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Cyclopropane Initiators. 3. Cationic Polymerization of *N*-Vinylcarbazole Initiated by Ethyl 1-Cyano-2-(*p*-methoxyphenyl)cyclopropanecarboxylate

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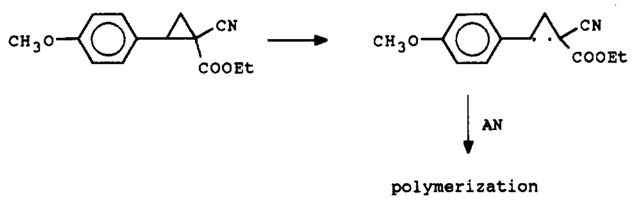
ABSTRACT: Ethyl 1-cyano-2-(*p*-methoxyphenyl)cyclopropanecarboxylate (ECMC) initiates the cationic polymerization of *N*-vinylcarbazole (VCZ) in 1,2-dichloroethane solution at temperatures above 60 °C. The experimental kinetic equation is $R_p \propto [\mathrm{VCZ}]^{1.5}[\mathrm{ECMC}]^{0.9}$ and the apparent activation energy is 20.3 kcal/mol. The obtained polymer shows a bimodal molecular weight distribution, which is attributed to free-ion vs ion-pair propagation. The factors favoring free-ion propagation include lower conversion, lower temperature, lower monomer concentration, higher initiator concentration, and more polar solvents.

Introduction

Our studies of the spontaneous polymerizations which occur upon mixing electron-rich olefins with electron-poor olefins, "charge-transfer polymerizations", have shown that these polymerizations are initiated by tetramethylene intermediates.[1,2] These tetramethylenes could be either predominantly diradical or zwitterionic. Evidence for this dual nature was provided from both experiments[1,2] and theoretical calculations.[3] In analogy to the tetramethylenes, Cram has found evidence for the dual nature, diradical or zwitterionic, of trimethylenes obtained by bond cleavage of cyclopropanes.[4-7] So we wanted to investigate the use of cyclopropanes as initiators of polymerizations.

In a previous paper, the polymerization of acrylonitrile initiated by ethyl 1-cyano-2-(*p*-methoxyphenyl)cyclopropanecarboxylate (ECMC) was investigated and a mechanism involving a diradical trimethylene as the initiator was proposed.[8]



Subsequently, ECMC in the presence of zinc chloride was shown to give diradical initiation of styrene polymerization.[9]

In this paper the ability of this trimethylene to act as a zwitterion and initiate cationic polymerization is examined. Specifically, the ability of ECMC to initiate the cationic polymerization of *N*-vinylcarbazole (VCZ), a monomer known to be very susceptible to such polymerization,[10] will be described. The trimethylene from ECMC can have a dual character due to its substituents. Moreover, the pentamethylene (after one monomer unit has been added) can have either zwitterionic or diradical character, and this character will determine the polymerization mechanism.

Results

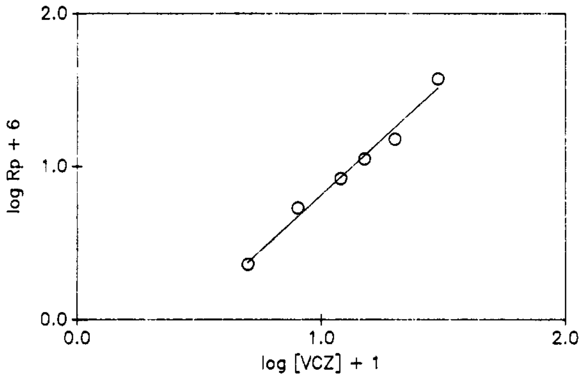
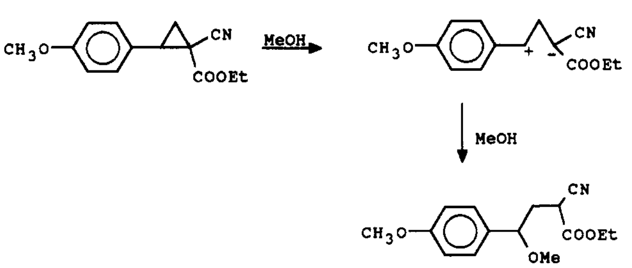


Figure 1. Relationship between R_p and [VCZ]. [ECMC] = 7 × 10^{-2} M, 100 °C, in DCE.

ECMC as Cationic Initiator. ECMC initiates the polymerization of VCZ above 60 °C, as shown in Table I. The self-initiation of VCZ is negligible under the conditions used: 1,2-dichloroethane (DCE) at 105 °C. Because VCZ is known to undergo both radical and cationic polymerizations,[10] inhibitors were added: the radical inhibitors DPPH (diphenylpicrylhydrazyl) and TEMPO (tetramethylpiperidine-*N*-oxyl) show no significant effect on the yield, but methanol completely stops the polymerization. These results demonstrate a cationic mechanism.

Heating ECMC for 14 h at 110 °C in methanol leads to the methanol adduct, ethyl 2-cyano-4-methoxy-4-(*p*-methoxyphenyl)butanoate in 73% yield. Thus the ability of ECMC to generate a zwitterionic trimethylene was demonstrated.



Bimodal Molecular Weight Distribution. Poly(*N*-vinylcarbazole) (PVCZ) obtained using ECMC as initiator in 1,2-dichloroethane shows a bimodal molecular weight distribution (MWD). This cannot be attributed to cationic vs radical polymerizations, since the polymer obtained in the presence of TEMPO shows the same bimodal MWD. The two different molecular weight peaks are ascribed to free-ion (high-MW) and ion-pair (low-MW) propagation (see the Discussion).

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Table I
Polymerization of VCZ Initiated by ECMC

[M], M	[ECMC], ×10^2 M	temp, °C	time, h	solvent/additive	yield, %	HMW,^{a} ×10^{-3}	LMW,^{b} ×10^{-3}	HMW/LMW
2	5	105	8	DCE	34.7			
2	5	105	8	DCE/DPPH^c	32.0			
2	5	105	8	DCE/MeOH^d	4.3			
2	5	105	8	MeOH	0			
1	5	100	1	DCE	5.2	15.6	1.1	7.1
1	5	100	4	DCE	13.5	14.1	1.0	4.5
1	5	100	7	DCE	19.4	11.8	1.1	3.0
1	5	100	13	DCE	34.3	8.7	0.9	2.0
1	5	100	23	DCE	38.1	6.2	0.9	1.8
1	4	70	24	DCE	5.4	15.7	1.1	10.2
1	4	80	20	DCE	9.1	18.0	1.15	5.5
1	4	90	7	DCE	6.3	13.9	1.2	5.2
1	4	110	1	DCE	5.1	11.7	1.1	4.6
1	0.58	100	28	DCE	11.7	8.1	0.9	2.0
1	0.92	100	19	DCE	10.7	7.7	1.1	2.2
1	2.0	100	9	DCE	7.4	9.3	1.0	5.2
1	3.5	100	9	DCE	7.9	10.3	1.0	3.6
1	5.0	100	3	DCE	13.5	14.1	1.0	4.5
2	100	100	1	DCE	5.5	15.1	1.2	0.43
2	100	100	2	DCE	9.1	14.0	1.1	0.53
2	100	100	3	DCE	19.7	14.8	1.1	0.74
2	100	100	5	DCE	26.2	16.8	1.1	0.93
2	100	100	9	DCE	40.8	17.0	1.0	0.84
0.5	7	100	5	DCE	11.0	10	0.9	10.2
0.8	7	100	5	DCE	12.0	14	1.1	3.9
1.2	7	100	5	DCE	12.4	23	1.1	3.8
1.5	7	100	5	DCE	13.4	23	1.1	1.4
2.0	7	100	5	DCE	13.5	25	1.2	0.93
2	5	105	2	C_6H_6^{e}	4.2	9.1	1.1	0.13
2	5	105	2	$CHCl_3$^{e}	19.7	9.0	0.9	0.23
2	5	105	2	DCE	23.8	8.7	0.9	1.8
2	5	105	2	CH_3NO_2^{e}	36.3			f
2	5	105	2	CH_3CN^{e}	49.2			f

[a] HMW: high molecular weight peak in SEC. [b] LMW: low molecular weight peak in SEC. [c] [DPPH] = 3 × 10^{-3} M. [d] DCE/MeOH = 5/1. [e] Dielectric constants: benzene, 2.0; chloroform, 4.7; nitromethane, 3.59; acetonitrile, 38.8. [f] Only one very broad peak.

The molecular weights and molecular weight distributions of PVCZ at different conversions are included in Table I. Both the high-MW (HMW) and low-MW (LMW) polymers exhibit a MW decrease, the latter very slight, as the conversion increases. This effect may be explained by the falling concentration during each run. Dilution leads to a lower ratio of HMW to LMW product at higher conversion. A similar effect of conversion on MWD was reported before.[12] Therefore, the conversions will be kept low when discussing the factors which affect the molecular weight distributions.

Effect of Monomer Concentration. Figure 1 shows the relationship between the polymerization rate and VCZ concentration. From the slope of the straight line, the monomer exponent is calculated to be 1.5.

As shown in Table I, increasing the monomer concentration leads to a higher MW for both MW fractions. It seems that a higher monomer concentration is more favorable to the ion-pair propagation; a lower HMW/LMW product ratio is obtained.

Effect of Initiator Concentration. Initial polymerization rates were determined from the initial slopes of the time–conversion plots. Figure 2 shows the effect of ECMC concentration on the rate of polymerization (R_p). From the slope of the log R_p–log [ECMC] plot, the exponent was calculated to be 0.9.

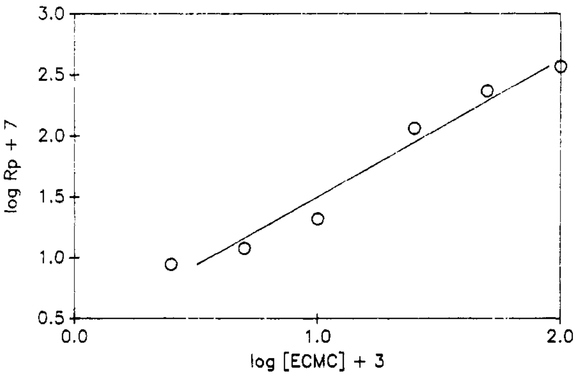
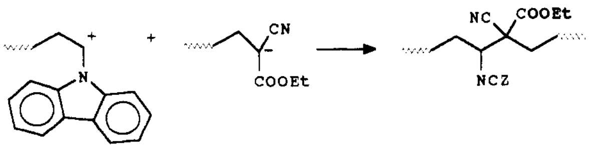


Figure 2. Relationship between R_p and [ECMC]. [VCZ] = 1 M, 100 °C, in DCE.

The effect of ECMC concentration on the molecular weight of PVCZ was investigated as shown in Table I. While the low molecular weight portion does not change much, the high molecular weight portion increases its MW with ECMC concentration, and the ratio of HMW to LMW product also increases.



On the basis of the assumption that the increase of MW is due to chain coupling (see Discussion), we carried out

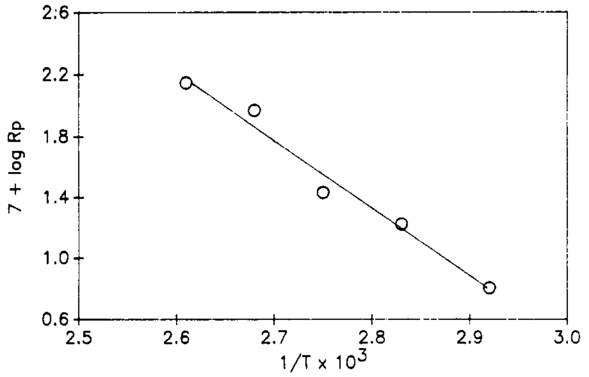


Figure 3. Arrhenius plot for VCZ polymerization initiated by ECMC. [VCZ] = 1 M and [ECMC] = 4 × 10^{-2} M, in DCE.

the polymerization at very high ECMC concentration (1 M). The data in Table I show a slight molecular weight increase with time or conversion, and the ratio of HMW to LMW product also increases. The methoxy peak in the NMR spectrum indicates incorporation of ECMC in the polymer.

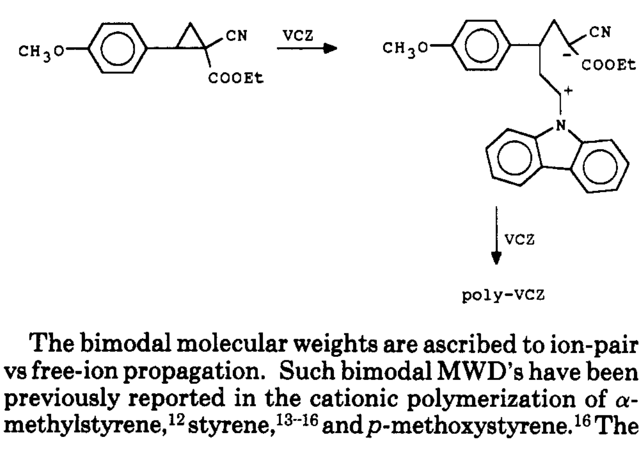
Effect of Temperature. From the Arrhenius plot for the rate of this polymerization (Figure 3) the composite activation energy was calculated to be 20.2 kcal/mol. Table I shows the molecular weight and molecular weight distribution of PVCZ at different polymerization temperatures. The low molecular weight portion does not change as the temperature rises, but the high molecular weight portion shows a decrease in MW.

Solvent Effect. The rate of polymerization increases with increasing solvent polarity (Table I). The ratio of HMW to LMW product also increases steadily from 0.13 (benzene) to 0.23 (chloroform) to 1.8 (1,2-dichloroethane). Finally, when acetonitrile and nitromethane were used, the polymer showed very broad MWD's.

Effect of Initiator Structure. Several different cyclopropanes were used as initiators: ethyl 1-cyano-2-phenylcyclopropanecarboxylate, ethyl 1-cyano-2-tolylcyclopropanecarboxylate, ECMC, and ethyl 1-cyano-2-(*o*,*p*-dimethoxyphenyl)cyclopropanecarboxylate. The yields obtained in the same conditions ([VCZ] = 2 M, [cyclopropane] = 0.05 M at 100 °C) were essentially the same, varying only from 18 to 23%.

Discussion

Mechanism. A S_N2 reaction of *N*-vinylcarbazole with ECMC, leading to a 1,5-zwitterion, is proposed. Such S_N2 reactions of cyclopropanes have been reported previously by Stewart and Westberg.[11] The cationic VCZ polymerization is initiated by the ECMC/VCZ pentamethylene zwitterion acting both as an ion pair and as free ions.



The bimodal molecular weights are ascribed to ion-pair vs free-ion propagation. Such bimodal MWD's have been previously reported in the cationic polymerization of α-methylstyrene,[12] styrene,[13-16] and *p*-methoxystyrene.[16] The high-MW portion is formed from the "dissociated" species, while the "nondissociated" species gives a low-MW polymer. Bimodal MW can thus only be obtained if the propagation is faster than the exchange between free ions and ion pairs. A slow exchange may occur if the growing cation and the counterion interact strongly.[16] Other possible explanations for the bimodality of MW are different aggregates or inter- and intramolecular ion pairs. The proposed free-ion vs ion-pair mechanism is supported by the effect of solvent polarity on MWD: increasing solvent polarity favors free-ion propagation. Moreover free-ion propagation (high MW) is favored at lower temperature as has been reported previously by Hayashi[12] and Higashimura.[13]

Several termination mechanisms can be postulated: β-proton transfer to a carbanion, chain transfer by β-proton abstraction by VCZ, and coupling of the growing cation with a carbanion on either its own or another chain. Termination by ion pair collapse, particularly for low molecular weight chains, might lead to an unusually high proportion of low molecular weight cyclics, but we have no direct evidence on this point. Termination by free-ion combination of different chains was postulated to explain the increase of the molecular weight of the HMW fraction at high initiator concentrations. Indeed the methyl signal of the *p*-methoxyphenyl substituent was present in the NMR spectrum of a polymer obtained at a very high initiator concentration.

Kinetics. A kinetics scheme can be devised on the basis of the proposed mechanism.

Let cyclopropane concentration = [C], *N*-vinylcarbazole concentration = [M], free-ion concentrations = [+] = [−], and ion-pair concentration = [±].

The initiation and termination can be written as follows:

$$R_i = k_i[C][M]$$

$$R_t = k_t^{\pm}[\pm] + k_t^{+}[+][-]$$

Because

$$K = \frac{[\pm]}{[+][-]} \text{ and } [\pm] = K[+]^2$$

the termination is transformed to

$$R_t = (k_t^{\pm}K + k_t^{+})[+]^2$$

In the steady state, $R_i = R_t$ and

$$k_i[C][M] = (k_t^{\pm}K + k_t^{+})[+]^2$$

Then

$$[+] = \left[\frac{k_i}{k_t^{\pm}K + k_t^{+}}\right]^{0.5}[C]^{0.5}[M]^{0.5} = A[C]^{0.5}[M]^{0.5}$$

and

$$[\pm] = KA^2[C][M]$$

For the rate of polymerization

$$R_p = \frac{-d[M]}{dt} = k_p^{\pm}[\pm][M] + k_p^{+}[+][M]$$

$$R_p = k_p^{\pm}KA^2[C][M]^2 + k_p^{+}A[C]^{0.5}[M]^{1.5}$$

From the bimodal molecular weight distributions, it is known that both terms contribute. The order in cyclopropane will be between 0.5 and 1, while the order in *N*-vinylcarbazole will be between 1.5 and 2. These expectations are in agreement with the experimental findings.

Conclusions

ECMC initiates the cationic polymerization of *N*-vinylcarbazole. We propose that the initiation step is a bimolecular S_N2 reaction of the cyclopropane with a monomer, that propagation proceeds via both free ions and ion pairs, and that termination occurs by free-ion combination and by ion-pair collapse.

This is the first example of cationic polymerization brought about by a cyclopropane derivative.

Experimental Section

Instrumentation. NMR spectra were recorded with a Bruker WM-250 nuclear magnetic resonance spectrometer. IR spectra were recorded with Perkin-Elmer spectrophotometer Model 983. Chemical 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.

The molecular weights and molecular weight distributions of the polymers were determined by size-exclusion chromatography (SEC), using Phenomenex 10^4- and 10^5-Å columns in series with chloroform as eluent and a Spectra-Physics UV detector at 254 nm. Polystyrene standards were used.

Ethyl 1-cyano-2-(*p*-methoxyphenyl)cyclopropanecarboxylate (ECMC) was prepared as described in the first paper of this series.[8]

Thermal Reaction of ECMC/Methanol. An ECMC (0.6 M) solution in methanol was heated at 110 °C for 14 h under an argon atmosphere. After the reaction, methanol was evaporated and the products were analyzed by GC/MS. The main product (72.7%) was ethyl 2-cyano-4-methoxy-4-(*p*-methoxyphenyl)butanoate. MS: *m/z* 277 (5, M^+), 246 (2, $M^+ - OCH_3$), 151 (100, $CH_3OC_6H_4C^+OCH_3$).

Ethyl 1-Cyano-2-phenylcyclopropanecarboxylate. The starting olefin methyl α-cyanocinnamate was prepared by a Knoevenagel condensation of benzaldehyde and methyl cyanoacetate. The methylene transfer step involved treatment of this olefin with dimethyloxosulfonium methylide in dimethyl sulfoxide to give the cyclopropane in 30% yield after vacuum distillation, as described before for ECMC.[8] ^{1}H NMR ($CDCl_3$): δ 1.30–1.40 (3 H, t), 2.10–2.40 (2 H, m), 3.10–3.20 (1 H, t), 4.20–4.40 (2 H, m), 7.30–7.50 (5 H, m). IR (KBr): 2241 (CN), 1736 (CO), 1601 (CC) cm^{-1}. Chem. Anal. Calcd: C, 72.59; H, 6.05; N, 6.51. Found: C, 72.42; H, 5.95; N, 7.02. MS: *m/z* 215 (45, M^+), 187 (20, $M^+ - CN$), 169 (100, $M^+ - OC_2H_5$), 141 ($M^+ - COOC_2H_5$), 115 (80, $M^+ - COOC_2H_5CN$).

Ethyl 1-cyano-2-(*p*-methylphenyl)cyclopropanecarboxylate was synthesized following the same procedure starting from methyl *p*-methyl-α-cyanocinnamate. Yield: 33%. ^{1}H NMR ($CDCl_3$): δ 1.20–1.30 (3 H, t), 2.20–2.40 (2 H, m), 3.10–3.20 (1 H, t), 3.40–3.60 (3 H, m), 4.30–4.40 (2 H, m), 6.90–7.20 (4 H, m). IR (KBr): 2242 (CN), 1738 (CO), 1612 (CC) cm^{-1}. Chem. Anal. Calcd: C, 73.36; H, 6.55; N, 6.11. Found: C, 73.48; H, 6.57; N, 6.05. MS: *m/z* 229 (40, M^+), 201 (15, $M^+ - CN$), 183 (100, $M^+ - OC_2H_5$), 156 (40, $M^+ - COOC_2H_5$).

Ethyl 1-cyano-2-(*o,p*-dimethoxyphenyl)cyclopropanecarboxylate was synthesized following the same procedure starting from methyl *o,p*-dimethyl-α-cyanocinnamate. Yield: 45%. ^{1}H NMR ($CDCl_3$): δ 1.30–1.40 (3 H, t), 2.10–2.40 (2 H, m), 3.10–3.20 (1 H, t), 3.80–4.00 (6 H, m), 4.20–4.40 (2 H, m), 6.50–7.10 (3 H, m). IR (KBr): 2241 (CN), 1729 (CO), 1609 (CC) cm^{-1}. Chem. Anal. Calcd: C, 65.45; H, 6.18; N, 5.09. Found: C, 65.24; H, 6.23; N, 4.72. MS: *m/z* 275 (45, M^+), 246 (45, $M^+ - CN$), 230 (20, $M^+ - OC_2H_5$), 202 (100, $M^+ - COOC_2H_5$), 175 (30, 202 − CN).

Other Chemicals. *N*-Vinylcarbazole (VCZ) was purified by recrystallization from hexane at low temperature and dried under vacuum. 1,2-Dichloroethane (DEC), acetonitrile, chloroform, nitromethane, and benzene were distilled from CaH_2.

Polymerization Procedure. The polymerizations were run in 15-mL Pyrex tubes 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, dissolved in chloroform, and poured into methanol again. The second solution-precipitation is to remove the remaining VCZ monomer from the polymer. The products were weighed and used for SEC analysis.

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