## Copolymerization of propylene oxide with carbon dioxide catalyzed by zinc adipate

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Copolymerization of carbon dioxide with propylene oxide in the presence of zinc adipate was studied. The effects of the temperature, nature of the solvent, and catalyst concentration on the molecular weight, molecular-weight distribution, and yields of the copolymer and propylene carbonate were examined. The structure of the polymer obtained was studied by <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy.

**Key words:** propylene oxide, carbon dioxide, zinc adipate, copolymerization, poly(propylene carbonate), propylene carbonate.

One of the promising areas of carbon dioxide utilization is its use as a reactant for the preparation of poly(alkylene carbonates), which are ecologically safe and biodegradable thermal plastics of the new generation.

Combustion of poly(alkylene carbonates) in air or an oxygen atmosphere produces  $CO_2$  and water as the only products. They are promising for the solution of technological, medical, and ecological problems due to a complex of valuable properties, such as a high adhesion to cellulose substrates in combination with a low oxygen permeability, oil resistance, easiness of processing, good compatibility with other polymers to form stable mixtures, and others.

Poly(alkylene carbonates) are prepared by the copolymerization of CO<sub>2</sub> with oxiranes in the presence of metal complex catalysts. The copolymer has an alternating structure of the polymeric chain with a minor content of ether fragments ( $\leq 10 \text{ mol.}\%$ ) randomly incorporated into the chain. A by-product, *viz.*, alkylene carbonate, is formed along with the copolymer.<sup>1</sup>

The most part of studies in this area are devoted to a search for catalytic systems involving no undesirable side processes and increasing the yield and molecular weight of the copolymer.<sup>2–7</sup>

Carbon dioxide is a stable compound, and its copolymerization with olefin oxides needs a highly active catalyst. A study of more than a hundred of catalytic systems based on metal (Zn, Co, Cr, Mg, Ca, Al, Y) complexes<sup>8</sup> showed that zinc coordination compounds exhibit the highest activity, and  $Zn_3[Fe(CN)_6]_2$  is the most active among them. However, poly(propylene carbonate) (PPC) obtained with this catalyst contains a noticeable number of ether units.

This disadvantage is much less pronounced for zinc carboxylates (next in the series of activity), which are prepared from ZnO and glutaric or adipic acids and allow synthesis of PPC with a fairly high molecular weight (>260000).

The catalysts of this type are characterized by such advantages as simplicity of synthesis and safety in use. The preparation of poly(alkylene carbonates) in the presence of zinc carboxylates is presently the single economically and technologically feasible industrial process.

The properties and composition of the polymer are substantially affected by copolymerization conditions, namely, temperature, pressure, solvent, and initial concentration of reactants. However, only few publications are devoted to this problem,  $^{9-12}$  and they contain only scanty information for different catalysts.

In this work we studied the effects of the temperature of the process, catalyst concentration, and nature of the solvent during propylene oxide (1) copolymerization with  $CO_2$  in the presence of zinc adipate on the molecular weight, molecular-weight distribution, and yields of copolymer 2 and by-product 3 (Scheme 1).

The structure of zinc adipate is likely similar to that of zinc glutarate studied elsewhere.<sup>1</sup>



The influence of the CO<sub>2</sub> pressure ( $p_{CO2}$ ) on copolymerization has earlier been described.<sup>10,12</sup> However, data

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Cat is zinc adipate

on the molar ratios of  $CO_2$  and propylene oxide are lacking, and it seems impossible to conclude about the influence of the pressure on the yield and molecular weight of the copolymer.

Our experiments were carried out at  $p_{CO_2} = 25-27$  atm, which ensured approximately twofold  $CO_2$  molar excess over oxide 1.

The yields of PPC 2 and propylene carbonate 3, number-average  $(M_n)$  and weight-average  $(M_w)$  molecular weights, and molecular-weight distribution  $(M_w/M_n)$  at different temperatures of the process (T) are presented in Table 1. The yield of PPC 2 increases, its molecular weight decreases, and the yield of by-product 3 increases with the temperature T (see Table 1).

The found increase in the yield of PPC 2 with T contradicts earlier theoretical calculations.<sup>13</sup> In the authors' opinion, the copolymerization of oxide 1 with CO<sub>2</sub> is accompanied by a decrease in the entropy and enthalpy, due to which this process should have the upper limiting temperature. It is known that for such transformations the equilibrium is shifted toward a decrease in the yield of the reaction products with T.

The increase in the yield of propylene carbonate 3 with T cannot be explained in terms of concepts that the

 Table 1. Yield of PPC 2 and its properties as functions of the reaction temperature

<i>T</i> /°C	Yield (%)		$M_{ m w} \cdot 10^{-3}$	$M_{\rm n} \cdot 10^{-3}$	$M_{\rm w}/M_{\rm n}$
	2	3			
65	23.0	5.5	300.1	34.3	8.73
75	28.8	8.5	268.1	31.6	8.48
85 90	64.7 46.0	10.0 16.0	218.5 122.2	28.7 37.5	7.61 3.26

*Note.* Catalyst is zinc adipate (0.308 mol L<sup>-1</sup>), reaction time is 10 h, solvent is  $CH_2Cl_2$ ,  $p_{CO_2} = 25-27$  atm.

**Table 2.** Effect of the catalyst concentration ( $C_{Cat}$ ) on the yield and properties of PPC **2** 

$C_{\text{Cat}}$ /mol L <sup>-1</sup>	Yield of <b>2</b> (%)	$M_{\rm w} \cdot 10^{-3}$	$M_{\rm n} \cdot 10^{-3}$	$M_{\rm w}/M_{\rm n}$
0.077	23.0	250.0	45.0	5.55
0.154	25.0	335.0	42.0	7.98
0.191	29.0	326.0	64.0	5.09
0.203	38.0	221.0	55.0	4.02
0.303	63.5	207.0	40.0	5.17
0.400	61.0	171.0	41.0	4.17

*Note.* Catalyst is zinc adipate, reaction time is 10 h, T = 81-83 °C, solvent is CH<sub>2</sub>Cl<sub>2</sub>,  $p_{CO_2} = 25-27$  atm.

only source of its formation is the polymeric chain, whose decomposition decreases the molecular weight<sup>14</sup> (degradation, depolymerization). It seems more probable that compound **3** is additionally formed<sup>15</sup> due to the direct interaction of the comonomers on the catalyst active sites, which differ from the active site of polymerization.

The data in Table 2 reflect the effect of the catalyst concentration on the yield and molecular-weight characteristics of PPC **2** and show that the maximum molecular weight of the polymer corresponds to a relatively low catalyst concentration (0.154 mol  $L^{-1}$ ). The maximum yield of the polymer is achieved at higher catalyst concentrations (0.303 mol  $L^{-1}$ ).

The dynamics of changing the characteristics of PPC **2** during copolymerization at a catalyst concentration of 0.29 mol  $L^{-1}$  is shown in Table 3.

It follows from the data presented that under the indicated conditions ( $p_{CO_2} = 25-27$  atm and T = 85-87 °C) the maximum yield of copolymer **2** is achieved in 10-12 h and remained at a constant level for the next 10-12 h, although such a behavior is accompanied by a decrease in the molecular weight.

The influence of the solvent nature on the yield of the polymer and its molecular-weight characteristics is determined by several factors, in particular, the basicity and polarity, solubility of  $CO_2$  (depending on the ex-

**Table 3.** Change in the characteristics of PPC **2** during copolymerization of propylene oxide (1) with  $CO_2$  (concentration of zinc adipate is 0.29 mol  $L^{-1}$ )

Reaction time/h	Yield of <b>2</b> (%)	$M_{ m w}$ • 10 <sup>-3</sup>	$M_{\rm n} \cdot 10^{-3}$	$M_{\rm w}/M_{\rm n}$
6	48.87	287.8	57.4	5.01
10	64.69	218.9	52.8	4.15
13	67.33	159.9	33.1	4.84
16	63.85	146.9	25.7	5.71
19	62.31	130.7	26.9	4.85
22	62.54	130.3	27.6	4.72

*Note.* T = 85 - 87 °C, solvent is  $CH_2Cl_2$ ,  $p_{CO_2} = 25 - 27$  atm.

Solvent	Yield (%)		$M_{\rm w} \cdot 10^{-3}$	$M_{\rm n} \cdot 10^{-3}$	$M_{\rm w}/M_{\rm n}$	Basicity	Polarity
	2	3				parameter <sup>16</sup>	parameter <sup>17</sup>
Perfluorodecalin <sup>a</sup>	67.1	5.5	180.0	67.0	2.69	_	_
<i>o</i> -Xylene <sup><i>b</i></sup>	67.0	6.0	158.0	33.0	4.82	0.157	0.641
Toluene <sup>b</sup>	66.4	6.0	194.0	77.0	2.50	0.128	0.655
$CH_2Cl_2^b$	65.4	8.0	299.0	57.0	5.26	0.178	0.876
Methylcyclohexane <sup>a</sup>	57.8	5.5	152.0	70.0	2.18	0.078	0.563
Benzene <sup>b</sup>	56.2	6.0	202.0	68.0	2.97	0.124	0.667
1,4-Dioxane <sup>b</sup>	54.1	4.0	282.0	25.0	11.49	0.444	0.701
<i>n</i> -Hexane <sup><i>a</i></sup>	52.2	5.5	172.0	59.0	2.94	0.056	0.519
Freon-113 <sup>a</sup>	50.0	4.0	216.0	73.0	2.94	0.038	0.616
Toluene—AcOEt $(1:1)^b$	38.2	5.5	95.7	13.0	7.19	_	_
AcOEt <sup>b</sup>	27.0	16.0	60.0	15.0	3.89	0542	0.795
Benzyl chloride <sup>b</sup>	13.7	5.0	161.0	20.0	8.18	_	_
THF <sup>b</sup>	4.1	30.0	15.0	_	_	0.591	0.838
MeCN	1.5	30.0	_	_	_	0.286	0.895
Monoglyme	Traces	50.0	_	_	_	0.636	_
Diglyme	0	0	_	_	_	0.623	_
Cyclohexanone	0	0	_	_	_	0.482	0.874
1-Methylpyrrolidin-2-one	0	0	_	_	_	0.613	0.970
Propylene carbonate	0	—	_	—	—	0.341	0.930

**Table 4.** Effect of the solvent nature on the copolymerization of propylene oxide (1) with CO<sub>2</sub> in the presence of zinc adipate  $(T = 75 - 78 \text{ °C}, p_{CO_2} = 26 - 28 \text{ atm}, 10 \text{ h})$ 

<sup>a</sup> The final reaction mixture exhibits syneresis.

<sup>b</sup> The final reaction mixture is a viscous heterogeneous paste.

perimental conditions and composition of the reaction mixture), and others.

The results of studying the effect of the solvent nature on the copolymerization of  $CO_2$  with propylene oxide (1) (Table 4) suggest that the yield (>50%) of PPC 2 with  $M_w = 150000-300000$  and the low content of by-product 3 are achieved by the use of solvents with mainly low basicity and polarity. In solvents with high polarity and basicity the process is inhibited or completely suppressed likely due to the competition between the solvent and oxide 1 for the active site of polymerization.

Advantages of fluorinated solvents are worth of special mentioning. They are nontoxic and incombustible, and  $CO_2$  is highly soluble in them. In addition, syneresis is observed in the reaction mixture at the final stage of copolymerization to considerably simplify solvent regeneration. Despite the polymer precipitates from the reaction mixture at the final stage of polymerization, the molecular weights of PPC **2** are rather high.

The structure of polymer 2 obtained at 75 °C in the presence of zinc adipate (see Table 1) was studied by  ${}^{1}\text{H}$  and  ${}^{13}\text{C}$  NMR spectroscopy.

The <sup>1</sup>H NMR spectrum of **2** contains signals with chemical shifts at 1.28-1.74 (m, CH(<u>Me</u>)), 4.04-4.38 (m, CH<sub>2</sub>), and 4.95-5.13 ppm (m, CH(Me)) and a ratio of integral intensities of 3:2:1, which corresponds to the PPC fragments with structure **A** (see Scheme 1).

Along with the main signals, the spectrum also contains minor signals with chemical shifts at 1.05-1.41(m, CH(<u>Me</u>)), 3.33-3.88 (m, CH<sub>2</sub>), and 4.81-5.23 ppm (m, C<u>H</u>(Me)) corresponding to the ether fragments of the polymeric chain with structure **B**. Their content could be determined from the ratio of integral intensities of signals from the carbonate and ether CH<sub>2</sub> groups because the identification of the ether fragments from other signals is impeded due to their superposition. In the presented example, the content of the ether fragments was 9%.

Analysis of the <sup>13</sup>C NMR spectra shows that all possible types of addition of the monomer units are accomplished in PPC **2**, *viz.*, "head-to-head" (HH), "tail-to-tail" (TT), and "head-to-tail" (HT). Based on the assumption that the relaxation times of the C atoms of the carbonyl groups in the <sup>13</sup>C NMR spectra are approximately the same for the three variants of addition (HH, TT, and HT, 153.0–155.0 ppm<sup>18</sup>), the content of these fragments in the chain of PPC **2** can quantitatively be estimated from the integral intensities of their signals. In the case considered, the ratio is HH : TT : HT = 0.817 : 1.000 : 3.142. The multiplicity of signals from other C atoms also points to different types of addition of the monomers.

The data presented completely coincide with the results of studies of the structure of PPC obtained with the catalytic system based on the  $Et_2Zn$  derivatives.<sup>18</sup>

## **Experimental**

Carbon dioxide was stored for 72 h at  $\sim$ 20 °C in an autoclave filled with activated silica gel (pressure 55 atm).

Zinc adipate was synthesized using a known procedure<sup>19</sup> and activated for 40 h at 130 °C (2 Torr), decomposition point 425–450 °C (*cf.* Ref. 19: decomposition point 425–450 °C). Its IR spectrum (Specord IR-75, 1540 cm<sup>-1</sup> (Zn $\rightarrow$ O=C), 1585 cm<sup>-1</sup> (terminal acidic groups)) coincides with that presented previously.<sup>1</sup>

Propylene oxide was refluxed above  $CaH_2$  until gas evolution ceased and distilled.

Solvents were purified using known procedures.<sup>20</sup>

The molecular weights of polymers were determined by gel permeation chromatography on a Gilson instrument (columns AM-Gel 500A, 2 Linear ( $300 \times 7$  mm), eluent velocity 1 mL min<sup>-1</sup>, eluent CHCl<sub>3</sub>). NMR spectra were recorded on a Bruker DRX-500 spectrometer (500 MHz) in CDCl<sub>3</sub>.

Copolymerization (general procedure). A solvent (50 mL) was loaded to a 200-mL steel reactor (maximum pressure 50 atm) with a heated jacket and a mechanical stirrer, and the catalyst (3 g) and propylene oxide (1) (15 g) were added with stirring. The reactor was sealed at ~20 °C, and CO<sub>2</sub> was conveyed with stirring until the pressure reached 16 atm. Then the reaction mixture was heated to the reaction temperature and stirred for a specified time ( $p_{\rm CO_2} = 26 \pm 1$  atm). After the end of the reaction, a heterogeneous mixture of the catalyst and a viscous solution of the polymer was unloaded and treated with a 6% solution of HCl to decompose the catalyst. The transparent organic layer was washed to the neutral reaction and slowly added with stirring to MeOH (200 mL) to precipitate the polymer. The precipitated polymer was additionally washed with MeOH (100 mL), and the precipitate was separated and dried at 80-90 °C (5 Torr) to a constant weight.

Poly(propylene carbonate) 3. <sup>1</sup>H NMR, δ: 1.28–1.74 (m, 3 H, Me); 4.04–4.38 (m, 2 H, CH<sub>2</sub>); 4.95–5.13 (m, 1 H, CH). <sup>13</sup>C NMR, δ: 16.10–16.40 (m, Me); 68.80–69.40 (m, OCH<sub>2</sub>); 71.90–72.50 (m, OCH); 153.00–155.00 (m, C=O).

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