

New copolymers from electrophilic trisubstituted ethylenes and electron-rich vinyl comonomers

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SUMMARY

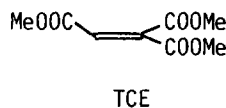
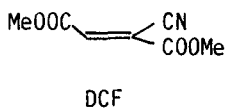
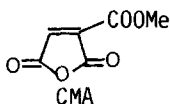
Ten new alternating, either 1:1 or 1:2, copolymers of electrophilic trisubstituted ethylenes with electron-rich vinyl monomers, were synthesized by free radical copolymerization.

Introduction

The search for new copolymer structures continues to be a challenge for the synthetic polymer chemist. We have extensively studied electrophilic trisubstituted ethylenes containing cyano and carbomethoxy substituents as novel comonomers. (1-5) They do not homopolymerize and undergo only limited anionic oligomerization, but readily form alternating 1:1 copolymers with monosubstituted electron-rich vinyl monomers such as styrene, *p*-methylstyrene, and vinyl acetate under free radical initiation.

One of the important driving forces for these copolymerizations may be in the free radical propagation mechanism. (6) Either a strong alternating polar effect in free radical copolymerization, or homopolymerization of the CT complexes as monomer can account for the observed 1:1 alternation. These effects can act to bring reluctant monomers such as stilbene into polymerization. Accordingly it seemed possible that other electron-rich monomers, even if they possess low reactivity, could be copolymerized with electrophilic trisubstituted ethylenes.

Three electrophilic trisubstituted ethylenes, carbomethoxymaleic anhydride (CMA), dimethyl cyanofumarate (DCF), and tricarbomethoxyethene (TCE) were copolymerized with further electron-rich vinyl monomers in this study.



The following electron-rich vinyl monomers, listed in order of decreasing reactivity, were selected for copolymerization with our electrophilic monomers: divinyl ether (DVE) > α -methylstyrene (AMS) > indene (In) > furan (Fu) > benzofuran (Bzf).

Results and Discussion

Ten new copolymers between electron-deficient olefins and electron-rich monomers were synthesized. Copolymer data are compiled in Table 1.

Conclusion - Copolymerizations of the electron-poor trisubstituted olefins have been extended to include copolymerization with 1,1- and 1,2-disubstituted olefins, copolymerization with disruption of aromatic systems, and cyclocopolymerization. These results support the idea that charge-transfer forces can bring otherwise reluctant monomers into copolymerization.

Experimental

The 60 mHz NMR spectra were run on a Varian T-60 or an EM-360 instrument. Infrared spectra were run on a Perkin-Elmer 740-A. Polystyrene equivalent molecular weights were determined using size exclusion chromatography in chloroform. Columns were DuPont Zorbax PSM60S and PSM300S. Detection was by UV absorbance (254 nm). Elemental analyses were performed by MicAnal of Tucson, AZ.

Monomers. Tricarbomethoxyethene was synthesized by the literature method. (2) Indene (Eastman Kodak) and α -methylstyrene (Aldrich) were dried over potassium hydroxide pellets, passed through a basic alumina column and distilled at 20 Torr vacuum. Benzofuran (Aldrich, 99.5%) was twice distilled from potassium hydroxide at 20 Torr and stored at 10°C. Furan (Alfa) was purified by distillation from KOH and stored at 0°C. Azo-bis-isobutyronitrile was recrystallized from methanol and dried.

New Synthesis of Dimethyl Cyanofumarate. Methyl glyoxylate was formed in situ by removal of methanol from its hemiacetal (then available as an 80% solution from Aldrich). Knoevenagel reaction of this highly reactive aldehyde with methyl cyanoacetate occurred and was forced to completion by the azeotropic removal of water.



All glassware was soaked for one hour in alcoholic HCl (4:1) to remove any traces of base. To a 300 ml, 3-necked round-bottomed flask fitted with an 8 inch Vigreux column, fractional take-off head and an addition funnel is added 30 g of methyl cyanoacetate (Aldrich, washed with aqueous bicarbonate and distilled), 72 g hemiacetal of methyl glyoxylate and 100 ml acetonitrile (distilled from phosphorus pentoxide). Methanol and water were removed by azeotropic distillation. Additional solvent was periodically added to maintain the volume of the reaction mixture. Reaction progress was monitored by following the head temperature. Pure acetonitrile distilling signified the end of reaction. The reaction product was stripped under aspirator vacuum to give a colorless oil. This oil was distilled in a Kugelrohr distillation apparatus (Aldrich, oven temperature 110°C, vacuum 0.3 mm Hg) to give an oily solid which was recrystallized from ethyl ether. The recrystallized product was fine white needles melting at 59.5-60.1°C. (lit(2) m.p. 60-61°), 44.6% yield.

Table 1 Properties of New Copolymers

Monomers	Synthesis Method	Yield(%)	Polymer Stoich.	Inherent Viscosity (dl/g)	Calculated Analysis		Observed Analysis			
					%C	%H	%C	%H		
CMA In	I	57	1:1	1.01	66.16	4.45	0.00	65.81	4.37	0.02
CMA Fu	I	64	b	0.13	53.57	3.60	0.00	53.39	3.56	0.05
CMA Bzf	I	62	1:1	0.44	61.31	3.68	0.00	61.19	3.60	0.00
CMA DVE	II	64	2:1	0.23	56.75	5.45	0.00	52.92	5.04	0.68 ^c
DCF In	II,III,IV	77	d	0.91	67.37	5.26	4.91	65.76	5.26	4.73
DCF AMS	III,IV	54	d	0.22	66.90	5.92	4.88	66.51	5.93	4.87
DCF Fu	II	61	e	0.51	55.50	4.65	5.92	55.93	5.04	5.54
DCF Bzf	II	9	f	-	62.71	4.57	4.87	60.31	4.21	4.99
DCF DVE	I,II,IV	50	2:1	0.43	52.98	4.95	6.85	53.01	4.90	6.78
TE DVE	I,II,IV	64	1:1	0.28	52.93	5.93	0.00	51.04	5.35	0.00

- Synthesis Methods - see copolymerization procedure, Experimental Section
- Reversible Diels-Alder cycloaddition between these two monomers did not adversely affect polymerization.
- A persistent residual amount of acetonitrile could not be removed.
- The DSC of the copolymer showed no glass transition temperature below its decomposition temperature.
- CMR was run on this copolymer in order to attempt to determine the mode of addition to furan. The CMR was δ 50.7, 51.1, 52.8, 54.0, 85.5, 86.0, 88.7, 115.1, 126.4 (olefin), 131.9 (olefin), 165.9 and 168.0 (ppm). This spectrum was consistent with 1,4-addition.
- CMR and APT (attached proton test) were run in deuteriochloroform on the solution copolymer in order to attempt to determine the mode of addition to benzofuran. Unfortunately the differences between calculated spectra for 2,3- and 3,2-additions were small, about the same size as the observed bandwidths, so no unambiguous assignment was possible.
- Attempts to synthesize the copolymer in bulk gave insoluble products.

New Synthesis of Carbomethoxymaleic Anhydride. Carbomethoxymaleic anhydride⁽⁴⁾ may be more conveniently synthesized from 1,2,2-tricarbomethoxyethanol, available from aldol reaction. To a three-necked, 100 ml round-bottomed flask fitted with an addition funnel, Vigreux column, thermometer, and fractional take-off head was added 12.0 g hemiacetal of methyl glyoxylate (distilled), 13.2 g dimethyl malonate (Aldrich, distilled) and 25 ml acetonitrile (refluxed over calcium hydride and distilled). The reaction solution was brought to a boil with an oil bath and methanol was removed as an azeotrope. Reaction progress may be observed by monitoring the head temperature and was complete when pure acetonitrile distilled. Acetonitrile was replenished during the reaction to maintain the volume of the reaction solution. Evaporation of the solvent gives a quantitative yield of 1,2,2-tricarbomethoxyethanol as a colorless oil suitable for the next step of the synthesis.

1,2,2-Tricarbomethoxyethanol, 5.0 g, and 10 g of phosphorus pentoxide were ground together with a mortar and pestle. The resulting mixture was placed in a 100 ml round-bottomed flask fitted with short path distillation head, drying tube, and receiver. The flask was immersed in a 180°C oil bath for one hour. The bath temperature was then lowered to 160°C. Vacuum (0.1 mm Hg) was applied, and about 1.0 g (40%) of the anhydride was distilled out. A heat gun was used to prevent the product from solidifying in the distillation head. The product was recrystallized from ethyl ether. The properties agreed with literature values¹¹ of monomer prepared from tricarbomethoxyethene.

Divinyl Ether. Divinyl ether was prepared by the method of Lott, Smith and Christiansen⁽⁷⁾ modified in that the solvent used was 2-ethylhexanol. A 500 ml Morton flask with mechanical stirring and a condenser was used to dissolve small pieces of sodium in 100°C solvent. Because the monomer is volatile, a jacketed vacuum adapter was used in addition to a 12 inch condenser. Circulating water for both was iced, and the receiver was cooled by an acetone-dry ice bath. The crude product was redistilled at ambient pressure and stored at 0°C.

Copolymerization procedure. Four different means of initiation were used to synthesize copolymers, and are described as follows. (I) Bulk polymerizations were done in a hydrolysis or polymerization tube. To a polymerization tube was added 0.003 moles of each monomer plus 1 mole % of AIBN. The monomer mixture was degassed by two freeze-thaw cycles. The polymerization tube was immersed in a 60°C oil bath for the indicated time. The resulting polymer was dissolved in acetonitrile and diluted to reasonable viscosity. The resulting solution was filtered if needed. This solution was twice precipitated into excess ethyl ether, isolated on a sintered glass funnel, and then dried over phosphorus pentoxide in a drying pistol at 56°C. (II) Solution polymerization was similar except 1 mL acetonitrile was added to the monomer mixture. (III) Redox polymerization was done by the system benzoyl peroxide-N,N-diethylaniline. (IV) Photopolymerization was done in a quartz tube fitted with a rubber septum. To the tube was added 0.003 moles of each monomer, 1 mL acetonitrile plus 1 mole % AIBN. The tube was flushed with nitrogen for ten minutes, then exposed to an ultraviolet (UV) light from a 254 nm Hg lamp. Reaction temperature was kept below 30°C at all times. Polymer was twice precipitated as described above.

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