Anionic Ring-opening Polymerization of Alkyl 1-Cyanocyclopropanecarboxylates

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ABSTRACT: Poly(alkyl 1-cyanotrimethylene-1-carboxylate)s $(CH_2CH_2C(CN)(COOR))_n$ are the next higher chain homologues of poly(α-cyanoacrylate)s. They were synthesized via the anionic ring-opening polymerization of the corresponding alkyl 1-cyanocyclopropanecarboxylate monomers initiated with thiophenolate salts (PhSM, with M = Li, Na, K, and NBu_4) and at temperatures above 50 °C. Precipitation of the growing polymer chains at an early stage during the polymerization did not prevent further propagation, probably via polymerization in the solid or at the solid surface. The propagating cyanoacetate carbanion is very stable in a normal air atmosphere, surviving for long periods of time in the absence of strong acids. Although monodisperse polymers were obtained in most experiments ($\bar{M}_w/\bar{M}_n < 1.10$), strong experimental evidence for a living polymerization could only be obtained when K^+ and NBu_4^+ counterions were used. Nonquantitative initiations characterized polymerizations initiated by PhSLi and PhSNa. Attempted polymerizations of ethyl 1-cyanocyclobutanecarboxylate failed under similar or slightly more energetic experimental conditions, with the thiophenolate initiator attacking the pendant ester rather than the cyclic methylene group.

Introduction

We recently reported that cyclopropanes activated by two ester groups placed on a geminal position of the three-membered carbon ring can readily polymerize via an anionic ring-opening polymerization mechanism.[1,2] Under controlled conditions, neither termination nor chain-transfer reactions were observed, and features typical of a living polymerization were obtained up to temperatures as high as 200 °C.[2] The increased reactivity compared to normal, unactivated cyclopropanes and the high stability of the propagating carbanions both result from the presence of the two esters acting as strong electron-withdrawing and carbanion-stabilizing substituents.

In this report, we extend the initial concept of using activated 1,1-disubstituted cyclopropanes as precursors to carbon-chain polymers substituted by polar substituents on every third carbon along the backbone. The effect of a pair of ester- and nitrile-activating substituents on the reactivity of cyclopropane and cyclobutane monomers is examined as an analogy to well-known highly electrophilic vinyl monomers such as α-cyanoacrylates (super glue). The structure of the investigated monomers and resulting polymers is depicted in Scheme 1. Procedures developed to synthesize the required ultrapure monomers and methodologies to accurately characterize these polymers with unusual structures are presented first. The influence of several polymerization conditions (in particular, the temperature and the nature of initiators and counterions) on the polymerization is described and discussed.

Experimental Section

Materials. Ethyl, butyl, and octyl cyanoacetates (98+%, 95%, and 99% purity, respectively), 1,2-dibromoethane (99%),

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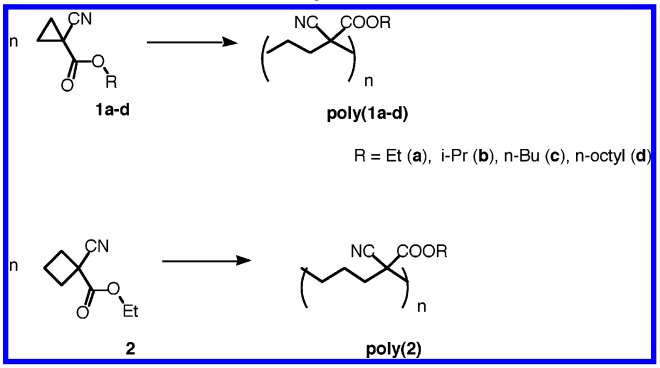
Scheme 1. Structures of the Alkyl 1-Cyanocyclopanecarboxylates Monomers 1a−d (R = ethyl (a), isopropyl (b), *n*-butyl (c), and *n*-octyl (d)) Investigated in This Study and of the Corresponding Polymers



and 1,3-dibromopropane (99%) were purchased from Aldrich and used without further purification. Isopropyl cyanoacetate (purum, ≥98.0%) and tetrabutylammonium thiophenolate (>97%) were obtained from Fluka, and anhydrous potassium carbonate (p.a.) from Acros. Dimethyl sulfoxide (DMSO) used for the polymerization was purified by distillation under vacuum (40 °C/2 mmHg), discarding the first and last 25%, and then drying over 4 Å molecular sieves. All other solvents were reagent grade and used without further purification.

Synthesis of Alkyl 1-Cyanocyclopropanecarboxylates 1a−d. A heterogeneous mixture of alkyl cyanoacetate (0.1 mol equiv), 1,2-dibromoethane (28 g, 0.15 mol), potassium carbonate (40 g, 0.29 mol), and 80 mL DMSO was vigorously stirred using a mechanical stirrer for 24 h at room temperature. Water (250 mL) was added to the reaction mixture, and the product was extracted with 3 × 150 mL portions of diethyl ether. The combined ether layers were concentrated by evaporation, washed with water (30 mL), and dried overnight over $MgSO_4$. The crude products were distilled under vacuum to yield the corresponding cyclopropane monomers **1a−d**. Yields, boiling points, and spectroscopic data (300 MHz NMR, $CDCl_3$) are provided below for each monomer.

1a: yield 69%, bp 45 °C/0.4 mmHg. ^{1}H NMR: δ 1.34 (t, CH_3), 1.59−1.72 (m, ring $2CH_2$), 4.27 (q, OCH_2). ^{13}C NMR: δ 13.3

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(ring CH_2), 14.1 (CH_3), 19.0 ($C_{quart.}$), 63.0 (OCH_2), 118.7 (CN). IR (liquid film, cm^{-1}): 3115 (cyclopropyl CH_2 stretch), 2986, 2941, 2250 (CN), 1737 (C=O), 1371, 1312, 1279, 1190, 1025, 972, 859, 747. Anal. Calcd for $C_7H_9NO_2$ (139.16): C, 60.41; H, 10.06; N, 6.53. Found: C, 60.16; H, 10.00; N, 6.60.

1b: yield 54%, bp 45 °C/0.3 mmHg. ^{1}H NMR: δ 1.31 (t, $2CH_3$), 1.58−1.71 (m, ring $2CH_2$), 5.1 (m, OCH). ^{13}C NMR: δ 13.5 (ring CH_2), 21.6 (CH_3), 19.1 ($C_{quart.}$), 71.0 (OCH), 118.8 (CN). IR (liquid film, cm^{-1}): 3121 (cyclopropyl CH_2 stretch), 2986, 2940, 2248 (CN), 1736 (C=O), 1361, 1309, 1281, 1190, 1106, 977, 933, 899, 749. Anal. Calcd for $C_8H_{11}NO_2$ (153.19): C, 62.72; H, 9.14; N, 7.14. Found: C, 62.50; H, 9.04; N, 7.32.

1c: yield 51%, bp 60 °C/0.3 mmHg. ^{1}H NMR: δ 0.93 (t, CH_3), 1.42 (m, CH_2), 1.58−1.74 (m, ring $2CH_2$ and OCH_2CH_2), 4.20 (t, OCH_2). ^{13}C NMR: δ 13.3 (ring CH_2), 13.6 (CH_3), 15.3 (CH_2-CH_3), 19.0 ($C_{quart.}$), 30.4 (CH_2CH_2O), 67.0 (OCH_2), 118.7 (CN). IR (liquid film, cm^{-1}): 3115 (cyclopropyl CH_2 stretch), 2962, 2934, 2879, 2249 (CN), 1740 (C=O), 1466, 1311, 1184, 1059, 936, 747. Anal. Calcd for $C_9H_{13}NO_2$ (167.23): C, 64.64; H, 8.38; N, 7.85. Found: C, 64.50; H, 8.36; N, 8.02.

1d: yield 31%, bp 98 °C/0.6 mmHg. ^{1}H NMR: δ 0.89 (t, CH_3), 1.24−1.44 (m, $5CH_2$), 1.57−1.75 (m, ring $2CH_2$ and alkyl CH_2), 4.19 (t, OCH_2). ^{13}C NMR: δ 13.3 (ring CH_2), 14.0 (CH_2), 15.3 (CH_2CH_3), 19.0 ($C_{quart.}$), 22.6 (CH_2), 25.7 (CH_2), 28.4 (CH_2), 29.1 (CH_2), 31.7 (CH_2CH_2O), 66.7 (OCH_2), 118.7 (CN). IR (liquid film, cm^{-1}): 3120 (cyclopropyl CH_2 stretch), 2960, 2928, 2857, 2249 (CN), 1740 (C=O), 1468, 1312,1176, 944, 747. Anal. Calcd for $C_{13}H_{21}NO_2$ (223.34): C, 69.91; H, 9.50; N, 6.27. Found: C, 69.85; H, 9.64; N, 6.29.

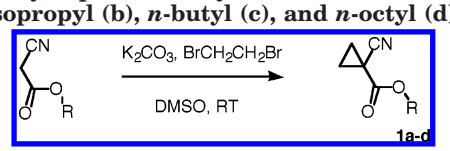
Synthesis of Ethyl 1-Cyanocyclobutanecarboxylate 2. The same general procedure as described above for **1a**−**d** was followed using 1,3-dibromopropane instead of 1,2-dibromoethane. Yield: 8%, bp 96−100 °C/ 1 mmHg. ^{1}H NMR: δ 1.34 (t, CH_3), 2.09−2.36 (m, cyclobutyl CH_2), 2.58−2.77 (m, cyclobutyl $2CH_2$), 4.27 (q, 2H, OCH_2). Anal. Calcd for $C_8H_{11}NO_2$ (153.19): C, 62.72; H, 7.25; N, 9.14. Found: C, 62.51; H, 7.23; N, 9.11.

Synthesis of Thiophenolate Initiators. Potassium and sodium thiophenolate initiators were synthesized according to a reported procedure.[1] Lithium thiophenolate was obtained using a slight modification of a previously reported procedure:[3] a 1.3 mol L^{-1} solution of *n*-BuLi (4.2 mL) in cyclohexane was slowly added to a solution of diphenyl disulfide (1.2 g, 0.005 mol) in 30 mL dry hexane at room temperature. The white precipitate was washed several times with hexane and dried in vacuo at 50 °C (0.9 mmHg). The final product was stored under argon. Yield: 1.05 g (88%). Anal. Calcd for C_6H_5SLi-$(H_2O)_{0.2}$ (119.65): C, 60.20; H, 4.55; S, 26.78; Li, 5.80. Found: C, 60.56; H, 4.94; S, 24.60; Li, 5.90.

Polymerization Procedure. Potassium and sodium thiophenolate initiators were dried just before use (200 °C/0.9 mmHg) using a Büchi Kugelrohr apparatus. While purging with nitrogen, weighed amounts of the initiator were dissolved in a specific volume of DMSO. The cyclopropane monomer was added to the initiator solution, and the polymerization tube was placed in an oil bath at 30 °C or 60 °C for a specified time. The polymer was precipitated in methanol, then filtered and washed several times with water and acetone. The polymers were dried in vacuo at 60 °C for 24 h.

A typical example is as follows: Sodium thiophenolate (0.018 g, 0.136 mmol) was dissolved under nitrogen in 5.0 mL of dry DMSO. Ethyl 1-cyanocyclopropanecarboxylate **1a** (0.500 g, 3.59 mmol) was added to this solution at room temperature and under nitrogen. The polymerization tube was placed in an oil bath at 60 °C for 15 min. The polymer was obtained by precipitation into 50 mL of methanol, filtered, washed with small aliquots of water (3× ∼50 mL) and acetone (3× ∼50 mL), and then dried under vacuum at 60 °C for 1 day. Yield: 0.1049 g (21%). GPC (DMF, 100 °C, polystyrene calibration): $\bar{M}_n$ = 6.9×10^3, $\bar{M}_w/\bar{M}_n = 1.06$. ^{1}H NMR: δ 4.3 (broad quartet, 2 ^{1}H, COO-CH_2), 1.9−2.2 (broad signal, 4 ^{1}H, backbone CH_2), 1.3 (broad triplet, 3 ^{1}H, $COOCH_2$−CH_3). ^{13}C NMR: δ 167.7 (COO), 118.3 (CN), 63.0 (COO-CH_2), 49.0 (C(CN)COOEt), 32.4 (backbone CH_2), 14.1 ($COOCH_2$-CH_3).

Scheme 2. Synthesis of Alkyl 1-Cyanocyclopanecarboxylates 1a−d (R = ethyl (a), isopropyl (b), *n*-butyl (c), and *n*-octyl (d))



Measurements. ^{1}H NMR and ^{13}C NMR spectra for the monomers were recorded on a Bruker DPX 300 spectrometer in $CDCl_3$ (at room temperature) and a Bruker AMX-2 500 spectrometer in DMSO-d_6 at 115 °C for the polymers. IR spectra were recorded on a BioRad FTS 175C FT-IR spectrometer. Elemental analysis was performed at the Micro Analysis Laboratory of the University of Massachusetts, Amherst. Gel permeation chromatography (GPC) analyses were obtained using a Polymer Laboratory PL-GPC ultrahigh-temperature chromatographic system with a Hewlett-Packard 1100 series isocratic pump and two PLgel 5 μm MIXED-D columns (linear range of molecular weights: 200−400000; column efficiency > 50000 plates m^{-1}). Dimethylformamide (DMF) was used as the eluent at 100 °C at a flow rate of 1 mL min^{-1}. The columns were calibrated with polystyrene standards.

Results and Discussion

Synthesis of Monomers 1a−d. A procedure initially developed by Zefirov et al.[4] and previously identified in our group as particularly effective for the synthesis of ultrapure cyclopropane-1,1-dicarboxylates[1] was used for the synthesis of ethyl 1-cyano-cyclopropanecarboxylate **1a**. The same procedure was extended to other alkyl 1-cyanocyclopropanecarboxylate monomers with isopropyl (**1b**), *n*-butyl (**1c**), and *n*-octyl (**1d**) groups on the ester substituent (Scheme 2). Vigorous mixing to finely disperse the solid potassium carbonate into the heterogeneous mixture was achieved by mechanical stirring and proved to be crucial to the success of the experiments. The monomers obtained were of high purity as indicated by high-field ^{1}H NMR and elemental analysis, with no residual starting reagents (cyanoacetates) that could act as chain-transfer agents during anionic polymerization. All monomers are colorless liquids and stable at room temperature.

Anionic Polymerization of 1a−d. Freshly synthesized sodium thiophenolate initiates the ring-opening polymerization of dialkyl cyclopropane-1,1-dicarboxylates.[1,2] In addition to their thermal stability and ease of drying, the use of soft bases such as thiophenolates of alkali metals increases the selectivity of the nucleophilic attack on the cyclopropane ring and prevents attack on the carbonyl of the ester. Other traditional anionic initiators such as organolithium compounds or Grignard reagents are hard bases that preferentially attack the carbonyl site on the ester and should be avoided as initiators.[5] The assumption was made at the beginning of this study that thiophenolates would also efficiently initiate the polymerization of cyclopropanes **1a**−**d**, and a series of polymerizations were carried out as shown in Table 1. Analysis of the structure by ^{1}H and ^{13}C NMR of the obtained powders established that the polymerization proceeded via a ring-opening mechanism, yielding polymers with cyanoester substituents on every third carbon (Table 2).

Structural Characterization of Poly(1a−d). The polymers were all isolated as white powders after precipitation in methanol. Poly(**1a**−**c**) were only soluble in highly polar solvents such as DMSO and DMF at temperatures above 100 °C. Poly(**1d**) with a longer alkyl side chain (*n*-octyl) was significantly more soluble,

Table 1. Ring Opening Polymerization of Monomers 1a−d

run no.	monomer	initiator[a]	time (h)	yield (%)	$\bar{M}_n$ (GPC)[b]	$\bar{M}_w/\bar{M}_n$[b]
1	**1a**	PhSK	0.25	39	7000	1.07
2	**1a**	PhSNa	0.25	21	6900	1.06
3	**1b**	PhSNa	0.25	34	6800	1.06
4	**1c**	PhSNa	0.25	10	4400	1.09
5	**1d**	PhSNa	0.25	21	4600	1.07
6	**1a**	PhSK	1.0	84	12400	1.05
7	**1a**	PhSNa	1.0	64	13400	1.06
8	**1b**	PhSNa	1.0	72	16100	1.07
9	**1a**	$PhSN(Bu)_4$	24	100	15000	1.06
10	**1b**	$PhSN(Bu)_4$	24	100	21900	1.15
11	**1a**	NMP[c]	24	100	8600	1.44
12	**1b**	NMP[c]	24	88	18200	1.20
13	**1c**	NMP[c]	24	81	5300	1.02

[a] 3.59 mmol monomer in 0.3 mL DMSO, 3.8 mol % initiator, 60 °C. [b] Determined in DMF at 100 °C, calibrated with polystyrene standards. [c] *N*-methyl pyrrolidine.

dissolving in toluene, THF, and chlorinated solvents at room temperature. However, higher molecular weight samples of poly(**1d**) (>3000) required moderate heating (30−60 °C) to dissolve in the same solvents. When solutions of poly(**1a**−**d**) in DMSO at 100 °C were cooled to ambient temperature, the polymers did not precipitate out of solution, but formed a clear, homogeneous gel.

The polymers were characterized by IR spectroscopy and high-temperature ^{1}H NMR and ^{13}C NMR. NMR spectra of poly(**1a**) (^{1}H NMR and ^{13}C NMR in DMSO-d_6 at 100 °C) are provided in Figure 1 as an illustration of the main features observed for the entire family of ester-substituted poly(**1a**−**d**). Full data corresponding to the individual polymers are summarized in Table 2.

The observed signals are fully consistent with the polymer structure expected of the ring-opened product, with the aromatic signal attributable to the phenylthiyl group from the thiophenolate initiators visible. The multiple peaks obtained for the backbone methylenes (from 1.9 to 2.2) produces a more complicated pattern than the single signal previously observed for poly(cyclopropane-1,1-dicarboxylate)s.[1] This is due to the presence of quaternary C(CN)COOR stereocenters on every third carbon along the backbone and the resulting absence of a plane of symmetry along that backbone. The presence of complex second-order AA′BB′ structures for the CH_2CH_2 subunits at the diad level, with the possibility of meso and dl arrangements, yields a complex pattern for the methylene units in the backbone. A complete analysis of the tacticity of these polymers on the basis of structurally related model compounds will be discussed in a forthcoming publication.

The main IR bands of the polymers include a nitrile stretching at 2249 cm^{-1}, a C=O stretching at 1740 cm^{-1}, and a C−O stretching at 1222 cm^{-1} (Figure 2). The strong peak at 1190 cm^{-1} in the monomer spectra (C−C stretching in the cyclopropane ring) has completely disappeared, providing further evidence that nucleophilic attack on the ester or cyano pending groups does not compete with the ring-opening reaction under the experimental conditions investigated in this study. Other spectroscopic features of interest that can be observed by IR will be discussed in the next section.

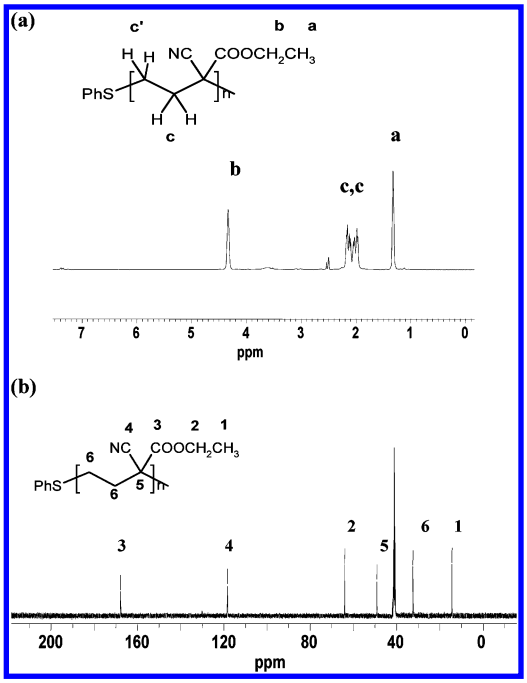


Figure 1. ^{1}H NMR and ^{13}C NMR spectrum in DMSO-d_6 of a typical sample of poly(**1a**) (poly(ethyl 1-cyanotrimethylenecarboxylate)) (GPC: $\bar{M}_n = 7 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.06$).

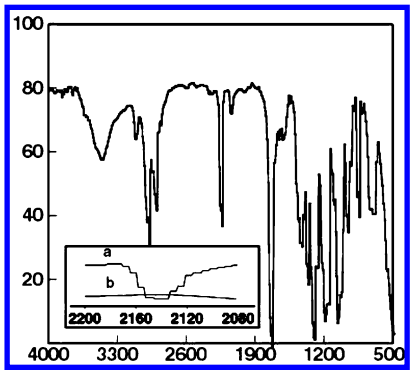


Figure 2. IR spectrum of poly(ethyl 1-cyanotrimethylenecarboxylate) (poly(**1a**)); the two curves in the inset correspond to (a) the absorption arising from the propagating end-group −C(CN)(COOEt)− in a "living" polymer isolated in the regular way, i.e., the absence of any strong acid and (b) after reaction with trifluoroacetic acid.

Determination of Absolute Molecular Weights. Poly(**1a**−**c**) are not soluble at room temperature in

Table 2. ^{1}H NMR and ^{13}C NMR Data (δ in ppm)[a] for Poly(1a−d)

	^{1}H NMR		^{13}C NMR				
			backbone			ester	
	backbone CH_2	R (ester)	CH_2	CN	C	COO	R
1a	1.9−2.2	1.3, 4.3	32.4	118.3	49.0	167.7	14.1; 63.0
1b	1.9−2.2	1.3, 5.1	32.0	118.8	49.0	167.2	21.6; 71.0
1c	1.9−2.2	0.9; 1.4; 1.6; 4.2	32.3	118.7	49.1	167.8	13.6; 15.3; 30.4; 67.0
1d	1.9−2.2	0.9; 1.2−1.4 (broad), 1.6, 4.2	32.2	118.7	49.1	167.8	14.0; 15.3; 22.6; 25.7; 28.4; 29.1; 31.7; 66.7

[a] TMS reference, DMSO-d_6 at 100 °C. [b] Poly(**1a**−**d**) initiated with PhSNa.

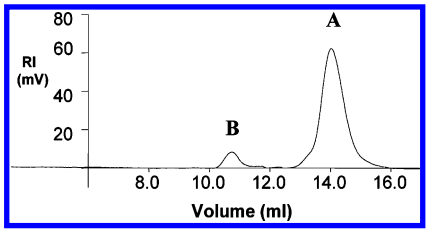


Figure 3. Typical GPC chromatogram of poly(ethyl 1-cyanotrimethylenecarboxylate) (poly(**1a**)) before treatment with trifluoroacetic acid.

organic solvents such as THF, chloroform, or even DMF. As a result, the molecular weights were initially obtained by GPC analysis in DMF at 100°C using a calibration based on polystyrene standards. GPC chromatograms of the polymers characterized under these conditions showed either single or bimodal distributions, without clear trends between the type of distribution observed and the polymerization conditions used to synthesize the polymer sample. The two peaks in the distribution were usually well separated, and both had narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.10$). A typical example of a GPC trace for a sample of poly(**1a**) displaying a bimodal distribution is shown in Figure 3. In this example, peak **A** corresponds to the lower molecular weight fraction ($\bar{M}_n = 1.8 \times 10^4$), while peak **B** corresponds to a much higher molecular weight ($\bar{M}_n = 2.6 \times 10^5$). For samples displaying a bimodal distribution, the area under peak **B** (high molecular weights) was typically 3−5% of the area under peak **A** (low molecular weight).

The very high molecular weights obtained for peak **B** is difficult to reconcile with the chemistry and experimental conditions used in the above experiments. Among other hypotheses to explain this behavior, it was suspected that the high molecular weight fraction was due to aggregation of a few polymer chains driven by the formation of ionic bridges between persistent cyanoacetate carbanions $-C(CN)(COOEt)^{(-)}$ possibly present as end groups on the polymers. To check this hypothesis, polymer samples displaying a bimodal distribution were redissolved in DMF and treated with trifluoroacetic acid (rather than the methanol used in the first precipitation step). Subsequent analysis by GPC showed the area of peak **B** diminished to less than 1% in relation to peak **A**, which provided convincing evidence that the initial hypothesis was indeed correct.

The persistence of the propagating carbanions on some of the polymer chains at room temperature, even when no special storage precautions against humidity are taken and after precipitation was carried out in a protic solvent such as methanol, was further demonstrated by IR spectroscopy. IR spectra of a poly(**1a**) sample obtained during the polymerization prior to termination by treatment with a strong acid is shown in an inset in Figure 2 (curve a). The spectrum contains a band at 2137 cm^{-1} that fully disappears upon termination with a strong acid (curve b) and can be correlated to a $-C(CN)(COOEt)^{(-)}$ moiety whose assignment had been described in the literature on the basis of the IR spectrum of the ethyl cyanoacetate tetrabutylammonium salt (absorption at 2140 cm^{-1}).[6] This 2137 cm^{-1} C≡N stretching band was also visible for a sample of **1a** polymerized under exposure to atmospheric oxygen, carbon dioxide, and moisture.

The high stability of the propagating carbanion is not completely unexpected. Typical propagating carbanions

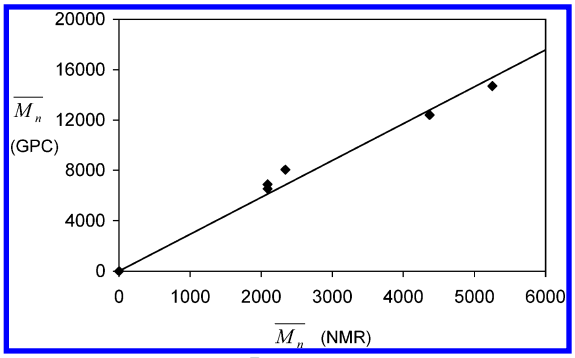


Figure 4. Comparison of $\bar{M}_n$ values obtained from NMR and GPC for poly(ethyl 1-cyanotrimethylenecarboxylate) (poly(**1a**)).

such as those of polystyrene or poly(methyl methacrylate) must be carefully protected against agents such as water, oxygen, alcohols, and carbon dioxide, but cyanoacetate carbanions are highly stabilized by two electron-withdrawing groups and, as a result, are extremely weak C−H bases ($pK_a = 16.4$ in DMSO at 25 °C, in contrast to a pK_a of 32 for H_2O under the same conditions[7]). The stability of the propagating cyanoacetate carbanion during the polymerization of α-cyanoacrylates (super glue) has been reported.[8,9] Weak acids such as acetic acid only retard the polymerization of α-cyanoacrylates, while the rapid termination of fully initiated chains requires strong acids such as *p*-toluenesulfonic acid.

The narrow distribution of molecular weights observed for peak **B** in the GPC chromatograms suggests that the obtained aggregates have a relatively well-defined stoichiometry. The exact aggregation numbers could not be determined, however, because of the lack of a suitable calibration curve for these starlike structures and the possibility of nonspecific interactions between the chromatography columns and the ionic core of the aggregates (analogous to the behavior observed for inverse micelles made of ionic macrosurfactants).

As a way to calibrate results obtained by GPC, molecular weight analysis of the polymers was also performed by end-group analysis via ^1H NMR spectroscopy. The peak area of the signal attributable to the aromatic protons of the PhS end group (7.2 ppm) was compared to the methylene protons (OCH_2, 4.2 ppm) of the ester group on the polymer (Figure 1). The absolute degree of polymerization using this method was compared to the apparent degree of polymerization obtained by GPC. $\bar{M}_n$ values obtained by NMR for poly(**1a**) were plotted against those obtained by GPC as shown in Figure 4. The slope of the straight line obtained by this methodology indicates that GPC overestimates the actual molecular weights by a factor of 3.

NMR spectroscopy of the polymers initiated with the thiophenolate initiators supports clean initiation and propagation steps, with no evidence for side reactions such as a Krapcho reaction (nucleophile-assisted decarboxylation) or backbiting reactions (Scheme 3).[10]

Kinetic Analysis of 1a Polymerization. The polymerization of **1a** initiated by potassium (K^+), sodium (Na^+), lithium (Li^+), and tetra-*n*-butylammonium (NBu_4^+) thiophenolate was analyzed kinetically, first at 60 °C. Experimental results are shown in Figures 5 and 6. In these figures, individual data points correspond to separate experiments. The degrees of polymerization were obtained by high-temperature SEC using a polystyrene calibration, and corrected to obtain absolute $\bar{x}_n$ according to the relationship provided in Figure 4.

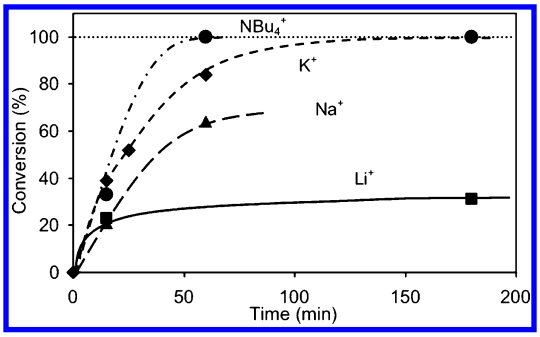


Figure 5. Dependence of the conversion (%) with time for the polymerization of ethyl 1-cyanocyclopropanecarboxylate **1a** with thiophenolate initiators: PhS$^-$X$^+$ [X = K (◆), Na (▲), Li (■), (NBu)$_4$ (●)]; 60 °C, 3.8 mol % initiator, 3.59 mmol **1a** in 0.3 mL DMSO.

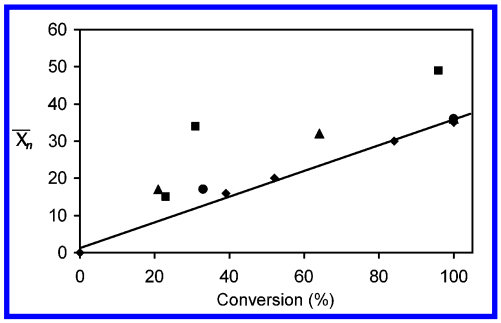
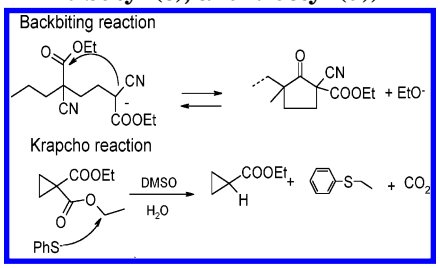


Figure 6. Evolution of the degree of polymerization with conversion for the polymerization of ethyl 1-cyanocyclopropanecarboxylate **1a** using PhS$^-$X$^+$ [X = K (◆), Na(▲), Li (■), (NBu)$_4$ (●)]; (3.8 mol % initiator; $[M_o]/[I_o]$ = 27/1, 60 °C, $\bar{X}_n$ obtained by GPC and corrected by NMR). The theoretical behavior expected for a living polymerization under the above experimental conditions is indicated by a solid line.

Scheme 3. Possible Side Reactions during the Polymerization of 1a−d (R = ethyl (a), isopropyl (b), *n*-butyl (c), and *n*-octyl (d))



The reaction mixture was initially homogeneous. After about 15 min, some polymer precipitated, consistent with the poor solubility of poly(**1a**) in DMSO below 100 °C even at low degrees of polymerization. Despite the precipitation, quantitative conversions were achieved in every case, albeit very slowly, when the counterion was lithium (quantitative polymer recovery was obtained for each four counterions after 24 h (1440 min); data point not included in Figure 5 for clarity).

The above observations can be rationalized on the basis of three hypotheses: (a) remaining soluble active species (thiophenolate initiator and/or propagating oligomers) maintain the polymerization after the precipitation has occurred, (b) the propagation can also occur in the solid polymer or at its surface, or (c) a fast equilibrium between soluble (active) and insoluble (inactive) propagating chains can develop in the range of molecular weights covered by the experiments. The evolution of the molecular weight distribution and degree of polymerization suggests the second or third hypothesis is correct; for all four initiators, the molecular weight distributions of the entire polymer sample (combined soluble and insoluble fractions) is indeed very narrow (PDI = 1.02−1.07) over the entire conversion range. This is also the case for the slow, PhSLi-initiated polymerization for which a PDI of 1.06 was observed at full conversion (24 h reaction time). Dialkyl cyclopropane-1,1-dicarboxylates, the diester equivalent of the cyanoester cyclopropane monomers investigated here, have previously been shown to display the opposite behavior, the early precipitation of the propagating polymer chains to a semicrystalline solid preventing any further propagation.[1,2] In contrast, there are many indications in the literature that α-cyanoacrylates can polymerize anionically from a solid polymer mass as seen in vapor deposition polymerizations or when used for the fast development of latent fingerprints from monomer vapors.[11,12] It thus appears on that basis that our experimental observations are not completely unforeseen.

Table 3. Polymerization of 1a at Varying Temperatures

run no.	monomer	initiator[a]	time (h)	temp (°C)	yield (%)	$\bar{M}_n$ (GPC)[b]	$\bar{M}_w/\bar{M}_n$ [b]
1	**1a**	PhSNa	0.25	60	*c*		
2	**1a**	PhSNa	0.25	100	12	8300	1.08
3	**1a**	PhSNa	0.25	120	72	17900	1.07

[a] 3.59 mmol **1a** in 5 mL DMSO, 3.8 mol % PhSNa. [b] Determined in DMF at 100 °C, calibrated with polystyrene standards. [c] No polymer isolated via precipitation

In the cases of PhSK and PhSNBu$_4$, the molecular weight increases linearly with conversion, reaching the theoretical limit at full conversion (Figure 6). These data, combined with the very low $\bar{M}_w/\bar{M}_n$ observed for each sample, strongly suggests that the polymerization is living as previously observed for the dialkyl cyclopropane-1,1-dicarboxylate monomers. Results summarized in Figure 6 for PhSLi and PhSNa display some significant upper deviation from the theoretical line. The low $\bar{M}_w/\bar{M}_n$ observed at low and high conversions and the almost linear relationship between degree of polymerization and conversion suggest that the deviation results from a nonquantitative initiation. As indicated by elemental analysis, the good initial purity of the starting initiators implies that some currently unidentified deactivation mechanism is responsible for the observed partial initiation.

This possible deficiency in the initiation of PhSLi- and PhSNa-initiated polymerizations makes it difficult to reach a firm conclusion on the effect of the counterion on k_p. In the case of dialkyl cyclopropane-1,1-dicarboxylate monomers such as diisopropyl cyclopropane-1,1-dicarboxylate, polymerizations initiated by PhSK proceeded about twice as fast as those initiated by PhSNa.[2] Such an order of magnitude is compatible with the results obtained for **1a**, the experimental data showing that, at the onset, the PhSK-initiated polymerization proceeds twice as fast with little or no precipitation observed.

Analysis of **1a** polymerization at varying temperatures showed that the rate of polymerization increased with temperature, as expected, while maintaining the living character of the polymerization up to at least 120 °C (Table 3).

α-Cyanoacrylates react with neutral nucleophiles such as amines and phosphines, generating 1,3-zwitterions by Michael addition on the C=C double bond.[13−19] These intermediate species have been identified by

Table 4. Ring-opening Polymerization of 1a with Neutral Initiators

run no.	monomer	initiator[a]	time (h)	yield (%)	$\bar{M}_n$ (GPC)[b]	$\bar{M}_w/\bar{M}_n$ [b]
1	**1a**	PhSK	1.0	84	12400	1.05
2	**1a**	NMP[c]	1.0	43	8800	1.20
3	**1a**	DBU[d]	1.0	59	8800	1.16
4	**1a**	Et_3N	1.0	*e*		
5	**1a**	pyridine	1.0	*e*		
6	**1a**	PhSK	3.0	100	14700	1.05
7	**1a**	NMP	24	100	8600	1.44
8	**1a**	Et_3N	24	94	3700	1.15
9	**1a**	pyridine	24	*e*		

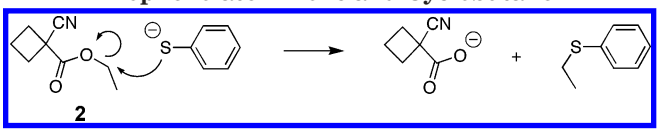
[a] 3.59 mmol of **1a** in 0.3 mL DMSO, 3.8 mol % initiator at 60 °C. [b] Determined in DMF at 100 °C, calibrated with polystyrene standards. [c] *N*-methyl pyrrolidine. [d] 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU)]. [e] No polymer isolated by precipitation

Pepper et al. as the key species in the polymerization of α-cyanoacrylates by neutral nucleophiles. To test whether these nucleophiles were also able to initiate the polymerization of activated cyclopropanes via a ring-opening attack and the formation of hypothetical 1,4-zwitterions, a study of the reactivity of various nucleophilic initiators toward the ring-opening polymerization of **1a** was conducted. The results are summarized in Table 4. Of the selected nucleophilic initiators, PhSK used here as a reference point is the most reactive, achieving quantitative conversion in 3 h. Lower yields and $\bar{M}_n$ were obtained for *N*-methyl pyrrolidine (NMP), 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU), and triethylamine (Et_3N) under the same conditions. A ^1H NMR analysis of the reaction mixture confirmed that pyridine does not initiate the polymerization of **1a** at 60 °C. The entire set of observations is globally consistent with the general trend of increasing the reactivity toward polymerization with an increase in the nucleophilic strength of the initiator.

Re-initiation from the Macroinitiator. As expected from a living polymerization, reinitiation from the macromolecular carbanion is also possible. Polymerization of **1a** at 60 °C for 4h (3.59 mmol **1a**, 0.3 mL DMSO, 3.8 mol % PhSNa) yielded poly(**1a**)$_1$, a polymer of $\bar{X}_n = 41$ (100% yield). When a second aliquot of **1a** (7 mmol) was added to the solid poly(**1a**)$_1$ prior to termination and allowed to run for 24 h, a second sample, poly(**1a**)$_2$, was obtained with a $\bar{X}_n = 102$ (50% yield). Despite the precipitation of the polymer from the reaction mixture during the polymerization of **1a**, the chains remained active and could propagate in the solid state in the presence of additional monomer, although (as expected) the reactivity was lower.

Tetrabutylammonium salts of cyanoacetates, ethyl dialkyl malonates, methyl malononitrile, and nitroalkanes have been used as efficient initiators for the living polymerization of acrylates and (methyl) methacrylates.[6,20−21] As a result, attempts were made to grow a block of PMMA from the polymeric carbanion of **1a** under conditions similar to those used for the polymerization of MMA.[6,21] The polymerization of **1d** was first carried out to quantitative conversion using $PhSN(Bu)_4$ (2.24 mmol **1d**, 3.8 mol %) at 60 °C in THF. Monomer **1d** was selected over **1a**−**c** because of the good solubility of poly(**1d**) in THF over the entire polymerization at 60 °C. After the monomer **1d** had been completely consumed, the solution was cooled to ambient temperature and MMA (2.24 mmol) was added. Analysis of the polymer mixture was performed by NMR and GPC, but no evidence was obtained for the presence of PMMA,

Scheme 4. Main Reaction Observed between Thiophenolate Anions and Cyclobutane 2



and the GPC data also showed no changes in $\bar{M}_n$. Tetrabutylammonium salts of cyanoacetates effectively initiate the polymerization of MMA under conditions identical to ours,[6,21] suggesting that the observed failure of the propagating carbanion to react with MMA is due to the physical inaccessibility of the MMA monomer to the propagating chains as a result of the precipitation of poly(**1d**) from solution at ambient temperature. If correct, this conclusion would support hypothesis (b) over (c), i.e., a direct polymerization in the solid state or at the solid surface rather than a fast equilibrium between soluble and insoluble propagating species.

Attempted Polymerization of Ethyl 1-Cyanocyclobutanecarboxylate 2. Because of the expected lower reactivity of cyclobutane monomers over the analogous cyclopropanes,[22] higher reaction temperatures between 140 and 180 °C were employed for the attempted polymerization of ethyl 1-cyanocyclobutanecarboxylate **2**. NMR analysis of the reaction mixture (4.5 mmol **2**, 4.6 mol % PhSNa, 0.5 mL DSMO, 160 °C) provided evidence that the main reaction is the attack of PhSNa on the ethyl carbon of the ester group (Krapcho reaction, Scheme 4),[10] yielding ethyl phenyl thioether and the salt of 1-cyanocyanocyclobutanecarboxylic acid as the main products. No polymers/oligomers could be identified for any of the reactions of **2** with either PhSK or PhSNa at 180 °C, even after long reaction times.

This sharp decrease in reactivity for the cyclobutane ring is not unexpected. Despite the almost identical strain energies of three- and four-membered rings, cyclobutane rings are much less reactive than cyclopropanes, in agreement with the reactivity ratio observed for their heterocyclic counterparts (oxetanes vs oxiranes, thietane vs thiiranes, azetidines vs aziridines, etc.).[22] As far as we are aware, the only example reported in the literature for the ring-opening polymerization of a cyclobutane is on the basis of 1,1,2,2-tetracyano-3-ethoxycyclobutane, for which polymerization was achieved at ambient temperature using various initiators including triethylamine.[23] In this case, the cyclobutyl ring is further activated toward the ring-opening nucleophilic substitution of the intra-annular C−C bond by the presence of a strong electron-donating substituent on the attacked carbon.

Conclusions

The synthesis of poly(alkyl trimethylene-1-cyano-1-carboxylate)s $(CH_2CH_2C(CN)(COOR))_n$, the next higher homologues of poly(α-cyanoacrylate)s, can be achieved via the anionic ring-opening polymerization of the corresponding alkyl 1-cyanocyclopropanecarboxylate monomers **1**. Despite the early precipitation of propagating polymer chains in the DMSO/monomer mixture used for the experiments, polymerizations were observed to proceed to full conversion, probably via addition of the monomer to propagating centers located in the solid or at its surface. Molecular weights obtained under the investigated experimental conditions (high initiator-to-monomer ratios) were rather low, as ex-

pected. Polymerizations initiated with thiophenolate salts, in particular potassium and tetra-*n*-butylammonium thiophenolates, were highly efficient, with no evidence for competing side reactions. Polymers with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.10$) were obtained in most cases, and the polymerizations (within the limits of this investigation) displayed characteristics typical of living systems, in particular for PhSK- and $PhSNBu_4$-initiated polymerizations. IR spectroscopy supported a very high stability of the poly(**1a**) carbanion, even under wet air atmospheres. Attempts to ring-open ethyl 1-cyanocyclopropanecarboxylate **2** were unsuccessful, even at elevated temperatures, because of the poor kinetics associated with the ring-opening of cyclobutanes.

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