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Diradical Polymerization of Acrylonitrile Initiated by Ethyl 1-Cyano-2-(*p*-methoxyphenyl)cyclopropanecarboxylate

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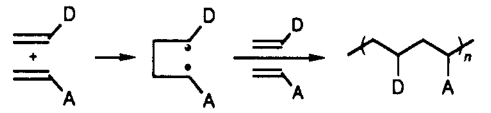
ABSTRACT: Ethyl 1-cyano-2-(*p*-methoxyphenyl)cyclopropanecarboxylate (ECMC) initiates the diradical polymerization of acrylonitrile (AN) at temperatures above 80 °C. The kinetic equation is $R_p = k[\mathrm{AN}]^{1.5}[\mathrm{ECMC}]^{0.5}$ and the apparent activation energy is 13.7 kcal/mol. Diradical propagation is supported by the GC/MS analysis of the small molecules formed competitively, the molecular weight increase with time, and the lack of solvent polarity effect. ECMC exhibits a slight chain-transfer and retarding effect on the polymerization. The molecular weight increase with time is more significant at lower initiator concentrations and at lower temperatures.

Introduction

We have investigated the ability of tetramethylenes, formed by reaction of electron-rich olefins with electron-poor olefins, to initiate the spontaneous polymerization of either or both components.[1,2] However, tetramethylenes formed in this way cannot be used to initiate a third monomer because the propagation sweeps out the initiating olefins by terpolymerization.

radical alternating copolymerization

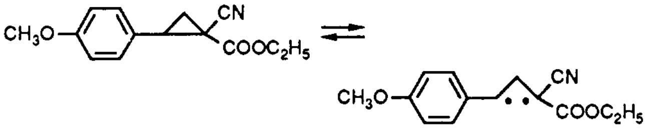


D = donor substituent, A = 1,4-acceptor substituents

Use of small-ring compounds to generate tri- or tetramethylene initiators is expected to have a significant advantage over generating these initiators by reaction of electron-rich with electron-poor olefins. The small-ring precursors are unaffected during propagation. So far, although we have found cyclobutanes that cleave to tetramethylene zwitterions and can initiate ionic homopolymerizations,[3] we have not found one that cleaves at reasonable temperatures to a tetramethylene diradical and initiates free-radical polymerizations. So in this paper we describe a cyclopropane that cleaves to a trimethylene diradical and initiates free-radical polymerizations.

Cyclopropanes are well-known to cleave to trimethylene diradicals at high temperatures (350 °C), but these temperatures are much too high for practical thermal initiations. To our knowledge, the only precedent for initiation of polymerization by a cyclopropane is a study by Imoto and his colleagues.[4] They found that methyl 1-methyl-2-(9-anthryl)cyclopropanecarboxylate at 70 °C initiated MMA polymerization by a free-radical mechanism. The severe structural limitations on the cyclopropane structure were shown in that methyl 2,2-diphenylcyclopropane-1-carboxylate initiated more slowly by a factor of ~10. From the Imoto study it seems that the combination of donor substituents on one carbon and acceptor substituents on the other was most favorable for bond cleavage.

We propose to generate polar 1,3-diradicals from the thermal ring opening of the donor–acceptor cyclopropane ethyl 1-cyano-2-(*p*-methoxyphenyl)cyclopropanecarboxylate (ECMC) and investigate if these diradicals can initiate the polymerization of acrylonitrile (AN). The polar substituents on the cyclopropane ring were chosen by analogy to our earlier tetramethylene work.[5]



Results

Exploratory Experiments. ECMC alone does not undergo any substantial thermal reaction at 120 °C for 10 h, either in bulk or in benzene solution. No new product or polymer was detected in HPLC and SEC. However, ECMC exhibits initiating ability for AN at temperatures above 80 °C, even though the reactions are very slow.

Heating AN alone at 90 and 140 °C confirmed that in each case no or very little polymer was produced after 20 h. The ECMC-initiated polymerization of AN, on the other hand, gave sufficient yields in our exploratory experiments. Anisole and ethyl α-cyano-β-(*p*-methoxyphenyl)acrylate, which do not contain cyclopropane structures, did not act as initiators under the same conditions, which supports the involvement of cyclopropane bond cleavage of ECMC in the initiation process.

DPPH (diphenylpicrylhydrazyl) can be used to monitor how fast radicals are formed in a system, by checking the fading time of its bright purple color. DPPH (0.002 M) was added to a solution of ECMC (0.3 M) at 120 °C. In benzene alone, the fading time was 12 min, in a 1/1 mixture of benzene/AN the color lasted 7.5 min, while in pure acrylonitrile the fading time was only 5 min.

Small-Molecule Formation. When an AN/ECMC mixture was heated for 45 min at 240 °C, sufficient low molecular weight products were obtained for identification. After the polymer was filtered and excess AN evaporated, the residue was analyzed by GC/MS. Besides ECMC, small amounts of various products with molecular weights 298 and 351 were detected, which correspond to 1:1 and 1:2 ECMC/AN adducts. The proposed structures **3** and **5** for these adducts shown in Scheme I agree with the mass spectral data. No other products were detected in GC/MS.

Polymerization Study. The rate of polymerization (R_p) is determined from the initial slopes of the time–conversion curves. From the slope of the log R_p vs log [ECMC] plot in Figure 1 the initiator exponent was calculated to be about 0.5.

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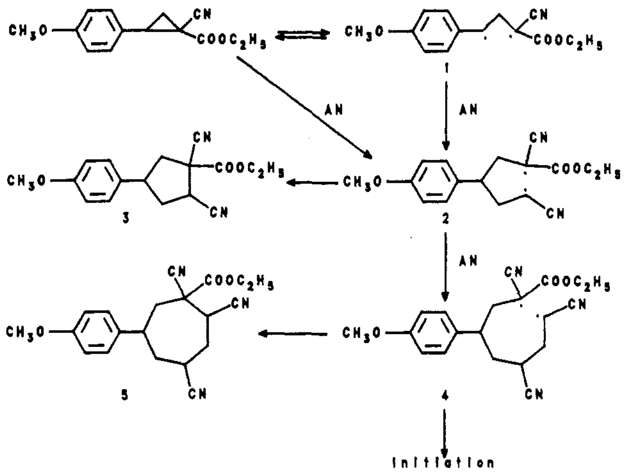
Scheme I



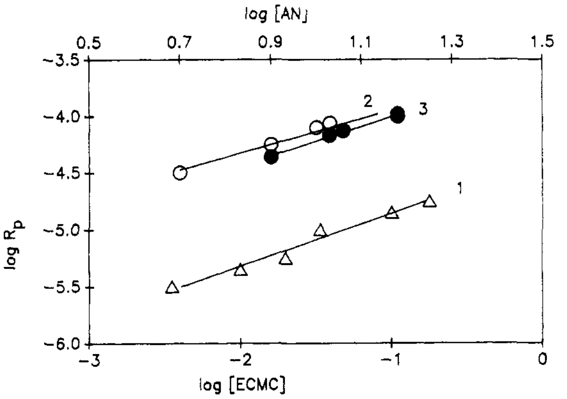


Figure 1. Rate of polymerization R_p as a function of (1) [ECMC] at 90 °C in bulk AN; (2) [AN] in benzene at 120 °C, [ECMC] = 0.1 M; and (3) [AN] in acetonitrile at 120 °C, [ECMC] = 0.1 M.

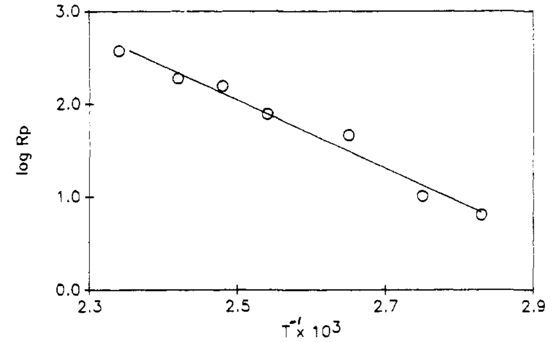


Figure 2. Arrhenius plot for AN polymerization initiated by ECMC. [ECMC] = 6.5 × 10^{-2} M.

Table I
Influence of ECMC and Anisole on the Polymerization of AN Initiated by AIBN[a]

[ECMC] or	ECMC		anisole	
[anisole], M	R_p, mol L^{-1} s^{-1}	MW	R_p, mol L^{-1} s^{-1}	MW
0	1.61×10^{-4}	6.3×10^5	1.61×10^{-4}	6.5×10^5
0.023	1.48×10^{-4}	5.2×10^5	1.26×10^{-4}	5.4×10^5
0.08	1.30×10^{-4}	4.8×10^5	1.02×10^{-4}	4.6×10^5
0.33	1.02×10^{-4}	3.5×10^5	0.87×10^{-4}	4.5×10^5
1.3	0.45×10^{-4}	2.0×10^5	0.46×10^{-4}	3.9×10^5

[a] [AN] = 7.6 M, in benzene, 50 °C, [AIBN] = 5 × 10^{-3} M. Reaction time: 70 min.

The relationship between the initial polymerization rate R_p and AN concentration is also shown in Figure 1. From the slope of the straight lines, the monomer exponents are calculated to be 1.4 and 1.5 in benzene and in acetonitrile, respectively, which is higher than the normal value 1.0.

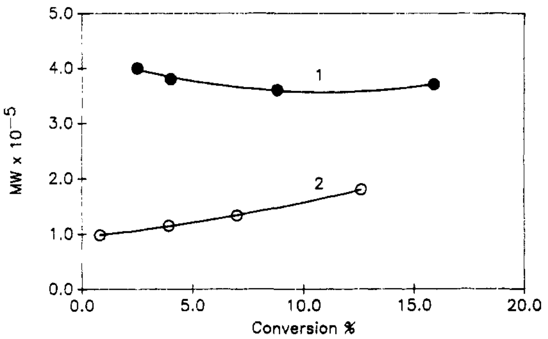


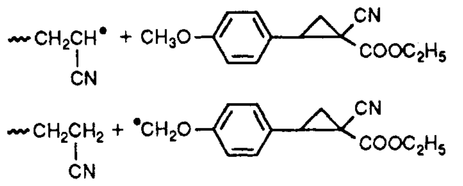
Figure 3. Relationship between MW and conversion: (1) [AIBN] = 5 × 10^{-3} M, 55 °C, 7.6 M in benzene; (2) [ECMC] = 0.53 M, 90 °C.

The polymerization rate equation can be written as follows:

$$R_p = k[\mathrm{ECMC}]^{0.5}[\mathrm{AN}]^{1.5}$$

The relationship between the polymerization rate and the temperature was measured between 80 and 155 °C. The activation energy is calculated to be 13.7 kcal/mol from the Arrhenius plot in Figure 2.

Table I shows that for the AN polymerization initiated by AIBN at 50 °C, addition of ECMC decreases R_p and the molecular weight. ECMC does not initiate at this temperature, and the retardation can be attributed to hydrogen abstraction from the methoxy group:



Anisole has already been reported as a chain-transfer agent and retarder in the free-radical polymerization of vinyl acetate.[6] For comparison, we also investigated the effect of anisole on the polymerization of AN under our conditions. The results in Table I support the chain-transfer and retarding ability of the $MeOC_6H_4$ group.

The polarity of the solvent had a minor effect on the conversion. The polymerizations were run in different solvents using the following conditions: [ECMC] = 0.1 M, [AN] = 5.1 M at 120 °C for 31 h. The yields varied from 2.6% in acetonitrile to about 5% in benzene, chloroform, and 1,2-dichloroethane.

Dependence of Molecular Weight on Time and Temperature. The molecular weight of PAN increases with time (or conversion) when initiated by ECMC, as shown in Figure 3. The control experiment of AN polymerization initiated by AIBN shows no such molecular weight increase.

Figure 4 shows the dependence of molecular weight on time at different ECMC concentrations. At higher ECMC concentration the molecular weight of AN increases more slowly with conversion. At higher temperature (140 °C) the molecular weight increases less with time than at 90 °C, as also shown in Figure 4.

Discussion

In this paper we investigated a donor–acceptor-substituted cyclopropane ECMC as initiator for polymerization. Our results show that a trimethylene diradical is produced by ring-opening of ECMC and is detected by the fact that it initiates the radical polymerization of AN.

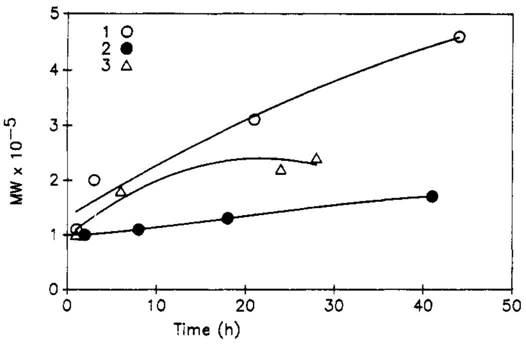


Figure 4. Relationship between MW and time at different [ECMC]: (1) [ECMC] = 0.13 M, 90 °C; (2) [ECMC] = 0.53 M, 90 °C; (3) [ECMC] = 0.13 M, 140 °C.

The sole cycloaddition products of ECMC/AN (five- and seven-membered rings) provide evidence for the formation of the trimethylene diradical intermediate.

The bond cleavage of ECMC to a diradical can occur without AN, but as shown by the fading times of DPPH, the presence of AN does accelerate the process. As shown in Scheme I, there are two possible pathways to form the initiating pentamethylene diradical 2. ECMC can monomolecularly form the trimethylene diradical 1, which adds a molecule of AN, leading to the pentamethylene diradical 2, but a bimolecular reaction of ECMC and AN is also possible. The accelerating effect of AN on the decomposition of ECMC and the 1.5 order in monomer in the polymerization rate equation both indicate involvement of the monomer in the initiation step. In analogy to the olefin–olefin reactions that can lead to diradical tetramethylenes,[1,2] an olefin can react with a cyclopropane to form a diradical pentamethylene.

In analogy to the tetramethylene-initiated polymerizations in our earlier studies,[5] we propose that the trimethylene-initiated polymerizations in this study also proceed via diradical propagation. It is not possible by kinetics to determine whether or not the propagating chains grow from both ends in a true diradical fashion. The dependence of the rate of polymerization on the monomer concentration, on the initiator concentration, and on the activation energy of polymerization are identical for diradical and monoradical propagations. However, the relationship between molecular weight and polymerization time (or conversion) can provide a crucial criterion. If termination occurs by recombination, polymer chains with a growing radical at each end will combine to form diradical chains of higher MW. Therefore diradical polymerization can be described as a combination of chain polymerization with step-growth polymerization. In one case of a diradical tetramethylene initiated polymerization, we have observed this molecular weight growth.[5] In the present study we do observe an increase of molecular weight with conversion, but not as large as expected. This may be due to chain transfer to initiator, which produces monoradicals. Therefore, at higher ECMC concentration the monoradical polymerization character is more significant. Temperature shows a similar effect. At higher temperature, more initiating diradicals are formed, but the chain-transfer reaction also becomes faster, disproportionation termination becomes significant, and other side reactions will produce monoradicals. The total effect is that at higher temperature a smaller increase of MW with time than expected is observed.

In conclusion, ECMC can serve as a diradical source to initiate polymerization at reasonable temperatures, although it induces some chain transfer.

Experimental Section

Instrumentation. NMR spectra were recorded with a Bruker WM-250 nuclear magnetic resonance spectrometer. IR spectra were recorded with a Perkin-Elmer Model 983 spectrophotometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. GC/MS spectra were obtained with a Hewlett-Packard GC/MS system: Model 5890 GC, Model 5970 mass spectrometer, and RTE-6 data system.

Ethyl 1-Cyano-2-(4-methoxyphenyl)cyclopropanecarboxylate (ECMC). Ethyl α-cyano-*p*-methoxycinnamate was prepared by a Knoevenagel condensation of *p*-anisaldehyde and ethyl cyanoacetate as described by Zabicky.[7] ECMC is synthesized by methylene transfer to this olefin with dimethyloxosulfonium methylide in dimethyl sulfoxide following Cram's procedure[8] in 55% yield after vacuum distillation. This product is a colorless cloudy oil that becomes colored on exposure to air or heat.

^{1}H NMR δ 1.27 (3 H, t), 2.03 (2 H, d), 3.07 (1 H, t), 3.74 (3 H, s), 4.23 (2 H, q), 7.0 (4 H, m); IR (KBr) 2243 (CN), 1730 (CO), 1611 (CC) cm^{-1}. Anal. Calcd: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.10; H, 6.16; N, 5.41. MS (70 eV) *m/e* (%) 245 (70, M$^+$), 216 (30, M$^+$ - COOC$_2$H$_5$), 145 (70, M$^+$ - COO$_2$H$_5$), 172 (M$^+$ - COOC$_2$H$_5$ - CN).

Other Chemicals. Acrylonitrile (AN), dichloroethane (DCE), acetonitrile, and benzene were distilled from CaH$_2$. AIBN was recrystallized from methanol. Anisole and chloroform were obtained from Aldrich and used without further purification.

Polymerization Procedure. The polymerizations were run in 15-mL Pyrex tubes equipped with vacuum-line Teflon valves. Nitrogen was bubbled through the reaction mixture for 3 min, and the valve was then closed off. After a period of time in a temperature-controlled bath, the reactants were poured into excess methanol. The precipitated polymer was filtered off, dried, and weighed. The viscosity of PAN solutions in DMF was measured at 25 °C, and the molecular weight was calculated with the equation[9]

$$[\eta] = 3.92 \times 10^{-4} \bar{M}_w^{\,0.75}$$

Oligomers of the ECMC/AN Reaction System. The structures of 2 and 4 were assigned on the basis of GC/MS analysis.

Adduct 3: MS (70 eV) *m/e* (%) 298 (35, M$^+$), 245 (5, M$^+$ - CH$_2$CHCN), 225 (80, M$^+$ - COOC$_2$H$_5$), 199 (10, M$^+$ - COOC$_2$H$_5$ - CN), 189 (30, M$^+$ - C$_6$H$_4$OMe).

Adduct 5: MS (70 eV) *m/e* (%) 351 (10, M$^+$), 278 (5, M$^+$ - COOC$_2$H$_5$).

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