated aqueous NaCl. The organic layer was separated, dried ($MgSO_4$), and filtered. Solvent was removed under reduced pressure. The crude product was vacuum distilled. Yield = 34.6 g (56%), B.P. = 80°C per 0.4 Torr; NMR δ ($CDCl_3$) 3.70 (q, 1H, J = 7 Hz, CH), 3.40 (m, 4H, J = 7 Hz, CH_2), 1.55(d, 3H, J = 7 Hz, CH_3), 1.28 (t, 3H, J = 7 Hz, CH_3), 1.15 (t, 3H, J = 7 Hz, CH_3); i.r. (neat), 2243, 1654 cm^{-1}.

N,N Diethyl 2-cyanopropionamide phenylselenide

This product was prepared by the same procedure as that for diethyl methylmalonate phenylselenide with sodium hydride (5.4 g, 215 mmol), THF (400 ml), N,N diethyl-2-cyanopropionamide (25.0 g, 162 mmol), diphenyl diselenide (30.0 g, 96 mmol), bromine (13.8 g, 86 mmol), and THF (100 ml). Yield = 37.1 g (74%); NMR δ ($CDCl_3$) 7.75 (d, 2H, Ph), 7.4 (m, 3H, Ph), 3.95 (m, 1H, CH_2), 3.50 (m, 2H, CH_2),3.25 (m, 1H, CH_2), 1.82 (s, 3H, CH_3), 1.35 (br t, 3H, CH_3),1.15 (br t, 3H, CH_3); i.r. (neat) 2221, 1646 cm^{-1}.

N,N diethyl 2-cyanoacrylamide (DECA, **11**)

This product was prepared by the same procedure as that for diethyl methylenemalonate with N,N diethyl-2-cyanopropionamide phenylselenide (37.1 g, 120 mmol), methylene chloride (250 ml), 30% hydrogen peroxide (51.1 g, 451 mmol), and water (35 ml). Yield = 13.8 g (76%), B.P. = 75°C per 0.95 Torr, NMR δ ($CDCL_3$) 6.4 (s, 1H,=CH_2), 6.3 (s, 1H,=CH_2), 3.45 (br q, 4H, CH_2), 1.25 (br t, 6H, CH_3); i.r. (neat) 3111, 2224, 1651, 1606 cm^{-1}.

1,4 Butanediol dicyanopropionate (**15**)

To a 1000 ml three-necked flask equipped with a Dean–Stark trap, condenser, thermometer and nitrogen inlet, was added ethyl 2-cyanopropionate (50.8 g, 400 mmol), 1,4 butanediol (15.8 g, 175 mmol), p-toluenesulfonic acid (3 g, 16 mmol), and toluene (500 ml) under nitrogen. The solution was heated to reflux with stirring. Solvent was removed through the Dean–Stark trap and replaced with an equal volume of fresh toluene. After refluxing for 8 h and removing 500 ml of solvent, the solution was cooled to room temperature. The solution was washed twice with 300 ml of saturated aqueous $NaHCO_3$, twice with 300 ml of H_2O, and once with 300 ml of saturated aqueous NaCl. The organic layer was separated, dried ($MgSO_4$) and filtered. Solvent was removed under reduced pressure. The crude product was purified by vacuum distillation. Yield = 22.3 g (51%), B.P. = 172°C per 0.6 Torr; NMR δ ($CDCl_3$) 4.35 (br t, 4H, OCH_2), 3.80 (br t, 4H, CH_2), 3.60 (q, 2H, J = 6 Hz, CH), 1.60 (d, 6H, J = 6 Hz, CH_3); i.r. (neat) 2252, 1745 cm^{-1}.

1,4 Butanediol dicyanopropionate bis-phenylselenide

To a 500 ml four-necked flask, equipped with a condenser, mechanical stirrer, thermometer, rubber septum and nitrogen inlet was added sodium hydride (2.7 g, 105 mmol) and anhydrous dimethyl formamide (200 ml) under nitrogen. Butanediol dicyanopropionate (10 g, 40 mmol) was added over 10 min at room temperature, and the reaction mixture was stirred for 2 h. A phenylselenium bromide solution, previously prepared from diphenyl diselenide (17.2 g, 55 mmol), bromine (7.2 g, 45 mmol) and THF (100 ml), was added by syringe and the reaction mixture was stirred for 2.5 h. The reaction mixture was added to 250 ml each of ether and saturated aqueous $NaHCO_3$. The organic layer was washed twice with 250 ml of H_2O and once with 250 ml of saturated aqueous NaCl. The organic layer was separated, dried ($MgSO_4$) and filtered. Solvent was removed under reduced pressure. Crude yield = 23.4 g (quant). To the crude product was

added 10 ml of ether and the mixture was cooled in an ice bath. The bis-phenylselenide precipitated was filtered and washed with 5 ml of cold ether. Yield = 6.5 g (29%), M.P. = 113°C; NMR δ ($CDCl_3$) 7.75 (d, 4H, Ph), 7.40 (m, 6H, Ph), 4.10 (m, 4H, OCH_2), 3.50 (m, 4H, CH_2), 1.85 (s, 6H, CH_3); i.r. (KBr) 2231, 1730, 1234 cm^{-1}.

1,4 Butanediol dicyanoacrylate (BDDCA, **4**)

To a 250 ml flask, equipped with a condenser, mechanical stirrer, thermometer, and addition funnel, was added the bis-phenyselenide (6.5 g, 12 mmol) and methylene chloride (50 ml). Hydrogen peroxide, 30% (11.6 g, 102 mmol) was dissolved in water (8 ml) and added slowly to the reaction flask over 10 min. The temperature was maintained at 20–30°C with an ice bath. After the addition was complete, the reaction mixture was stirred for 2 h at room temperature. The organic layer was separated and washed with 50 ml of water. The organic layer was separated, dried (anhydrous silicic acid) and filtered into a flask containing 0.015 g of methanesulfonic acid. The solution was condensed under reduced pressure. Because of its reactivity, BDDCA was kept as a CH_2Cl_2 solution until just prior to use. Solvent was evaporated under vacuum in a dessicator from a plastic beaker, which had been immersed overnight in 0.5 M H_2SO_4 and air dried. The solid BDDCA was used immediately. M.P. = 80°C (by DSC); NMR δ ($CDCl_3$) 7.10 8 (s, 2H,=CH), 6.65 (s, 2H,=CH), 4.35 (br t, 4H, OCH_2), 3.75 (br t, 4H, CH_2); i.r. (KBr) 3.32, 2237, 1729, 1615 cm^{-1}.

*2'-Octyl 2-cyanopropionate (***18**)

To a 500 ml three-necked flask equipped with a Dean–Stark trap, condenser, thermometer and nitrogen inlet, was added ethyl 2-cyanopropionate (50 g, 394 mmol), 2-octanol (60 g, 462 mmol), p-toluenesulfonic acid (3 g, 16 mmol), and toluene (250 ml) under nitrogen. The solution was heated to reflux with stirring. Solvent was removed through the Dean–Stark trap and replaced with an equal volume of fresh toluene. After refluxing for 7 h and removing 500 ml of solvent, the solution was cooled to room temperature. The solution was washed twice with 250 ml of saturated aqueous $NaHCO_3$, twice with 250 ml of H_2O, and once with 250 ml of saturated aqueous NaCl. The organic layer was separated, dried ($MgSO_4$) and filtered. Solvent was removed under reduced pressure. The crude product was purified by vacuum distillation. Yield = 33.9 g (41%), B.P. = 85–88°C per 0.7 Torr; NMR δ ($CDCl_3$) 5.0 (m, 1 H, OCH), 3.55 (q, 1 H, J = 7 Hz, CH), 1.2–1.8 (m, 16 H, CH_2, CH_3), 0.9 (br t, 3 H, J = 7 Hz, CH_3); i.r. (neat) 2250, 1742 cm^{-1}.

2'-Octyl 2-cyanopropionate phenylselenide

This product was prepared using the same procedure as diethyl methylmalonate phenylselenide with sodium hydride (3.9 g, 153 mmol), THF (250 ml) and 2-octyl-2-cyanopropionate (20 g, 115 mmol). Phenyl selenium bromide was prepared with diphenyl diselenide (20.9 g, 67 mmol) and bromine (9.8 g, 61 mmol) in THF (100 ml). Yield = 43.2 g (quant.); NMR δ ($CDCl_3$) 7.75 (d, 2 H, Ph), 7.40 (m, 3 H, Ph), 4.85 (m, 1 H, OCH), 1.80 (s, 3 H, CH_3), 0.8–1.70 (m, 16 H, CH_2, $2CH_3$); i.r. (neat) 2233, 1734, 1251 cm^{-1}.

*2-Octyl 2-cyanoacrylate (***19**)

This product was prepared by the same procedure as for diethyl methylenemalonate with 2-octyl-2-cyanopropionate phenylselenide (43.2 g, 115 mmol), CH_2Cl_2 (300 ml), 30% hydrogen peroxide (27 g, 418 mmol), and water (30 ml). Yield = 14.4 g (60%), B.P. = 95°C per 1.0 Torr; NMR δ ($CDCl_3$) 7.05 (s, 1 H, =CH), 6.60 (s, 1 H, =CH), 5.05 (m, 1 H, OCH), 0.8–1.7 (m, 16 H, CH_2, 2 CH_3); i.r. (neat) 2236, 1732, 1649, 1287 cm^{-1}.

General polymerization procedure

To a three-necked 250 ml flask, equipped with a nitrogen inlet, mechanical stirrer and rubber septum, was added a monomer or monomer mixture (5 g) and THF (100 ml) under nitrogen. Pyridine (0.1 ml) was added by syringe and the reaction was allowed to stir overnight at room temperature. The solution was quenched with 0.5 ml of concentrated HCl and added to 500 ml of methanol containing 0.5 ml of concentrated HCl. If the polymer was soluble in methanol, it was coagulated in 500 ml of 50:50 methanol/water containing 0.5 ml of concentrated HCl. The polymer was filtered and dried overnight under a vacuum at room temperature. Spectral data are provided in *Table 1*. Yields, GPC results and TGA data are shown in *Table 2*.

ECA/BDDCA swelling procedure

To a steel lap shear was applied *ca.* 100 mg of ECA or a ECA/BDDCA mixture. The monomer was polymerized by exposure to dimethyl-p-toluidine vapours and the weight of the polymer was measured. The lap shears were immersed in methylene chloride overnight at room temperature. They were removed and the weight of the polymer was again measured. Each experiment was performed in triplicate.

RESULTS AND DISCUSSION

Monomer synthesis

All of the precursors for the desired monomers, with the exception of diethyl methylmalonate, were prepared in this laboratory. The dicyanopropionate ester of butanediol, **15**, was prepared by the transesterification of ethyl 2-cyanopropionate, **17**, with 1,4 butanediol in toluene and p-toluenesulfonic acid as the catalyst. N,N diethyl 2-cyanopropionamide, **16**, was prepared in toluene from **17** and a trimethyl aluminium/diethyl amine complex[10], while

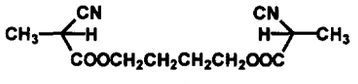
Table 1 Infrared and ^1H NMR data for polymers

Polymer	i.r. (cm^{-1})	NMR [δ($CDCl_3$)]
ECA	2246, 1748	4.3 (br s, 2H), 1.3 (br s, 3H). Backbone CH_2 peak is too broad to detect
75:25 ECA/DECA	2245, 1748, 1647	3.8–4.8 (br s), 1.0–2.0 (br s). Backbone CH_2 peak is too broad to detect
50:50 ECA/DEMM	2248, 1747	4.0–4.8 (br m), 2.2–3.1 (br m), 0.9–1.8 (br m)
DEMM	1730	4.0 (br s, 4H) 2.7 (br s, 2H), 1.2 (br s, 6H)
DECA	2230, 1647	2.5–3.7 (br m, 4H), 1.3 (br s, 3H), 1.1 (br s, 3H). Backbone CH_2 peak is too broad to detect
2-OCA	2248, 1744	5.0 (br s, 2H), 2.3–2.9 (m, 2H), 1.0–2.0 (m, 12H), 0.8–1.0 (br s, 3H)
50:50 ECA/2-OCA	2248, 1747	5.0 (br s), 4.4 (br s), 2.5 (m), 0.8–2.0 (m)

Table 2 GPC and TGA data for polymers

Polymer	Mn	MW	P.D.	Decomposition onset temperature (°C)	Midpoint temperature (°C)
ECA	287600	615300	2.14	190	242
75:25 ECA/DECA	166,700	246300	1.55	205	239
50:50 ECA/DEMM	121600	198600	2.28	198	273
DEMM	39300	89500	1.63	276	300
DECA	12200	19000	1.57	203	247
2-OCA	13500	18300	1.40	185	211
50:50 ECA/2-OCA	12000	24300	2/00	188	215

2′-octyl 2-cyanopropionate, **18**, was obtained from a transesterification reaction between **17** and 2-octanol.



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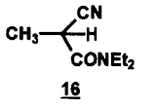

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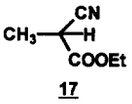

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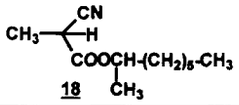
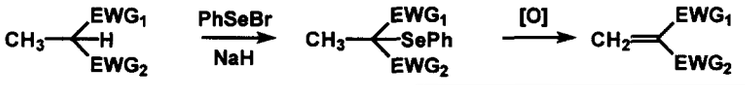


18

The precursors, **13**, **15**, **16** and **18** were treated with sodium hydride and phenyl selenium bromide to form their respective phenylselenides, as shown in equation (3), where EWG represents



eq. 3 (3)

the various electron withdrawing groups. Treatment of the phenylselenides with aqueous hydrogen peroxide produced the desired olefin monomers, butanediol dicyanoacrylate ester (BDDCA), **4**, diethyl methylenemalonate (DEMM), **8**, N,N diethyl 2-cyanoacrylamide (DECA), **11** and 2′-octyl 2-cyanoacrylate (2-OCA), **19**. Phenylseleninic acid is a by-product of the oxidation reaction, and acts as a stabilizer for these base-sensitive olefins. The acid is easily removed by filtration and a water wash. The monofunctional monomers were purified by distillation, while BDDCA, **4**, was isolated from the reaction solution without further purification. The monomer structures, their yields and purity are provided in *Table 3*.

BDDCA, **4**, is an extremely reactive solid that polymerizes in the solid state within *ca.* 20 min after solvent removal, despite the addition of 0.5wt.% methanesulfonic acid as a stabilizer. Difunctional monomer **4** must be dissolved in the polymerization solvent, THF, immediately after it is isolated from the oxidation reaction to perform the polymerization studies. The other monomers are clear liquids that are stable for several weeks, without added acid, provided they are stored in a freezer.

Cross-linked ECA polymer

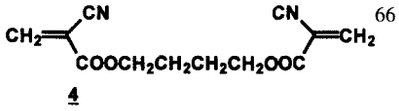
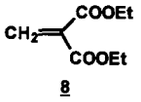
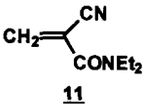
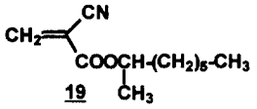
Because of the earlier difficulties in the preparation of pure difunctional cyanoacrylate monomers, the properties of cross-linked alkyl cyanoacrylate polymers have not been adequately studied. The facile preparation of BDDCA, **4**, now allows the comparison of the cross-linked ECA polymer properties with those of the linear ECA homopolymer.

To test whether the addition of BDDCA, **4**, to ECA improves solvent resistance of the polymer, solvent swelling experiments were performed with the linear and cross-linked polymers. BDDCA, **4**, was added to ECA at 5, 10 and 20wt.% levels immediately after its isolation from the reaction solution, and the mixtures were polymerized in a bulk reaction, without solvent. The uncross-linked and cross-linked ECA polymers were immersed in CH_2Cl_2 overnight and the percentage increase in weight was calculated. The percentage weight increases are compared in *Figure 1*.

Because the addition of BDDCA, **4**, significantly reduces solvent swelling, the solvent resistance of the polymer[11] should improve, which can be an important consideration in adhesive applications.

ECA was cross-linked with 1, 5, 10 and 20% of BDDCA, **4**, in THF solution with pyridine as the initiator. The cross-linked polymers precipitated as gels from solution. After isolation of the polymer and removal of residual solvent, TGA analyses of the cross-linked polymers were performed and the thermal decomposition data are compared in *Figure 2*.

Table 3 Electron deficient monomers

Monomer	Yield (%)	Purity (%)
 **4**	66	98
 **8**	76	> 99
 **11**	60	98
 **19**	80	98

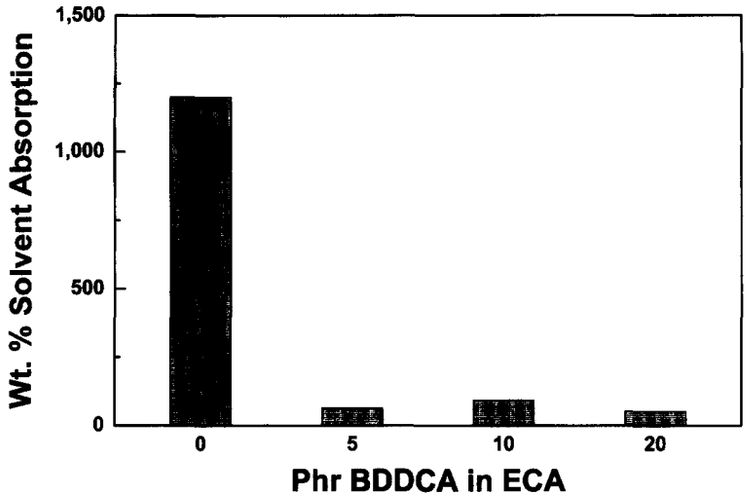


Figure 1 Degree of solvent swelling with 0, 5, 10 and 20% BDDCA added to ECA.

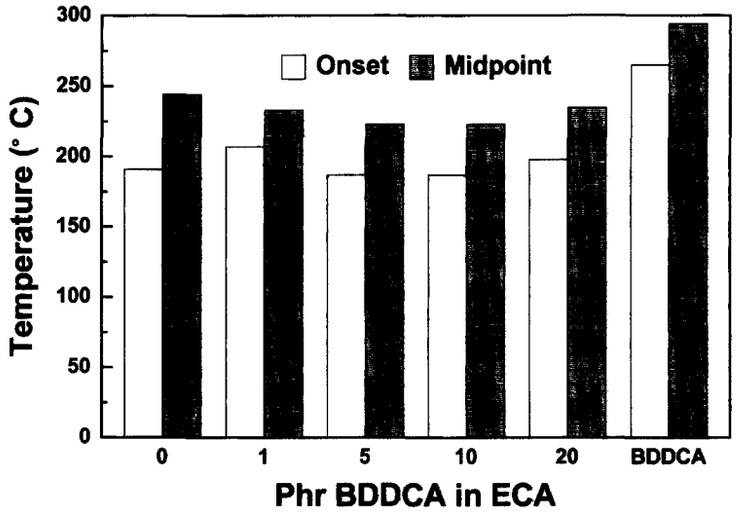


Figure 2 Comparison of TGA decomposition temperatures for cross-linked ECA polymers and the BDDCA homopolymer.

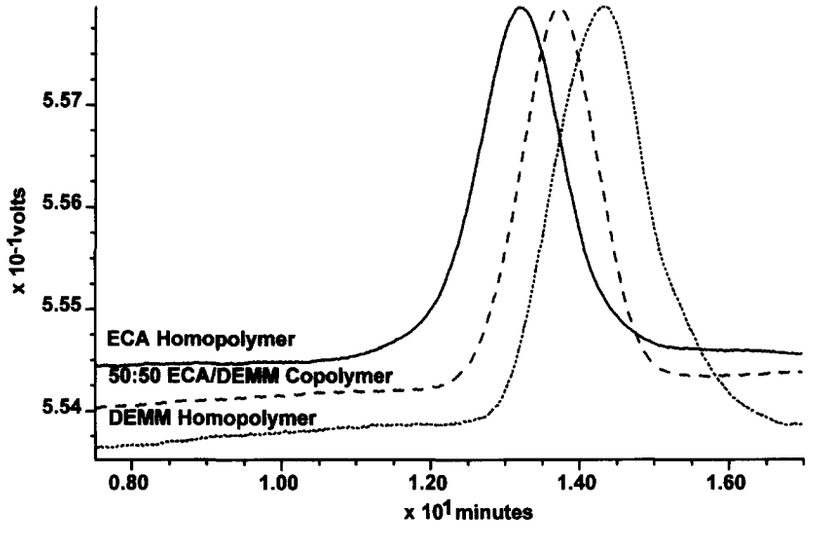


Figure 3 GPC curves for the ECA, 50:50 ECA/DEMM and DEMM polymers.

While the highly cross-linked BDDCA, **4**, homopolymer does exhibit a higher decomposition temperature than the ECA homopolymer, the cross-linked ECA polymers show little or no improved thermal stability over the ECA homopolymer.

ECA copolymerization

After the monofunctional monomers **8**, **11** and **19** were isolated and characterized, these monomers were polymerized in dry THF with pyridine as the initiator. Copolymers with ECA were also prepared under the same reaction conditions.

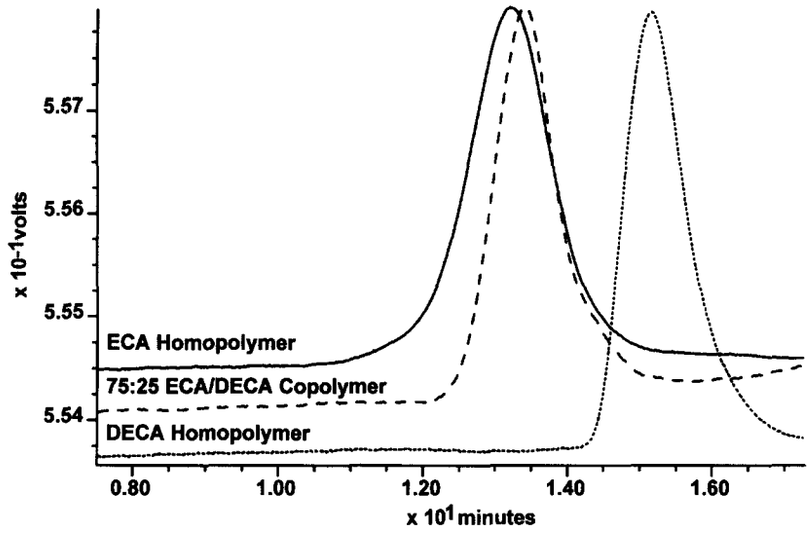


Figure 4 GPC curves for the ECA, 75:25 ECA/DECA and DECA polymers.

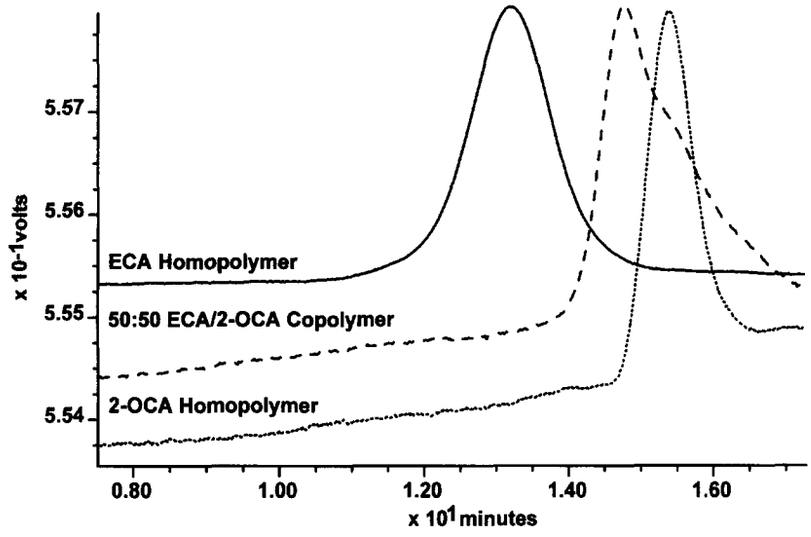


Figure 5 GPC curves for the ECA, 50:50 ECA/2-OCA and 2-OCA polymers.

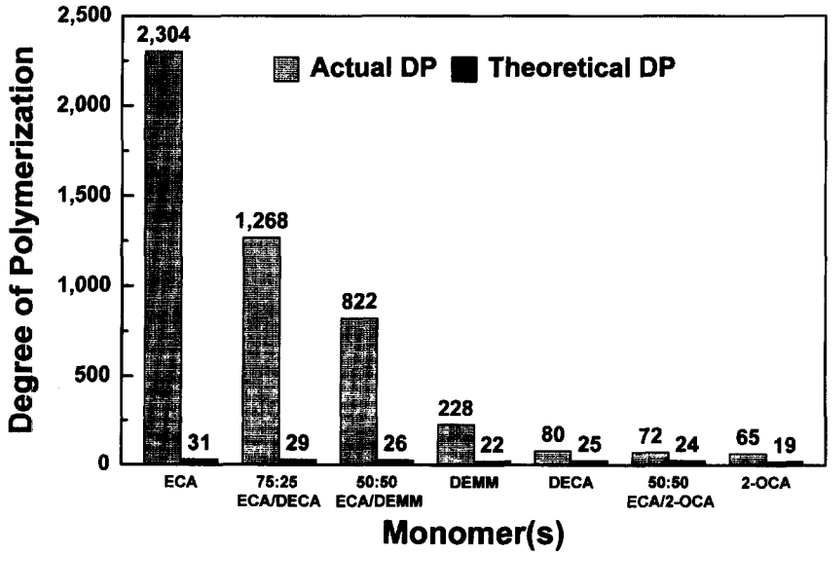


Figure 6 Comparison of actual and theoretical degrees of polymerization.

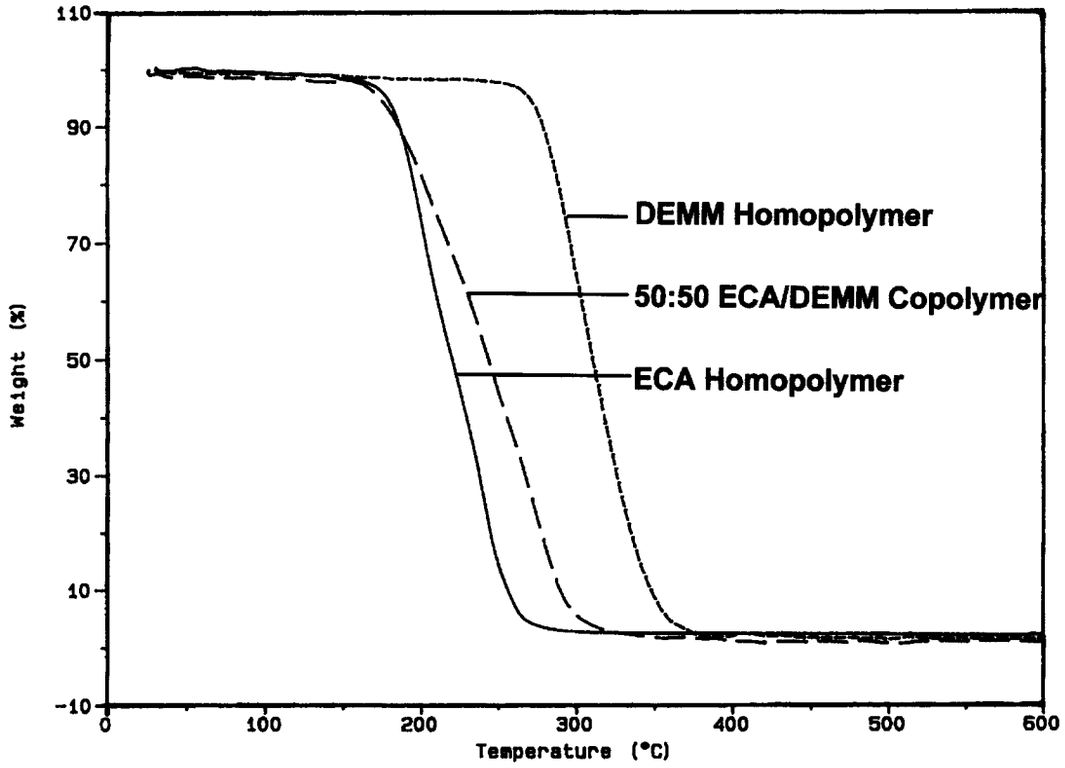


Figure 7 TGA curves of the ECA, 50:50 ECA/DEMM and DEMM polymers.

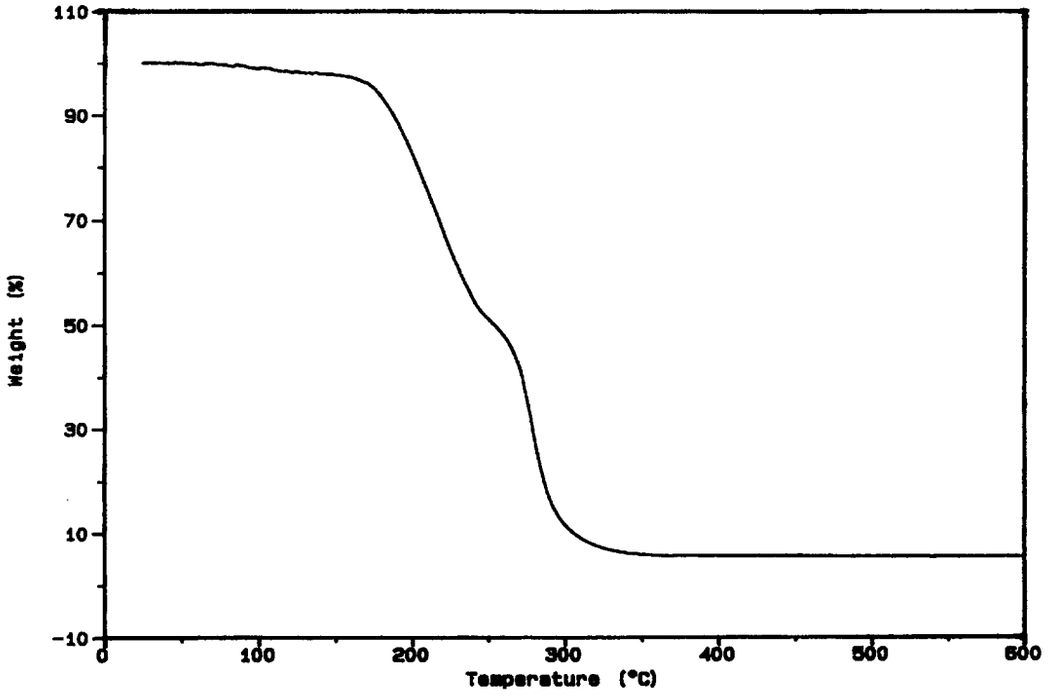


Figure 8 TGA curve for a 50:50 mixture of the ECA and DEMM homopolymers.

The monomer weight ratios of the copolymers are provided in *Table 4*. All polymers were analysed using gel permeation chromatography (GPC), thermogravimetric analysis (TGA), nuclear magnetic resonance spectroscopy (NMR) and infrared spectroscopy (i.r.).

All NMR chemical shifts and i.r. absorptions of the resulting polymers were evident in the expected regions (see Experimental Section).

The GPC curves for the DEMM, **8**, DECA, **11**, and 2-OCA, **19**, homopolymers, their copolymers with ECA and the ECA homopolymers are provided in *Figures 3–5*. Because the molecular weights of the monomers are all different, the degree of polymerization was utilized, instead of the actual molecular weights, to obtain an accurate comparison of polymer chain lengths. The degree of polymerization for the copolymers is intermediate between the ECA homopolymer and that of the homopolymer of the respective monomer. The copolymers exhibited a single peak in the GPC, which is an indication that a true copolymer is formed and that the product is not simply a mixture of homopolymers.

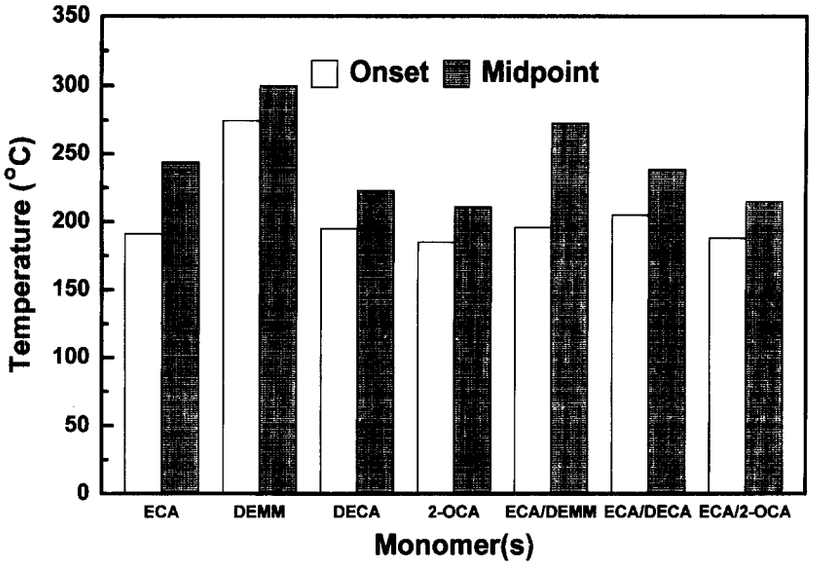


Figure 9 A summary of the onset and midpoint decomposition temperatures of the homopolymers and copolymers.

Table 4 Monomer weight ratios for copolymer reactions

Monomers	Weight ratio
ECA/DEMM	50:50
ECA/DECA	75:25
ECA/2-OCA	50:50

In all cases, the actual degree of polymerization is significantly larger than the theoretical, which is predicted from the initiator/monomer ratio, as demonstrated in *Figure 6*. Obtaining high molecular weight polymers from alkyl cyanoacrylate monomers, regardless of the composition of the initiator and the monomer/initiator molar ratio, is a well-documented phenomenon. However, the reason or reasons for this are still unclear[12]. While ECA provided the largest difference between the theoretical and actual degrees of polymerization, electron deficient monomers DEMM, **8**, DECA, **11**, and 2-OCA, **19**, as well as their ECA copolymers, exhibited similar behaviour.

The monomers that produced polymers with lower degrees of polymerization must polymerize more slowly than ECA. This allows competing reactions, such as chain termination on chain transfer to occur more readily[13], thereby reducing the degree of polymerization.

The DEMM homopolymer exhibits a substantially higher decomposition temperature than the ECA homopolymer, as seen in *Figure 7*. The 50:50 ECA/DEMM copolymer demonstrated an intermediate thermal stability between that of the two homopolymers and revealed a one-step decomposition curve. This is another indication that a true copolymer formed, because a 50:50 mixture of the two homopolymers shows a distinct two-step decomposition curve, as seen in *Figure 8*. The DECA and 2-OCA homopolymers, as well as their ECA copolymers, all possessed similar thermal stabilities to the ECA homopolymer. TGA data for all of the polymers is summarized in *Figure 9*.

CONCLUSIONS

A convenient procedure for the preparation of difunctional alkyl cyanoacrylate esters, such as BDDCA, **4**, as well as other monofunctional 1,1 disubstituted electron deficient olefins, such as DEMM, **8**, DECA, **11**, and 2-OCA, **19**, by the oxidation of a phenylselenide precursor has been demonstrated. Cross-linking ECA with BDDCA improves solvent resistance, but does not improve polymer thermal stability. The monofunctional monomers do homopolymerize and copolymerize with ECA by nucleophilic initiation, but their rate of polymerization is slower and their homopolymers possess a lower degree of polymerization than the ECA homopolymer. However, the DEMM homopolymer and its 50:50 copolymer with ECA do possess improved thermal stability over the ECA homopolymer.

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