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Ring-opening polymerization of activated cyclopropanes: polymerization of diethyl 1,1-cyclopropanedicarboxylate by metallic sodium*

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Summary

Diethyl 1,1-cyclopropanedicarboxylate undergoes ring-opening polymerization under anionic conditions. If the cyclopropane is contaminated by diethyl malonate $CH_2(COOEt)_2$, polymerization can be initiated by metallic sodium. The mechanism of this initiation was found to involve an initial reduction of the malonate by sodium to give the salt $(EtOOC)_2CH^{(-)}$ $Na^{(+)}$ which acts as the real initiator. Poly(diethyl 1,1-cyclopropane dicarboxylate) is soluble in halogenated solvents and was characterized by GPC, IR, ^1H- and ^{13}C-NMR. Molecular weights are low to moderate (typically 10^3-10^4) and are compatible with the low monomer / initiator ratios used in these experiments.

Introduction

Only a few communications in the literature report on the ring-opening polymerization of cyclopropanes.(2) This situation results from the low reactivity of cyclopropyl rings towards both nucleophiles and electrophiles and contrasts with the good polymerizability observed for analogous heterocycles like oxiranes. Some authors showed that the presence of activating substituents on the cyclopropane has a beneficial influence on the ring-opening. For example, Cho and al. were able to polymerize anionically 1,1-cyclopropanedicarbonitriles and ethyl 1-cyano-cyclopropane carboxylates substituted on position 2 by an additional activating substituent (vinyl or phenyl).(3,4) They postulated that the presence of this additional activating substituent is a prerequisite to the polymerization.

In this paper, we will show that the presence of an additional activating substituent on position 2 is not necessary for the polymerization to proceed. In particular, we will analyze the anionic polymerization of diethyl cyclopropanedicarboxylate 1 induced by the presence of metallic sodium.

*See ref. [1]

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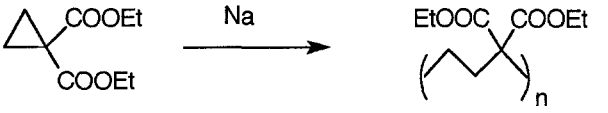


1

Experimental part

Materials. Diethyl malonate (99%, Janssen), DMSO (99+%, Janssen) and K_2CO_3 (anhydrous, p.a., Janssen) are commercial products and were used as received.

Synthesis of ultra-pure 1 . A mixture of 96.0 g (0.60 mol) of diethyl malonate, 237.0 g (1.26 mol) of 1,2-dibromoethane, 690.0 g (4.99 mol) of potassium carbonate and 500 mL of DMSO was vigorously stirred at room temperature during three days. 1.5 L of demineralized water were added to the suspension, and the resulting solution was extracted with six 500 mL-portions of diethyl ether. The combined ether extracts were concentrated by evaporation of the ether. The organic residue was washed twice with 500 mL of water, dried overnight on $MgSO_4$, and distilled *in vacuo* to furnish 1 in 95% yield (105.8 g), b.p. 95-7 °C/22 mmHg.

Samples of 1 containing 4-7 mol-% of diethyl malonate were synthesized by a phase-transfer catalysis procedure, as described in the literature. (5)

Polymerizations. All polymerizations were carried out in bulk under argon. After the cyclopropane had been introduced in a polymerization tube, a flow of argon was bubbled during 15 min and a known amount of metallic sodium, freshly scraped, cut in small pieces and weighted as rapidly as possible, was introduced. An additionnal purging by argon at room temperature was carried out during 15 min. The tube was finally placed in an oil bath under the conditions described in Table I. The reaction mixture containing poly(1) was dissolved in DMSO and reprecipitated in a large volume of methanol. The solid was filtered and dried at 50°C during two days in vacuo.

Measurements. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer using $CDCl_3$ as solvent, and TMS as an internal reference. IR spectra were recorded on a Nicolet FT-IR 205. GPC was performed on a Waters system equiped with two SHODEX K80M and one K802.5 columns using chloroform as the eluent; the calibration was based on polystyrene standards.

Results and discussion

Synthesis of the monomer

Polymerization under anionic conditions requires a synthetic route to a very pure grade of the monomer to be used. Particularly important from that point of view is the absence of acidic impurities. This fundamental requirement of purity is

not met however for diethyl 1,1-cyclopropanedicarboxylate 1, which is available commercially or can be easily synthesized by condensation of diethyl malonate with 1,2-dibromoethane under basic conditions. Samples of different origins (synthetic and commercial) were analyzed by 200 MHz ^{1}H-NMR: spectra always exhibited a peak at 3.35 ppm, characteristic of the methylene protons of diethyl malonate $CH_2(COOEt)_2$. Quantitative analysis of the commercial samples by gas chromatography revealed the presence of quantities ranging from 0.5 to 3 mol-% of diethyl malonate in the cyclopropane. Attempts to remove diethyl malonate from the mixture with 1 proved to be extremely difficult in our hands, a conclusion previously reached by others. (6)

A systematic screening for the purity of samples synthesized by condensation of diethyl malonate with dibromoethane under different sets of experimental conditions (type of base, solvent, temperature) revealed finally a satisfactory technique. The successful method, originally described by Zefirov and coll.(7), uses solid K_2CO_3 as the base and dimethylsulfoxide (DMSO) as the solvent. We improved the original experimental procedure to avoid a new contamination, by DMSO this time. The final procedure is described in the experimental part. A very pure monomer is obtained with no impurity detectable by 200 MHz ^{1}H-NMR and gas chromatography.

Polymerization of 1

Attempts to polymerize commercial samples of 1 (i.e. samples containing 0.5-3.0 mol-% of malonate) under different conditions proved to be relatively inefficient except when metallic sodium was used as the initiator. Results for experiments with sodium are described in Table I.

Experiments 1-5 were carried out with samples of 1 containing either 4 or 7 mol-% of residual diethyl malonate. They led to a mostly quantitative conversion of the monomer. During the reaction, viscosity of the medium progressively increased and a solid was finally obtained after a few hours. Times given in Table I for experiments 1-3 corresponds to what is necessary to reach this point.

The reprecipitated polymer is a white powder soluble in dimethylsulfoxide, $CHCl_3$, and CH_2Cl_2 but insoluble in acetone, N,N-dimethylformamide, CCl_4, and $(ClCH_2)_2$. Gel permeation chromatography (GPC) analysis were run in chloroform (polystyrene calibration) and indicated low to medium molecular weights. Molecular weights are compatible however with the low cyclopropane/malonate ratio used in these experiments (see table I). A direct comparison between the degree of polymerization obtained by GPC and the cyclopropane/malonate ratio is not possible due to the inability of our GPC experiments to provide absolute molecular weights.

Table I. Polymerization of cyclopropane 1 in the presence of sodium
(DEM: diethyl malonate)

#	mol-% DEM[a]	1 (mmol)	Na (mmol)	DEM (mmol)	1/DEM (b)	T (°C)	t (h)	$\overline{M}_n$ GPC[c]	$\overline{x}_n$ GPC	$\overline{M}_w/\overline{M}_n$
1	4	15.6	4.35	0.8	20.8	80	60	2200	12	2.27
2	7	26.6	7.80	2.3	11.6	90	80	9000	48	2.47
3	4	16.4	4.80	0.8	20.8	90	80	6900	37	5.18
4	7	4.9	0.44	0.4	11.6	80	24	1100	6	1.24
5	0	5.4	0.44	0.0	-	80	24	-	-	-
6	7	4.9	0.44	0.4	11.6	80	48	1300	7	1.19
7	0	5.5	0.44	0.0	-	80	48	-	-	-

[a] mole percentage of DEM in the cyclopropane/ malonate initial mixture; [b] cyclopropane/malonate ratio in the initial mixture; [c]polystyrene calibration

These results can be rationalized by the two-steps mechanism depicted in Figure 1: conversion of the malonate into its sodium salt (step a) and use of the *in situ* generated anion as the initiator of the polymerization (step b). Step (b) is a known reaction, described by Bone and Perkin at the end of the last century. (8)

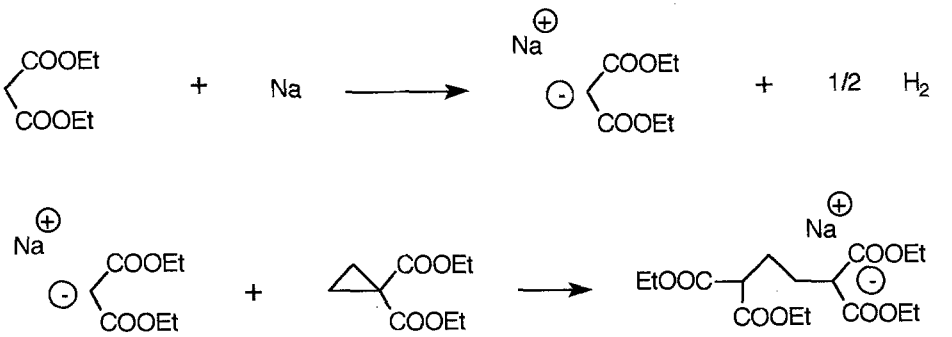


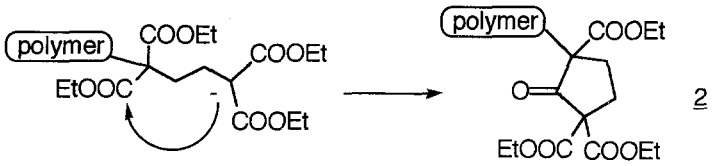
Fig.1. Suggested mechanism for the initiation of the polymerization of cyclopropane 1 in the presence of metallic sodium

To check the hypothesis depicted in Fig. 1, an additional experiment was conducted: 0.0407 equivalent of diethyl malonate and 0.0690 equivalent of sodium were added to ultra-pure 1. After 24 hours at room temperature, no polymer was produced. The residual sodium was then filtered and the solution was kept

at 80 ± 1°C for an additional 24 h-period. Poly(1) gradually appeared and conversion was mostly complete at the end of the period. A similar result was obtained when thiophenol was used instead of diethyl malonate. Interestingly, thiophenolate anions can also be generated by a redox reaction with sodium and are known to ring-open diethyl 1,1-cyclopropane dicarboxylate. (9)

Characterization of poly(1)

I.R., ^{1}H- and ^{13}C-NMR spectra (figs. 2-4) are compatible with the structure expected for a polymer resulting from the ring-opening polymerization of 1. Assignments of main peaks are indicated directly on figures 3 and 4. On fig.4 (^{13}C spectrum), upper-case letters correspond to the main chain and lower-case letters to the chain end $-CH(COOEt)_2$. (10) Additional tiny peaks identified by a question mark probably result from the carbon atom of substructure 2. This type of structure is due to a backbiting attack of the polymeric malonate anion on the ester of the penultimate unit:



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These condensations (Dieckmann reaction) are well documented in the literature. (11)

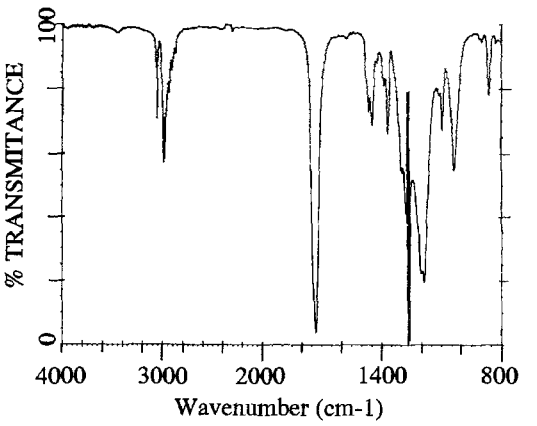

Fig.2. IR spectrum of poly(1)

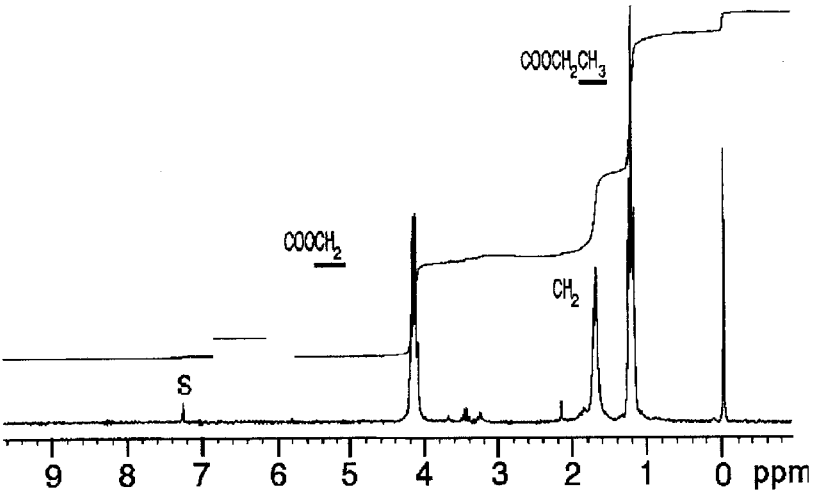

Fig.3. ^{1}H-NMR spectrum of poly(1) in $CDCl_3$

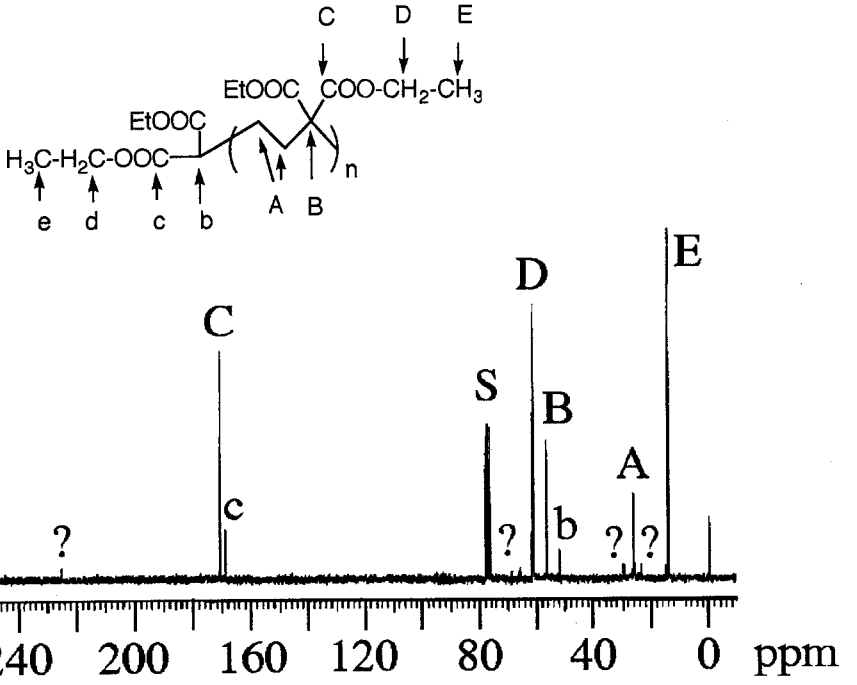

Fig.4. ^{13}C-NMR spectrum of poly(1) in $CDCl_3$

Conclusion

Poly(1,1-diethoxycarbonyl trimethylene) has been synthesized by the ring-opening polymerization of diethyl 1,1-cyclopropane dicarboxylate. The polymerization can be induced by metallic sodium, but the real initiating species is the sodium salt of diethyl malonate present in the cyclopropane as an impurity.

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