Ring-Opening Polymerization of Diisopropyl Cyclopropane-1,1-dicarboxylate under Living Anionic Conditions: A Kinetic and Mechanistic Study

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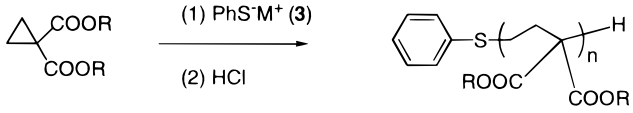
ABSTRACT: Diisopropyl cyclopropane-1,1-dicarboxylate (**1**) undergoes ring-opening polymerization in the presence of thiophenolate anions acting as initiator. A carbon-chain polymer, substituted on every third carbon atom by two isopropyl ester substituents, is obtained, whose structure and molecular weight were characterized by several analytical techniques. Under typical reaction conditions, only the expected ring-opened structure with a phenylthio end group is obtained, with no evidence for side reactions during the initiation and propagation steps. A kinetic study of the polymerization, at 140 °C in the presence of sodium thiophenolate, showed that the degree of polymerization increases linearly with conversion. The final polymers have narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ < 1.13), and the reaction follows a first-order kinetics with respect to the monomer over the entire conversion range. These results support a living mechanism for the polymerization. The nature of the counterion and the presence of counterion complexing agents, like crown ether and cryptand, significantly increase the reaction rate. A linear Arrhenius behavior was found in the 130−190 °C range, with an activation energy of 21.3 kcal mol^{-1}. At higher temperatures deviation from the linear Arrhenius behavior and appearance of new peaks in ^{1}H NMR can be observed. Thermogravimetric analysis shows that the polymer is thermally stable up to 270 °C. Poly(**1**) is highly crystalline, with a melting point in the 168−76 °C range.

Introduction

In the course of our study on the ring-opening polymerization of activated carbon cycles, we recently described the anionic ring-opening polymerization of diethyl cyclopropane-1,1-dicarboxylate (**2**).[1,2] Cyclopropane **2** polymerizes easily in the presence of soft nucleophilic initiators such as thiophenolate anions **3** to provide a carbon-chain polymer substituted by two esters on every third atom. The polymerization reaction is schematized in Scheme 1. It involves an initial ring opening by the thiophenolate anion and the subsequent propagation of a malonate carbanion. The propagating species is stabilized by two electron-withdrawing groups, providing a stability approaching those of an alcoholate that is probably key to the cleanliness of the ring-opening reaction. Indeed, cyclopropanes are known for their reluctance to polymerize under ring-opening mechanisms.[3] In all cases reported in the literature, polymers either were insoluble and difficult to characterize or had their molecular weights and/or structure deeply affected by side reactions.[4−16] Conversely, the polymerization of **2** showed some indications of a living character, in particular a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ < 1.14) and an increase of the degree of polymerization with conversion.[2] A careful spectroscopic analysis of the polymers displayed no evidence of side reactions. However, the dependence of the degree of polymerization with conversion gave a linear plot that did not intersect at the origin. Also, a detailed mechanistic analysis of the rection was prevented by the insolubility of the polymer and its gradual precipitation over time. The poor solubility of poly(**2**) in other solvents, possibly compatible with the reaction conditions, precluded a more complete investigation of the polymerization and its possible livingness.

Scheme 1. Ring-Opening Polymerization of Cyclopropane-1,1-dicarboxylates 1 and 2



R = *i*Pr (**1**), Et (**2**)

M = Na (**3a**), K (**3b**)

This paper presents a detailed mechanistic and kinetic analysis on the ring-opening polymerization of a new cyclic monomer, diisopropyl cyclopropane-1,1-dicarboxylate (**1**). A separate study on the polymerizability of several dialkyl cyclopropane-1,1-dicarboxylates, whose complete results will be reported later, had shown that, among all tested cyclopropyl monomers, poly(**1**) had the best solubility in its own monomer over an extensive range of experimental conditions.

Experimental Section

Materials. Dimethyl sulfoxide (DMSO), 2-propanol, *p*-toluenesulfonic acid monohydrate, 1,2-dibromoethane, potassium carbonate (anhydrous, p.a.), thiophenol, and Kryptofix 2.2.2 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) were obtained from Aldrich or Acros. Sodium thiophenolate (**3a**) was synthesized according to a procedure described in a previous publication.[2] DMSO was purified by distillation under vacuum (35 °C/1 mmHg), discarding the first and last 25%. The recovered fraction was further dried on 4 Å molecular sieves, stored under nitrogen, and used in the next 8 weeks or discarded.

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Table 1. Ring-Opening Polymerization of 1 at 140 °C[a]

reaction time (h)	conversion (%)	yield (%)	$\bar{M}_n$ (NMR)	$\bar{M}_n$ (VPO)	$\bar{M}_n$ (GPC-LS)	$\bar{M}_n$ (MALDI-ToF)	$\bar{M}_w/\bar{M}_n$ (GPC-LS)	$\bar{M}_w/\bar{M}_n$ (MALDI-ToF)
2	30.7	9.5	3040	2420	2490		1.13	
5	52.0	48.8	6040	5990	5960	5609	1.08	1.029
8	66.1	62.8	7900	6570	6560	6625	1.08	1.027
12	84.3	81.4	9200	8490	8310	8290	1.05	1.021
16	100	95.9	>10000	9700	9100	9417	1.06	1.018

[a] 22.2 mmol of **1** in 1.6 mL of DMSO, 2.3 mol % **3a**.

Synthesis of Potassium Thiophenolate (3b). A 3.39 g (87 mmol) sample of freshly scraped potassium was added into 250 mL of dry ether. A 10.70 g sample of previously distilled thiophenol was added dropwise to the suspension. The resulting mixture was left at room temperature under magnetic stirring until no metallic potassium remained (about 4 h). Ether was evaporated, and the resulting powder was washed five times with 200 mL of dry ether. The recovered solid was dried under vacuum for 24 h to yield 11.8 g of a white powder (yield: 92%). **3b** was stored under nitrogen and further dried (200 °C/ 0.3 mmHg in a Buchi Kugelrohr oven) right before use. Its ^{1}H NMR spectrum is identical to the one reported for **3a** and can be used as an indicator of its purity and to monitor its degradation over time.[2]

Monomer Synthesis. Diisopropyl malonate was synthesized by refluxing a benzene solution (300 mL) containing malonic acid (0.6 mol), 2-propanol (1.2 mol), and *p*-toluenesulfonic acid monohydrate (5.7 g) until no more of the azetropic mixture added in a Dean-Stark trap (3−5 h). The resulting solution was washed with saturated aqueous potassium carbonate. The solvent was evaporated, yielding a residue that was distilled at low pressure (∼60 °C/1 mmHg) to give a colorless liquid (yield: 88%). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.3 (d, 12 H), 3.3 (s, 2 H), 5.1 (sept, 2 H).

A mixture of diisopropyl malonate (94 g, 0.50 mol), 1,2-dibromoethane (197.4 g, 1.05 mol), anhydrous potassium carbonate (410 g, 3.0 mol), and DMSO (560 mL) was stirred vigorously for 3 days at room temperature. One liter of water was added to the resulting mixture, and the obtained solution was extracted with three 400 mL ether fractions. The combined ether extracts were dried overnight over sodium sulfate. The ether was evaporated and the residue distilled under vacuum (∼60 °C/1 mmHg) to yield 88.8−96.3 g of **1** (0.42−0.45 mol, 84−90% yield). ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 1.3 (d, 12H), 1.5 (s, 4H), 5.1 (sept, 4H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ (ppm) 15.4 (CH_2), 21.4 (CH_3), 28.5 (C(COOiPr)$_2$), 68.5 (COO−CH), 169.1 (C(=O)−O). IR (liquid film): 2983, 2940, 2878, 1722, 1375, 1359, 1317, 1212, 1158, 1146, 1102, 906, 896, 807, and 754 cm^{-1}.

Polymerization Procedure. Weighed amounts of sodium or potassium thiophenolate were dissolved in the required volume of dried DMSO. The slightly yellow solution was introduced into a polymerization tube, and monomer **1** was rapidly added. A flow of argon gas was bubbled for 10 min into the solution via a capillary tube. The polymerization tube was closed, placed in a thermostated oil bath at the required temperature, during the desired amount of time, and then removed from the oil bath. The polymerization was stopped by adding 2 mL of concentrated aqueous chlorhydric acid. A 2−6 mL aliquot of hot chloroform (depending on the amount of polymer precipitated) was used to redissolve the polymer. Poly(**1**) was precipitated from the cooled chloroform solution using methanol as the nonsolvent. A white powder was recovered by filtration and dried for 24 h at 45 °C in a high-vacuum oven.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on 200 or 300 MHz Varian spectrometers using CD_2Cl_2, d_6-DMSO, or $CDCl_3$ as the solvent. IR spectra were recorded on a Nicolet FTIR 205. Elemental analysis were carried out at the University College London. Gel permeation chromatography−light scattering (GPC-LS) analyses were obtained using a Waters 510 pump, two SHODEX K80M, and one K802.5 column, using chloroform as the eluent and a flow rate of 1 mL min^{-1}. A Wyatt DAWN DSP multiangle light scattering photometer and a Wyatt OPTILAB DSP interferometric refractometer were used as detectors. (d*n*/d*c*) for poly(**1**) was measured in chloroform at room temperature, using the Wyatt OPTILAB DSP refractometer in its stand-alone configuration. Molecular weights were also determined from toluene solutions at 51 °C using a vapor pressure osmometer (Jupiter VPO 833 instrument) and by MALDI-ToF (matrix-assisted laser desorption/ionization time-of-flight) mass spectrometry using a Bruker Reflex III. The matrix for the MALDI-ToF experiment was prepared by evaporating a THF solution (5 g L^{-1}) of a 1:1 dithranol/polymer mixture on a KCl crystal. The instrument was externally calibrated. Differential scanning calorimetry (DSC) studies were carried out on a DSC 7 Perkin-Elmer instrument (helium, 10 K min^{-1}). Purity of the monomer was controlled by capillary gas chromatography (GC) using a Carlo Erba HRGC oven and a poly(dimethylsiloxane) column (30 m × 0,25 mm). Thermal decompositions were evaluated by thermogravimetric analysis (TGA) using a SETARAM TGC 85 apparatus (10 K min^{-1}, nitrogen).

Results

Polymerization Kinetics. Our previous study on the polymerizability of diethyl cyclopropane-1,1-dicarboxylate (**2**) had shown that ring-opening polymerization requires a temperature of at least 80 °C to proceed at an acceptable rate.[2] The same study demonstrated that sodium thiophenolate (**3a**) initiates efficiently the polymerization, which agreed with a previous report that **3a** reacts quantitatively with **2** to provide the ring-opened adduct only.[17] While other soft bases are also known to efficiently ring-open cyclopropane-1,1-dicarboxylates,[18,19] thiophenolates offer the advantage of being easy to synthesize, store, dry, and use. It was used througout this study. Hard bases typically used in anionic polymerizations, like Grignard reagents or organolithium species, cannot be used, as they attack on the ester rather than on the cycle.[18]

An initial attempt to polymerize **1** under the same conditions as those reported previously for **2** showed that, contrary to its diethyl analogue, **1** yields entirely soluble polymers over the full conversion range, allowing a mechanistic analysis of the reaction to be carried out. Typical polymerization conditions are listed in Table 1. Conversions were obtained by analyzing final reaction mixtures by ^{1}H NMR and comparing methylene signals for **1** and poly(**1**) at 1.3 and 1.7 ppm, respectively. Yield values refer to isolated yields of poly(**1**) obtained by gravimetry after precipitation in methanol and drying. Both values are very close except at low conversion, where the amount of recovered polymer was far from quantitative. The discrepancy probably results from the low molecular weight of the polymer obtained under these conditions, which prevented a full precipitation in the nonsolvent (methanol) used to recover the polymer.

Kinetic experiments at 140 °C are summarized in Figure 1 for polymerizations initiated with sodium thiophenolate (**3a**). Each experimental data point corresponds to a separate experiment. A value of 4.6×10^{-4}

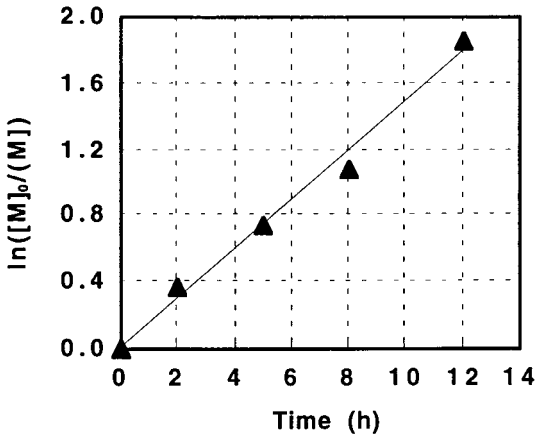

Figure 1. First-order kinetic plot of for the ring-opening polymerization of DiPC (% represents the polymer conversion; same experimental conditions as in Table 1).

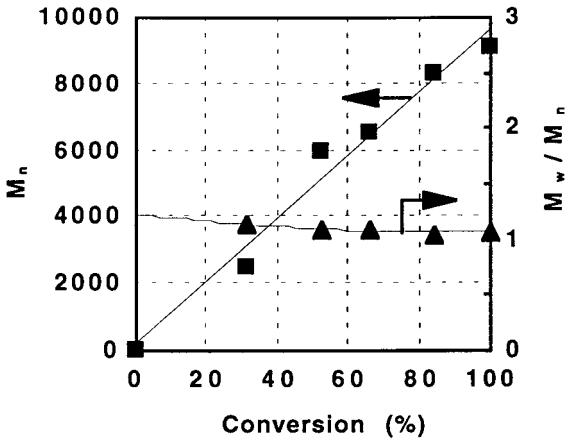

Figure 2. Dependence of the number-average molecular weight (squares) and polydispersity index (triangles) on monomer conversion for the polymerization of **1** at 140 °C (22.2 mmol of **1** in 1.6 mL of DMSO, 2.3 mol % **3a**).

Table 2. Influence of the Counterion on the Polymerization of 1[a]

initiator[b]	time (h)	conversion (%)	yield (%)
PhSNa	5	49	52
PhSK	5	86	83
PhSK + 18-crown-6	0.67	53	50
	1.33	73	70
PhSK + Kryptofix 222	0.67	100	96

[a] 140 °C, 22.2 mmol of **1** in 1.6 mL of DMSO. [b] 2.3 mol %.

L mol^{-1} s^{-1} for the rate constant of the propagation step k_p was calculated from the slope of the regression line ($[I]_0 = 0.081$ mol L^{-1}). Results on the influence of the counterion on the polymerization rate are summarized in Table 2. Propagation rate constants at various temperatures were calculated from conversion data using a first-order kinetic equation:

$$\ln\left(\frac{1}{1-([M]/[M]_0)}\right) = k_p[I]_0 t \qquad (1)$$

where $[M]_0$ and $[I]_0$ are the initial concentrations in monomer and initiator, and [M] is the monomer concentration at polymerization time t. Results are reported as an Arrhenius plot in Figure 3.

End Group Functionalization. In all previous experiments, propagating polymer chains were terminated by adding hydrochloric acid. This acid−base reaction introduces an hydrogen atom as an end group. Malonate carbanions are also known to react with alkylating agents such as *n*-alkyl, allyl, or benzyl iodides, bromides, or tosylates, offering the interesting prospect of end-capping the polymer with a large set of potential end groups.[20] To test this possibility, the following experiments were carried out. In the first experiment, monomer **1** was polymerized for 2 h at 140 °C (0.8 mL of DMSO, 22.2 mmol of **1**, 2.3 mol % **3a**) and terminated in the usual way, i.e., by adding hydrochloric acid. The conversion reached 31%, and the number-average molecular weight was 2.5×10^3, as measured by GPC-LS ($\bar{M}_w/\bar{M}_n = 1.17$). The same experiment was then repeated, except that exactly half an equivalent of 1,2-dibromoethane was added after 2 h, instead of the traditional hydrochloric acid. Once again, the conversion was 30%, but the number-average molecular weight was now 4.6×10^3, almost double that observed in the previous experiment. The distribution was monomodal and monodisperse ($\bar{M}_w/\bar{M}_n = 1.12$), and no peak at $\bar{M}_n = 2.5 \times 10^3$ was detectable on the GPC chromatogram.

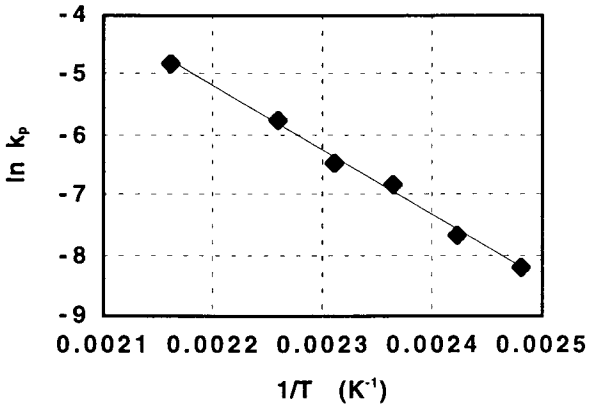

Figure 3. Arrhenius plot for the polymerization of **1** (experimental conditions: 22.2 mmol of **1** in 1.6 mL of DMSO, 0.052 mmol **3a**).

Polymer Characterization. Obtained polymers were characterized by ^{1}H and ^{13}C NMR and FT-IR. Spectra of polymers obtained below 190 °C are fully compatible with the expected structure. The general appearance is very simple due to the high symmetry of poly(**1**) and the absence of tacticity. Alongside the aromatic signal of the phenylthiyl end groups at 7.1−7.4 ppm whose intensity decreases with increasing molecular weights for the polymer, signals with the expected 2:4:12 ratio were observed around 4.2 (O−C*H*), 1.7 (main-chain CH_2), and 1.2 ppm (CH_3), respectively. The multiplicity for each signal is as expected: septuplet and doublet for the isopropyl side groups and a singlet for the four equivalent protons on the main chain. For low molecular weight samples, a small signal was observed at 2.4 ppm and assigned to the PhS−CH_2 protons, adjacent to the end group. The ^{13}C NMR spectrum consists of five peaks at 22.9, 29.2, 69.9, 57.9, and 171.6 ppm. These signals were assigned to the *C*H$_3$, *C*H$_2$, *C*(COOR)$_2$, *C*H, and *C*=O carbons, respectively.

A detailed analysis of the spectra revealed no indication of side reactions. Particular attention was paid to some possible side reactions that, due to precedent in the organic chemistry literature, appeared possible, especially at high temperarures. They include the Krapcho reaction (alkylation−decarboxylation of malonate esters by good nucleophiles),[21] the Dieckmann

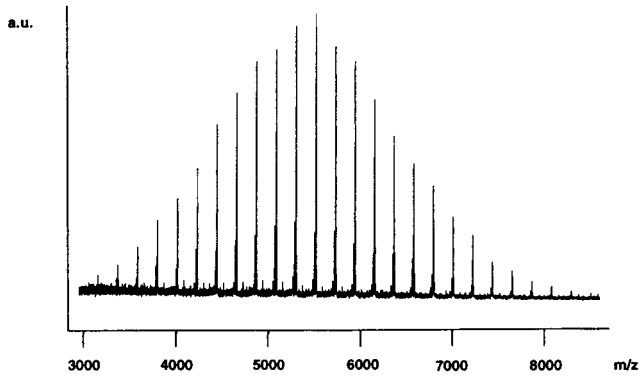

Figure 4. MALDI-ToF mass spectrum of a typical poly(**1**) sample terminated using hydrochloric acid.

condensation (backbiting of the malonate carbanion on the ester of the neighboring unit with the release of a alcoholate anion and formation of a cyclic ketoester),[22] and the formation of a thioester by direct nucleophilic substitution of an ester of the monomer or polymer by the thiophenolate initiator. This last reaction had been suggested by a referee of one of our recent papers on **2** polymerization, based on an analogy with biochemical reactions where intermediate formation of thioester as activated species is common. However, formation of a thioester from the direct attack of an organosulfur species on an ester requires normally more stringent conditions.[23,24] Also, as mentioned above, thiophenolate had been reported to quantitatively ring-open cyclopropane **2**,[17] but our reaction conditions are slightly different and the possible formation of a thioester could not be entirely ruled out only on the basis of that argument. At the end of our study, all spectroscopic techniques indicate that, if present, structures corresponding to the products of these side reactions are below the detection limit of our instruments. At temperatures higher than 190 °C, however, an additional singlet appears in the ^{1}H NMR spectra at 2.15 ppm.

Molecular weights were measured using four different techniques known to theoretically provide absolute molecular weights (quantitative ^{1}H NMR analysis of the PhS− end groups, VPO, GPC-LS, and MALDI-ToF). It was unclear whether GPC-LS would be really effective in the molecular weight range under consideration, despite the manufacturer's claims in that direction.[25] Experimental results are summarized in Table 1; very close results were obtained by all four techniques (Table 1). In all cases, polymers had a narrow molecular weight distribution (<1.13). A full account of the analytical procedure, detailing the experimental design and precautions taken to ensure a fair comparison between the four techniques, will be reported separately. It is worthwhile to mention at this point that results obtained so far support the manufacturer's claim that GPC-LS can be used as an absolute technique for the determination of molecular weights in the low molecular weight range (10^3−10^4). Accuracy is limited mainly by the broadness of the molecular weight distribution, low-polydispersity polymers providing the best results. MALDI-ToF analysis of the polymer is exceptionally easy in a dithranol matrix and provides excellent spectra. A typical example is shown in Figure 4. The major peak distribution corresponds to the expected polymer cationized by a potassium ion and end-terminated by a phenylthio group (M_r = 109) on one side and by a hydrogen on the other. This finding is consistent with both the initiation and termination mechanisms. (Anionic chain ends were killed by adding hydrochloric acid.) Other distributions of much lower intensities, corresponding to cationization by proton, lithium, or sodium ions, can also be observed on the spectrum. Here again, special precautions were taken to identify specific side reactions (see above), but none of these reactions nor any other side reactions could be identified on the spectrum.

Physical Properties. Poly(**1**) is a white solid soluble in benzene, chlorobenzene, toluene, THF, acetone, and chloroform. The polymer is also soluble in its own monomer but is insoluble in alkanes and methanol. Poly(**1**) is a semicystalline polymer with a melting point in the 170−174 °C range. A detailed experimental study on its crystalline structure is presently under way. Poly(**1**) exhibits a good thermal stability as measured by TGA, with no weight loss below 270 °C.

Discussion

Polymerization Mechanism. All data gathered during this study confirm the basic mechanism previously described for the polymerization of cyclopropane-1,1-dicarboxylates and summarized in Scheme 1. Spectroscopic evidence in particular supports very clean inititiation and propagation steps, with no evidence for the presence of side groups in the final polymer structure. This conclusion is reinforced by the kinetic analysis and molecular weight measurements for polymerizations carried out at 140 °C. Two conclusions can be drawn from the kinetic experiments summarized in Figures 1 and 2. First and foremost, the reaction is first-order with respect to the monomer over the entire conversion range (Figure 1). Second, the degree of polymerization increases linearly with conversion over the same conversion range and reaches the theoretical limit of 9400 at full conversion (Figure 2). The first set of results proves conclusively that the concentration of propagating species remains constant during the polymerization and that no termination takes place. The second set demonstrates that a chain-transfer reaction does not compete with the propagation step under the investigated experimental conditions. These kinetic results, coupled with the very narrow molecular weight distribution observed for the various polymers (Figure 2), fully support a living polymerization mechanism.

Polymerization conditions, temperature in particular, are far from being typical of experimental conditions typically used in living anionic polymerization, and it may even seem strange for a polymerization to be living at such a high temperature. It must be remembered, however, that the propagating species involved in the polymerization of **1** is a very stable malonate carbanion stabilized by two powerful electron-withdrawing groups. The pK_a of an alkylmalonate ester in DMSO is very low (18.0−18.5), closer to the acidity of an O−H group than a typical C−H.[26] From that perspective, cyclopropane-1,1-dicarboxylate monomers resemble an epoxide more than a classical cyclopropane. The extra stabilization of the malonate propagating carbanion, coupled with the known poor stabilization of an hydroxide anion in DMSO (pK_a = 32 for H_2O in DMSO),[27] may also explain why traces of water can be tolerated in the reaction mixture without losing the livingness. In all experiments, reactions were typically run without drying the glassware or the monomer.

The living nature of the malonate carbanion is further substantiated by the end-capping experiment with 1,2-

dibromoethane. A quantitative reaction with this bisalkylating agent was observed, while the monodispersity of the obtained polymer was maintained. This experiment suggests that a wide range of electrophilic reagents can potentially be used to place a variety of end groups on these polymers. It also indicates that, by reacting with polyalkylating agents, several architectures can be obtained by an "arm-first" approach, including star, branched, or comb copolymers. The reaction with 1,2-dibromoethane, as reported here, introduces an additional $-CH_2CH_2-$ segment in the middle of the chain. It allows to synthesize a polymer containing the exact same end groups on both ends of the chain. Placing functional groups compatible with the malonate carbanion on both the thiolate initiator and the end-capping reagent allows to obtain identical or completely different end groups at both ends.

Influence of Temperature. The value of 4.6×10^{-4} L mol^{-1} s^{-1} observed for the propagation rate constant at 140 °C places the ring-opening polymerization of **1** on the low side of the typical range of reactivity observed for ring-opening polymerizations, even at lower temperatures. As a practical consequence of this slow propagation, a relatively large amount of initiator must be used, limiting in practice the degree of polymerization, in this case to a value of 42−43 at full conversion. Increasing the temperature can be used to overcome this practical limitation and increase the reaction rate. In the temperature range from 130 to 190 °C, a linear Arrhenius behavior can be observed (Figure 3), with an activation energy of 21.3 kcal mol^{-1}. At higher temperatures, a progressive deviation from the linear Arrhenius relationship was found. This finding relates very well with the appearance of a new peak in the ^1H NMR spectra of polymers synthesized above 190 °C. It suggests that above this critical temperature a side reaction, whose nature has not yet been discovered, competes with the propagation reaction.

Influence of the Counterion. The counterion also plays an important role in the rate and selectivity of the polymerization as shown in Table 2. Substituting the sodium cation by a potassium almost doubles the reaction rate at 140 °C. Complexing the potassium ion, using a crown ether or a cryptand, makes the carbanion naked, further increasing the polymerization rate by approximately 1 order of magnitude. In this last case, the livingness of the polymerization is partly lost, as demonstrated by the appearance of two molecular weight distributions. These experiments suggest that, as is often the case in anionic polymerizations, several propagating species (free ion and ion pairs, possibly some aggregates) coexist in solution, the relative contribution of each being dependent on the nature of the counterion and physical conditions (solvent and temperature). The observed bimodal distributions imply that the rate of interconversion between these species is slow.

These results on the influence of the counterion correlate partly with Harrelson and Arnett's kinetic data on the alkylation of dimethyl ethylmalonate carbanion with methyl iodide in DMSO at 25 °C.[26,28,29] Their work demonstrated that the counterion (Li, Na, K) of the ethylmalonate carbanion has an influence on the second-order rate constant of about the same order of magnitude as in our polymerization. The authors unambiguously proved that, in the alkylation, the only reactive species is the free ion and that strong ion pairing by lithium and sodium cations transforms the active species into unreactive ones. A linear correlation was observed between ion-pair degrees of dissociation and rate constants, strongly supporting this hypothesis. By extrapolating to complete dissociation into free ions, it was possible to calculate the reactivity of the free carbanion. Here again, the increase in reaction rate was of about the same magnitude as in our experiments with the cryptand. An equilibrium between a reactive free carbanion and unreactive ion pairs cannot explain entirely our results, as shown by the bimodal distribution obtained when the counterion was complexed by a cryptand. It indicates however that several species are under equilibrium.

Conclusion

This study unambiguously proves for the first time that the ring-opening polymerization of a cyclopropane monomer can be made living when enough stabilization is provided to the carbon-centered propagating species. The detailed mechanistic study on the anionic polymerization of diisopropyl cyclopropane-1,1-dicarboxylate (**1**), as reported in this paper, demonstrates the livingness of the polymerization for that particular monomer. It also suggests that other activated cyclopropane-1,1-dicarboxylates can be polymerized livingly, provided the solubility of the highly symmetrical polymer is good enough or the concentration is low enough to avoid precipitation when some critical degree of polymerization is reached. Recent preliminary results on cyclopropanedicarboxylates bearing long *n*-alkyl chains support this view and will be reported separately. It is also supported by our recent study on the polymerization of diethyl cyclopropane-1,1-dicarboxylate (**2**), which showed some indication of livingness (linear increase of degree of polymerization with time, extremely low polydispersity) but precipitated at 70−80% conversion.

The substitution pattern provided by the polymerization of cyclopropane-1,1-dicarboxylates, i.e., two side substituents on every third atom of a carbon-chain backbone, allows bulky substituents to be introduced as ester groups. Higher degrees of polymerization than those reported in this study should be accessible by working at higher temperatures (but not higher than 190 °C) and finding the most appropriate counterion at the working temperature. The possibility of quantitatively end-capping the propagating polymer with alkylating agents has been demonstrated, opening the way to the synthesis of highly substituted polymers with well-controlled end groups. This last feature makes the design of various macromolecular architectures, including graft, star, cyclic, and comb copolymers, possible.

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