# Polyester from Dimethylketene and Acetaldehyde: Direct Copolymerization and $\beta$ -Lactone Ring-Opening Polymerization

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Received 27 May 2011; accepted 22 June 2011; published online 12 July 2011 DOI: 10.1002/pola.24854

**ABSTRACT:** Two ways to obtain aliphatic polyesters (PEs) from dimethylketene and acetaldehyde were investigated. On the one hand, a direct anionic copolymerization was carried out in toluene at -60 °C. The resulting polymer was mainly composed of PE units. On the other hand, a two-step process involving the synthesis of 3,3,4-trimethyl-2-oxetanone by [2+2] cycloaddition, followed by its ring-opening polymerization, with various initiators and solvents, led to the expected PE. Molecular weights up to 9000 g mol<sup>-1</sup> (measured by nuclear magnetic resonance (NMR)), with narrow polydispersity

around 1.2, were obtained. These polymers were found stable up to 274 °C under nitrogen and a broad and complex endothermic peak attributed to crystallinity was observed near 139 °C by differential scanning calorimetry (DSC). The crystallinity, measured by X-ray diffraction, was close to 0.45. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4129–4138, 2011

**KEYWORDS**: anionic polymerization; dimethylketene; polyesters; ring-opening polymerization; synthesis

**INTRODUCTION** Ketenes are derivatives of carboxylic acids which contain two consecutive double bonds (C=C=0). First isolated by Staudinger in 1905 with the synthesis of diphenylketene,<sup>1</sup> ketenes have been greatly studied and several reviews have been published.<sup>2-7</sup> These substances, containing two double bonds in adjacent position, show a particular high reactivity so that most of them are unstable products that cannot be isolated and must be handled very carefully. The chemistry of ketenes is dominated by addition reactions with nucleophiles, electrophiles, or reagents having labile hydrogen atoms,<sup>2,8-10</sup> and they characteristically undergo cycloaddition.<sup>11,12</sup> One of the most interesting properties of these compounds is their ability to be used as monomers. Indeed, in the absence of ketenophiles, simple ketenes undergo self-addition to lead to oligomers and polymers. For example, a polyester (PE) was obtained by polymerizing ethylketene,<sup>13</sup> and several studies on the polymerization of dimethylketene (DMK) showed that a selective reaction of the double bonds is possible with a suitable choice of both initiator and solvent to form three different polymer units: (1) acetal, (2) ketone, and (3) ester (Scheme 1).<sup>4,14-20</sup> With anionic initiators such as *n*-butyllithium (*n*-BuLi) or sodium methoxide, and depending on temperature and solvent, the PE structure can be obtained predominantly.<sup>21–25</sup>

DMK can also copolymerize with carbonyl compounds, namely ketones and aldehydes, such as acetone and deriva-

tives,<sup>26–29</sup> benzaldehyde and derivatives,<sup>30–32</sup> formaldehyde,<sup>33</sup> and furfural.<sup>34</sup> The preferred initiators are anionic ones, such as alkaline metals with aromatic organic compounds (sodium-naphtalene<sup>27,30,34</sup>), bases<sup>33,34</sup> (amines, tertiary phosphines, lithium alcoholates), and organometallic compounds<sup>26–32,34</sup> (*n*-BuLi, diethylzinc ZnEt<sub>2</sub>). The obtained polymer presents a strictly alternated structure between ketene and the carbonyl compound to form an ester unit depicted in Scheme 2. Among the researches undertaken during the 1960s, only brief analyses such as infrared spectroscopy, LiAlH<sub>4</sub> reduction, elementary analysis, and X-ray diffraction were presented.<sup>15,26–32,35</sup>

Another way to reach the same PE structure lies in the ringopening polymerization (ROP) of a  $\beta$ -lactone. In a first step, the latter can be synthesized by a [2+2] cycloaddition between DMK and a carbonyl compound, provided an appropriate catalyst is chosen (Scheme 3).<sup>36</sup> Thus, the use of metal halides such as AlCl<sub>3</sub>, HgCl<sub>2</sub>, FeCl<sub>3</sub>, and, especially, ZnCl<sub>2</sub> enabled the synthesis of a wide range of substituted propiolactone and butyrolactone.<sup>37–40</sup> Another useful catalyst is the boron trifluoride diethyl etherate (BF<sub>3</sub>-O(Et)<sub>2</sub>).<sup>41,42</sup> More complex catalysts, such as zinc, cobalt, and lead salts of difluorophosphoric acid were also efficient with other carbonyl compounds.<sup>43,44</sup>

The second step is the polymerization of the obtained  $\beta$ -lactone. Several publications dealt with the ROP of different  $\beta$ -

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**SCHEME 1** Dimethylketene polymer units main chain structures (1: PA, 2: PK, and 3: PE).

lactones such as  $\beta$ -propiolactone,<sup>45–55</sup>  $\beta$ -butyrolactone,<sup>51–63</sup> and  $\beta$ -pivalolactone,<sup>47,64,65</sup> as well as  $\beta$ -monosubstituted<sup>66–69</sup> and  $\alpha$ -disubstituted<sup>55,70–72</sup> ones, mainly with anionic initiators such as carboxylates and alcoholates, and occasionally with zwitterionic, cationic, or coordination-insertion initiation.<sup>73,74</sup> However, only few publications mentioned the polymerization of  $\alpha, \alpha', \beta$ -trisubstituted  $\beta$ -lactones initiated by tetraethylammonium benzoate (TEAB).<sup>75,76</sup>

In this article, we investigated two ways to obtain aliphatic PEs from DMK and acetaldehyde because (i) to our knowledge, the literature has never mentioned the direct copolymerization between DMK and acetaldehyde; (ii) only few studies mentioned the use of the DMK/acetaldehyde  $\beta$ -lactone (3,3,4-trimethyl-2-oxetanone),<sup>77-80</sup> and no literature was found about its synthesis by [2+2] cycloaddition; and also (iii) no literature concerning the ROP of 3,3,4-trimethyl-2-oxetanone could be encountered. Thus, a direct copolymerization initiated by *n*-BuLi in toluene at -60 °C was carried out on the one hand, and on the other hand, a two-step process involving the ROP, with various initiators and solvents, of the  $\beta$ -lactone previously synthesized by [2+2] cycloaddition between DMK and acetaldehyde was carried out. The structure, molecular weights, and thermal properties of these polymers were determined by Fourier transform infrared-attenuated total reflection spectroscopy (FTIR-ATR), <sup>1</sup>H and <sup>13</sup>C spectroscopies, steric exclusion chromatography, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction.

#### **EXPERIMENTAL**

#### **Materials**

Tetrahydrofuran (THF; Acros Organics; 99.5%) was dried over potassium hydroxide, distilled over sodium benzophenone, and packaged in sealed bottles on molecular sieves (4 Å) before use. *n*-Decane (Acros Organics; 99+%) was distilled over sodium under reduced pressure and packaged in sealed bottles on molecular sieves (4 Å) before use. Toluene (Acros Organics; 98%) and diethyl ether (VWR; 99%) were distilled over sodium and packaged in sealed bottles on molecular sieves (4 Å) before use. Absolute ethanol (99.8%),



**SCHEME 2** Polyester obtained by direct copolymerization between dimethylketene and a carbonyl compound.



**SCHEME 3** Polyester obtained by ring opening polymerization of a  $\beta$ -lactone, previously synthesized by a [2+2] cycloaddition between dimethylketene and a carbonyl compound.

dimethylsulfoxide (DMSO; 99.7+% extra dry), isobutyric anhydride (IBAN) (97%), *n*-butyllithium 1.6 M in hexanes solution (diluted when needed), zinc chloride 1.0 M in diethyl ether, sodium acetate (99+% anhydrous), potassium acetate (99+% anhydrous), and 18-crown-6 (99%) were purchased from Acros Organics and used as received. Acetaldehyde (Acros Organics; 99.5%) was dried then distilled over calcium sulfate, and packaged in sealed bottles before use. Boron trifluoride diethyl etherate, sodium formate (>99%), potassium formate (>99%), potassium benzoate (KB; >99%), and TEAB (>99%) were purchased from Sigma-Aldrich and used as received. Aluminum bromide (Acros Organics; 98+%) was purified by distillation under reduced pressure. Aluminum chloride (Acros Organics; 98.5%) was purified by sublimation under reduced pressure.

Every solution made from the aforementioned initiators was realized under very low impurity level nitrogen atmosphere (Alphagaz<sup>TM</sup> 2 from Air Liquide) in a glove box and then stored in sealed bottles. All the following steps were also carried out under Alphagaz<sup>TM</sup> 2 nitrogen atmosphere, to prevent the reaction of DMK with water and the formation of highly explosive peroxides in the presence of oxygen.

#### **Dimethylketene Synthesis**

DMK was synthesized by pyrolysis of IBAN according to Scheme 4. The apparatus (Scheme 5), inspired by those described in the literature,<sup>24,81–83</sup> was optimized and can be decomposed into three different parts corresponding to the three steps: DMK synthesis by IBAN pyrolysis, DMK purification, and DMK reaction.

IBAN (600 g, 3.793 mol) was introduced, with a flow rate around 240 g h<sup>-1</sup> using a dosing pump and under nitrogen atmosphere, into the pyrolysis oven A brought to 625 °C under a reduced pressure of 40 mbar. In parallel, the resulting gaseous mixture was purified by passing through condensers B, C, and D, respectively at 60, -24, and -30 °C: unreacted IBAN, isobutyric acid, and other by-products were mainly condensed. Most of DMK, still gaseous at this stage,



**SCHEME 4** Synthesis of dimethylketene by pyrolysis of isobutyric anhydride.



SCHEME 5 Dimethylketene synthesis, purification, and reaction apparatus.

then bubbled through *n*-decane (200 g) at -15 °C in flask E and get caught by liquid nitrogen in flask F. To achieve its purification, DMK was distilled from F to the reaction reactor G, where it was trapped by liquid nitrogen. Once the synthesis and purification steps were over, DMK was gently warmed up to the desired temperature and brought to atmospheric pressure, giving a yellow solution (58.41 g, 834 mmol). The overall synthesis yield, determined by mass balance, was 22%.

## Anionic Copolymerization Between Dimethylketene and Acetaldehyde

First of all, the authors highlight the danger of this direct polymerization which turned out to be very exothermic and unpredictable. Freshly distilled DMK collected in reactor G (58.41 g, 834 mmol) was brought to the desired reaction temperature using an acetone/carbon dioxide ice bath at -60 °C. Then toluene (298 mL) and acetaldehyde (45.90 g, 1042 mmol) were added slowly so that [DMK] = 2.8 mol  $L^{-1}$  and [DMK]/[acetaldehyde] = 0.8. When the temperature was stabilized, 16.7 mL of a solution of n-BuLi in hexanes  $(0.5 \text{ mol } \text{L}^{-1})$  were added dropwise very carefully, to obtain [DMK]/[n-BuLi] = 100. The reaction was so exothermic that the temperature increased from -60 to 0 °C in only few seconds. The reactive medium was kept during 12 h at -60 °C and then, allowed to reach room temperature. Absolute ethanol was poured into the reactor to react with and neutralize residual DMK and initiator. Then the mixture was precipitated in large amounts of absolute ethanol. The obtained polymer was filtered, washed several times with ethanol, dried under vacuum at room temperature, and retrieved (8.6 g, yield 9%).

#### 3,3,4-Trimethyl-2-oxetanone Synthesis

Freshly distilled DMK collected in reactor G (58.41 g, 834 mmol) was brought to the desired reaction temperature using an acetone/carbon dioxide ice bath at -15 °C. Then diethyl ether (253 mL) and acetaldehyde (36.74 g,

834 mmol) were added slowly so that  $[DMK] = 3.3 \text{ mol } \text{L}^{-1}$ and [DMK]/[acetaldehyde] = 1. When the temperature was stabilized, 3.0 mL of a solution of  $\text{ZnCl}_2$  in diethyl ether  $(1.0 \text{ mol } \text{L}^{-1})$  were added, to obtain  $[DMK]/[ZnCl_2] = 275$ . The reaction was exothermic; the temperature increased from -15 to 10 °C in only few seconds. The reactive medium was kept during 12 h at -15 °C and then allowed to reach room temperature. Absolute ethanol was poured into the reactor to react with and neutralize residual DMK and catalyst. The obtained product was retrieved by evaporating the mixture: 92.30 g of crude liquid product were obtained (yield 97%).

#### 3,3,4-Trimethyl-2-oxetanone Polymerization in Bulk

In a 10-mL round-bottomed flask previously dried in an oven, 3,3,4-trimethyl-2-oxetanone (5.02 g, 44 mmol) and TEAB (40.2 mg, 0.44 mmol) were introduced under nitrogen atmosphere, to obtain [ $\beta$ -lactone]/[TEAB] = 100. The mixture was brought, under stirring, at 37 °C during 15 days. Absolute ethanol was poured into the reactor to neutralize reactive species. Then the mixture was precipitated in large amounts of absolute ethanol. The obtained polymer was filtered, washed several times with ethanol, dried under vacuum at room temperature, and retrieved (3.26 g, yield 65%).

#### Measurements

Fourier Transform Infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum 2000 FTIR, equipped with a diamond ATR (Attenuated Total Reflection) device. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC-P 300 MHz apparatus. Chemical shifts are expressed in ppm relative to CDCl<sub>3</sub> which was used as internal reference and solvent. Gas chromatography was carried out on a PerkinElmer 1020 GC Plus.  $\overline{M}_n$  and  $\overline{M}_w/\overline{M}_n$  ratios were determined by size exclusion chromatography (SEC). Samples were solubilized in CH<sub>2</sub>Cl<sub>2</sub>, filtered (0.45  $\mu$ m) and analyzed at room temperature using a Varian PL-GPC50 device equipped with two mixed packed columns (PL gel mixed type C). The mobile phase





FIGURE 1 Dimethylketene/acetaldehyde copolymer FTIR spectrum.

was CH<sub>2</sub>Cl<sub>2</sub>, and polystyrene standards were used for calibration. Thermogravimetric analysis (TGA) measurements were performed on a TGA Q500 system (TA Instruments) under nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Starting degradation temperatures were determined at 1% weight loss. Differential scanning calorimetry (DSC) was performed on a DSC Q2000 apparatus (TA Instruments), under nitrogen with a heating rate of 10 °C min<sup>-1</sup> and a cooling rate of 5 °C min<sup>-1</sup>.  $T_g$  were measured at the midpoint, and  $T_f$  at the maximum of the fusion peak. X-ray diffractograms were performed on a Siemens D5000 diffractometer ( $\lambda_{Co} = 1.78897$  Å) by using Diffract AT Software.

#### **RESULTS AND DISCUSSION**

### Direct Copolymerization Between Dimethylketene and Acetaldehyde

DMK was prepared as described in the Experimental section. As there is no information in the literature for the copolymerization between DMK and acetaldehyde, the initiator, solvent, and concentrations used for the copolymerization between DMK and acetone described by Natta were tried.<sup>26</sup> This reaction turned out to be very exothermic and so unpredictable and dangerous that we made, for safety reasons, only one attempt. Nevertheless, full characterization of this unique polymer was carried out.

The obtained polymer was found soluble in most organic solvents and insoluble in alcohol and water. Its FTIR-ATR spectrum (Fig. 1) showed strong absorption bands at 1725, 1265, 1098, and 1049 cm<sup>-1</sup>, which indicated a PE structure even if these bands were slightly shifted compared with the DMK/acetone copolymer.<sup>18,26</sup>

However, as demonstrated by Bunel et al.,<sup>19</sup> it is hazardous to attest the structure of a polyketene only based on its FTIR analysis; thus, NMR was used to confirm the PE structure. In the <sup>1</sup>H NMR spectrum, the signals at ( $\delta$  = 5.1 ppm, m), ( $\delta$  =

1.1 ppm, d), and ( $\delta = 1.2$  ppm, d) were attributed, respectively, to protons H<sub>3</sub>, H<sub>4</sub>, and H<sub>5</sub>, which corroborated the copolyester structure (Fig. 2). Other nonattributed signals were also observed around 1.3, 3.8, 3.9, and 5.9 ppm, which were not consistent with the homopolymers of DMK<sup>19</sup> and were linked to the very exothermic and uncontrolled polymerization that could lead to undesired defects in a general PE structure.

However, it was demonstrated for polydimethylketene homopolymers that even if their <sup>1</sup>H NMR spectra are quite similar, polyketone (PK), PE, and polyacetal (PA) structures give distinct chemical shifts by <sup>13</sup>C NMR.<sup>19</sup> In particular, the PK structure exhibited a peak at 214 ppm, and the PE structure exhibited a peak at 177 ppm for their carbonyl, whereas the PA structure exhibited a peak at 99 ppm attributed to the ethylenic carbon of the main chain. According to the <sup>13</sup>C NMR spectrum of DMK/acetaldehyde copolyester, the peaks at  $\delta = 174$ , 74, 46, 21, and 15 ppm were attributed to a PE structure with a strict alternation of DMK and acetaldehyde to form ester units (Fig. 3). Moreover, the absence of signal  $\sim$ 214 ppm attested that no PK units were present in the polymer. However, as already mentioned in the <sup>1</sup>H NMR spectrum, several unidentified low-amplitude signals were also observed in particular at 99 ppm, which could be attributed to polydimethylketene acetal units.

This polymer exhibited a molecular weight  $\overline{M_n^{\text{SEC}}} = 2000 \text{ g} \text{mol}^{-1}$ , with a polydispersity of 2.0, which corresponds to  $\overline{M_n^{\text{NMR}}} = 7400 \text{ g} \text{mol}^{-1}$  by using the relationship  $\overline{M_n^{\text{NMR}}} = 3.7 \overline{M_n^{\text{SEC}}}$  to be established further. This molecular weight is quite good when compared with the theoretical value of 11,400 g mol<sup>-1</sup>, considering the ratio [DMK]/[BuLi] = 100.

The thermal properties of the obtained copolyester were investigated by TGA and DSC in nitrogen atmosphere. This



FIGURE 2 Dimethylketene/acetaldehyde copolymer <sup>1</sup>H NMR spectrum.





FIGURE 3 Dimethylketene/acetaldehyde copolymer <sup>13</sup>C NMR spectrum.

polymer was found stable until 200  $^{\circ}$ C, before a quick and complete degradation. Its thermal stability is, therefore, limited, which is probably due to the presence of impurities such as acetal units and a low molecular weight.

The DSC thermogram did not permit to determine  $T_{\rm g}$  but showed a broad and complex endothermic peak attributed to fusion at 143 °C, with  $\Delta H_{\rm f_1} = 40.2$  J g<sup>-1</sup>: the obtained polymer is, therefore, semicrystalline. The cooling of this polymer revealed a crystallization at 93 °C, with  $\Delta H_{\rm c} =$ -30.9 J g<sup>-1</sup>, and subsequent heating showed a still broad and complex fusion peak at 139 °C with  $\Delta H_{\rm f_2} = 31.8$  J g<sup>-1</sup>, in agreement with  $\Delta H_{\rm c}$ . This complex thermogram is probably due to a polymorphism within the polymer, already observed with DMK homopolymers.<sup>18,20</sup>

#### 3,3,4-Trimethyl-2-oxetanone Synthesis

The DMK/acetaldehyde  $\beta$ -lactone was prepared as described in the Experimental section. No information could be found in the literature concerning its synthesis, so different catalysts, previously encountered in the literature for the synthesis of other ketene-based  $\beta$ -lactones, were tested in diethyl ether to obtain the best yield and purity. All the parameters for these syntheses are gathered in Table 1.

FIGURE 4 3,3,4-Trimethyl-2-oxetanone FTIR spectrum.

Thus, BF<sub>3</sub> etherate, used for the [2+2] cycloaddition between ketene and acetaldehyde by Küng<sup>41</sup> (Table 1, Run 1), ZnCl<sub>2</sub>, previously used by McConnell et al.<sup>84</sup> with DMK and butyraldehyde (Table 1, Run 2), and other Lewis acid catalysts AlBr<sub>3</sub> and AlCl<sub>3</sub> (Table 1, Runs 3–4) were tried with diethyl ether as solvent. For safety reasons, because of the incontrollable exothermy observed during the copolymerization, the temperature advocated by Küng and McConnell, ranging, respectively, between 10–15 and 20–28 °C, was decreased to -15 °C. Each reaction was exothermic but could be controlled, and the maximal temperature reached by the medium was limited to 10 °C.

All catalysts gave satisfactory results in terms of reaction yield, ranging from 69 to 97%. The best yield was obtained with ZnCl<sub>2</sub> catalyst (97%). Hence, the following spectra correspond to Run 2. Whatever the catalyst used, FTIR-ATR showed a major absorption band at 1815 cm<sup>-1</sup>, characteristic of the  $\beta$ -lactone cyclic ester<sup>36</sup> (Fig. 4). However, another band located at 1740 cm<sup>-1</sup>, more or less intense depending on the catalyst, was also observed. To confirm the synthesis of the  $\beta$ -lactone and to identify and quantify this by-product, NMR spectroscopy was used.

In the <sup>13</sup>C NMR spectrum (Fig. 5), the peaks observed at  $\delta$  = 176, 80, 53, 22, and 16 ppm were all attributed to the  $\beta$ -

**TABLE 1** 3,3,4-Trimethyl-2-oxetanone Syntheses by [2+2] Cycloaddition BetweenDimethylketene and Acetaldehyde, in Diethyl Ether at -15 °C

Run	Catalyst	[DMK]/ [acetaldehyde]	[DMK] (mol L <sup>-1</sup> )	[DMK]/ [catalyst]	Maximum Temperature Reached (°C)	Yield (%)
1	$BF_3-O(Et)_2$	0.9	3.9	30	-4	69
2	ZnCl <sub>2</sub>	1	3.3	275	10	97
3	AICI <sub>3</sub>	1	3.3	275	2	77
4	$AIBr_3$	1	3.3	275	-7	81



FIGURE 5 3,3,4-Trimethyl-2-oxetanone <sup>13</sup>C NMR spectrum.

lactone structure, especially the characteristic  $C_3$  at 80 ppm and  $C_2$  at 53 ppm instead of 74 and 46 ppm in the PE.

Moreover, the  $\beta$ -lactone structure was fully verified by <sup>1</sup>H NMR (Fig. 6). Indeed, this spectrum was found very different from the PE one, and the signals at ( $\delta = 1.2$  ppm, s), ( $\delta = 1.4$  ppm, s), ( $\delta = 1.4$  ppm, d), and ( $\delta = 4.4$  ppm, q) were all attributed to the  $\beta$ -lactone structure 3,3,4-trimethyl-2-oxetanone, respectively to protons H<sub>5</sub>, H<sub>4</sub>, H<sub>6</sub>, and H<sub>3</sub>. Nevertheless, this spectrum showed an additional peak at ( $\delta = 1.3$  ppm, s), in accordance with the more or less intense by-product signal observed by FTIR in Figure 4. Actually, this signal complied with the presence of the DMK symmetric dimer, namely 2,2,4,4-tetramethyl-1,3-cyclobutanedione. Indeed, the temperature increased to 10 °C during the reaction, and ketenes are known to be unstable products that can dimerize all the more that the temperature increases.<sup>2</sup>



FIGURE 6 3,3,4-Trimethyl-2-oxetanone <sup>1</sup>H NMR spectrum.

TABLE 2 3,3,4-Trimethyl-2-Oxetanone Purity

Run	Catalyst	$\beta$ -Lactone Purity (%)
1	BF <sub>3</sub> O(Et) <sub>2</sub>	85.1
2	ZnCl <sub>2</sub>	98.4
3	AICI <sub>3</sub>	93.1
4	AlBr <sub>3</sub>	88.8

Taking into account the integrations of the different <sup>1</sup>H NMR signals corresponding to 3,3,4-trimethyl-2-oxetanone, on the one hand, and 2,2,4,4-tetramethyl-1,3-cyclobutanedione, on the other hand, the molar proportion of dimer and consequently the purity of the  $\beta$ -lactone were calculated. The results were summarized in Table 2. It appeared that the best purity was obtained with ZnCl<sub>2</sub> catalyst, with a very low proportion of 2,2,4,4-tetramethyl-1,3-cyclobutanedione. As this catalyst already afforded the best yield, the improved conditions for the  $\beta$ -lactone synthesis were those retained for Run 2.

Numerous tests were carried out to purify crude 3,3,4-trimethyl-2-oxetanone, but unfortunately, neither distillation nor chromatography was able to separate efficiently these two products, which have very similar chemical structure and hence high affinity. Therefore, for the ROP, the crude 3,3,4-trimethyl-2-oxetanone synthesized according to Run 2 was used without further purification, because 2,2,4,4-tetramethyl-1,3-cyclobutanedione was expected to be inert.

### 3,3,4-Trimethyl-2-oxetanone Ring-Opening Polymerization

Various tests of ROP were conducted to determine the best conditions (initiator, solvent) in terms of yield and molecular weights. A first series (Table 3, Runs 5-12) corresponded to the conditions already widely used with success in literature for less substituted  $\beta$ -lactones, namely in THF ( $\varepsilon = 7.6$ F m<sup>-1</sup>) and DMSO ( $\varepsilon = 46.7$  F m<sup>-1</sup>) as solvents, with a feed ratio [ $\beta$ -lactone]/[initiator] = 100 and [ $\beta$ -lactone] = 1.5 mol  $L^{-1}$ , in the presence of a crown ether ([initiator]/[18-crown-6] = 1), at 30 °C.<sup>52,53,55,65</sup> A second series corresponded to some initiators mentioned in the polymerization of more substituted  $\beta$ -lactones, namely KB and TEAB in THF and DMSO ([eta-lactone] = 1.5 mol L $^{-1}$ ), and in bulk, at 37  $^\circ$ C (Table 3, Runs 13-20).<sup>69,72,75,76</sup> As mentioned in the literature, the polymerizations were carried out with reaction times up to 30 days. Nevertheless, in DMSO, the reaction time was shortened to 10 days to avoid gelation in the reactor. In addition, some tests were stopped earlier when an important increase of the viscosity was noticed (Table 3, Runs 15, 16, 18-20). In all cases, the reaction was terminated by adding ethanol.

The obtained polymers were analyzed as previously described. Their FTIR-ATR spectra were strictly the same as for the direct copolymerization (Fig. 1). By  $^{1}$ H and  $^{13}$ C NMR, only the peaks observed and attributed to the PE structure in the direct copolymerization were obtained (e.g., Figs. 7 and 8, Run 16). Thus, the ROP afforded the expected PE.

	TABLE 3	3,3,4-Trimeth	vl-2-Oxetanone	<b>Ring-Opening</b>	Polymerization
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Run	Initiator	<i>T</i> (°C)	Solvent	M/I <sup>a</sup>	Reaction Time (days)	Yield (%)	$\overline{M_{n}^{SEC}}$ (g mol <sup>-1</sup> )	$\overline{\textit{M}_w}/\overline{\textit{M}_n}$	$\overline{M_{\rm n}^{\rm NMR}}$ (g mol <sup>-1</sup> )
5	HCO₂Na	30	THF	100	30	35	1,700	1.3	6,300 <sup>b</sup>
6	HCO <sub>2</sub> Na	30	DMSO	100	10	10	500	1.3	7,000 <sup>b</sup>
7	HCO <sub>2</sub> K	30	THF	100	30	25	2,500	1.4	9,300 <sup>b</sup>
8	HCO <sub>2</sub> K	30	DMSO	100	10	35	2,900	1.5	10,700 <sup>b</sup>
9	CH₃CO₂Na	30	THF	100	30	52	700	1.2	2,600 <sup>b</sup>
10	CH <sub>3</sub> CO <sub>2</sub> Na	30	DMSO	100	10	52	1,100	1.2	4,100 <sup>b</sup>
11	CH <sub>3</sub> CO <sub>2</sub> K	30	THF	100	30	60	2,400	1.2	8,900 <sup>b</sup>
12	CH <sub>3</sub> CO <sub>2</sub> K	30	DMSO	100	10	30	1,700	1.3	6,300 <sup>b</sup>
13	KB	37	Bulk	100	30	-	-	-	-
14	KB	37	THF	100	30	-	-	-	-
15	KB	37	DMSO	100	3	50	1,300	1.1	4,800
16	TEAB	37	Bulk	100	15	65	2,500	1.2	9,000
17	TEAB	37	THF	100	30	27	1,400	1.3	5,300
18	TEAB	37	THF	50	20	30	1,000	1.3	4,100
19	TEAB	37	DMSO	100	3	55	1,800	1.2	6,600
20	TEAB	37	DMSO	50	1	60	1,500	1.1	5,500

<sup>a</sup>  $M/I = [\beta$ -lactone]/[initiator].

<sup>b</sup>  $\overline{M_n^{\text{NMR}}}$  calculated from  $\overline{M_n^{\text{NMR}}} = 3.7 \overline{M_n^{\text{SEC}}}$ .

Additional information on molecular weights was given by the <sup>1</sup>H NMR spectra of the polymers initiated by benzoates (e.g., Fig. 9, Run 16). Indeed, taking into account the integrations of the different signals corresponding on the one hand to the benzoate aromatic ring ( $\delta = 7.4$ , 7.5, and 7.9 ppm, respectively for *m*-, *p*-, and *o*-H) and on the other hand to the polymer-repeating units and assuming only one benzoate in each polymer chain, the molecular weights of Runs 16–20 (Table 3) were computed. These latter results showed higher molecular weights than those measured by SEC, indicating that dichloromethane was a worse solvent for these polymers than for polystyrene. The relation between these two molecular weights was linear, with  $\overline{M}_n^{\rm NMR} = 3.7 \, \overline{M}_n^{\rm SEC}$  (mean value obtained by linear regression). The yield was always calculated on the amount of precipitated polymer. Thus, this yield cannot be linked to the monomer conversion as it does not include oligomers.

These experiments showed that the ROP was faster in DMSO whatever the initiator. This could be attributed to a better ability to dissociate ion pairs due to its higher polarity ( $\varepsilon_{\text{DMSO}} >> \varepsilon_{\text{THF}}$ ). In addition, for equivalent yields (Runs 17–18 and 19–20), increasing the initiator concentration led, as expected, to an increase in the kinetics and, to a lower extent, to a decrease in molecular weight. Finally, the system



**FIGURE 7** <sup>13</sup>C NMR spectrum of 3,3,4-trimethyl-2-oxetanone ring-opening polymerization product.





FIGURE 8 <sup>1</sup>H NMR spectrum of 3,3,4-trimethyl-2-oxetanone ROP product.



**FIGURE 9** <sup>1</sup>H NMR spectrum of 3,3,4-trimethyl-2-oxetanone ROP product (Table 3, Run 16).

that offered the best compromise in terms of kinetics, molecular weights, and yield was TEAB in DMSO or in bulk.

#### **Polymer Properties**

The thermal stability of the obtained PEs was investigated by TGA in nitrogen atmosphere. All these polymers were found stable until temperatures ranging from 268 to 274 °C, before they degraded rapidly and totally. Their thermal stability is therefore better than the PE obtained by direct polymerization, surely because these polymers, synthesized by ROP, cannot contain thermally unstable defects like acetal units observed in the copolymer.



**FIGURE 10** DSC thermogram of 3,3,4-trimethyl-2-oxetanone ROP product (Table 3, Run 19) (— first heating, - - - cooling, and .... second heating)

**TABLE 4** DSC Analysis of Polymers Obtained by 3,3,4 

 Trimethyl-2-oxetanone ROP

	Peak Temperature (°C)	Standard Deviation	$\Delta H$ (J g <sup>-1</sup> )	Standard Deviation
First heating	139	11	40.1	8.4
Cooling	107	10	-36.6	4.4
Second heating	138	11	37.9	4.3

Among all the DSC thermograms, either no  $T_{\rm g}$  could be determined, or only a weak  $T_{\rm g}$  around 54 °C (stdev = 6 °C), could hardly be measured. A broad and complex endothermic signal was attributed to fusion (e.g., Fig. 10, Run 19). These data were collected in Table 4.

All these results were very close to the values obtained with the direct copolymerization, and their complexity still reveals a polymorphism. Generally speaking, fusion enthalpies, and, hence, crystallinity, were higher for the PEs with greater molecular weights. For example, X-ray diffraction concerning Run 18 revealed a main peak at 15.5 ° and smaller peaks at 12.7, 14.7 and 17.7°, giving a crystallinity of 0.45 (Fig. 11).

#### CONCLUSIONS

For the first time, a new DMK-acetaldehyde-based PE was synthesized, using two different synthetic routes. DMK, synthesized by IBAN pyrolysis, was on the one hand copolymerized with acetaldehyde in toluene at -60 °C, with *n*-BuLi initiator. On the other hand, DMK was reacted with acetaldehyde in diethyl ether, with Lewis acid catalysts such as ZnCl<sub>2</sub>, to afford 3,3,4-trimethyl-2-oxetanone in a [2+2] cycloaddition mechanism. This  $\beta$ -lactone was subsequently subjected to ROP initiated by various species in THF, DMSO, or



**FIGURE 11** X-ray diffractogram of 3,3,4-trimethyl-2-oxetanone ROP product (Table 3, Run 18).

in bulk. In both cases, the obtained polymer presented a strict alternation between DMK and acetaldehyde to form ester repeating units even if the direct copolymerization afforded an uncontrollable and dangerous polymerization, leading to defects in a globally copolyester scheme. For safety reasons, the ROP should therefore be preferred to obtain such a PE structure involving a ketene and an aldehyde. This second path gave molecular weights up to 9000 g mol<sup>-1</sup>, with narrow polydispersity around 1.2. These polymers were found stable up to 274 °C under nitrogen, and exhibited a  $T_{\rm g}$  near 54 °C and a broad and complex endothermic peak around 139 °C, suggesting a complex polymorphism. The crystallinity, measured by X-ray diffraction, was close to 0.45.

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