

# (Co)polymerization Reactions with Participation of Cyclic Monomers Catalyzed by Double Metal Cyanide Catalysts

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Received November 7, 2023; revised December 12, 2023; accepted December 25, 2023

**Abstract**—Double metal cyanide catalysts are unique heterogeneous catalysts having no alternative in the industrial polymerization of propylene oxide to produce poly(propylene oxide) with properties demanded for special-purpose applications: a low degree of unsaturation and high molecular weights and hydroxyl values. These catalysts are known since the 1960s, but academic publications addressing them started to appear only in the early 2000s, which coincided with interest in epoxide/CO<sub>2</sub> copolymerization and other catalytic processes. The present literature review aims to systematize information on the application of double metal cyanide catalysts in (co)polymerization reactions involving epoxides and other cyclic monomers. Much attention is paid to chemo- and regioselectivity issues and mechanistic aspects of epoxide/CO<sub>2</sub> copolymerization. Due to the use of ionic liquids and other homo- and heterogeneous catalyst in the reaction of epoxides and CO<sub>2</sub>, double metal cyanide catalysts can be tuned for the selective synthesis of poly(ether carbonates), polycarbonates, or cyclic carbonates. Information on the application of these processes for the synthesis of functionalized (co)polymers is covered. Epoxide/cyclic anhydride copolymerization and epoxide/cyclic anhydride/CO<sub>2</sub> and epoxide/ε-caprolactone/CO<sub>2</sub> multicomponent reactions, including those using multicomponent catalytic systems based on the catalysts under consideration, are highlighted. Progress in this area suggests that double metal cyanide catalysts and multicomponent catalytic systems based on them will hold a prominent position in the synthesis of polymer materials of the future.

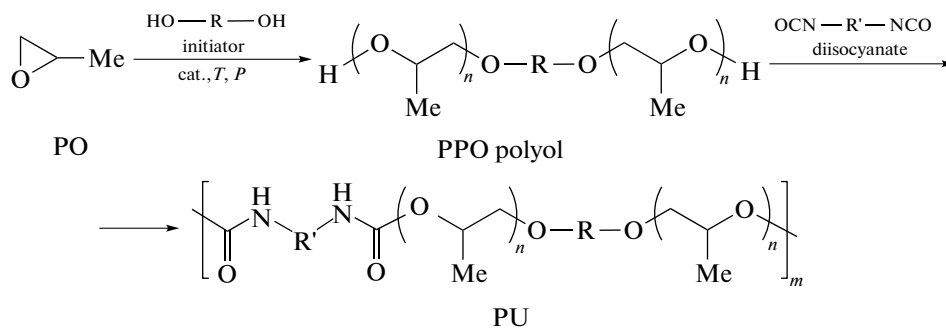
DOI: 10.1134/S1560090423600328

## INTRODUCTION

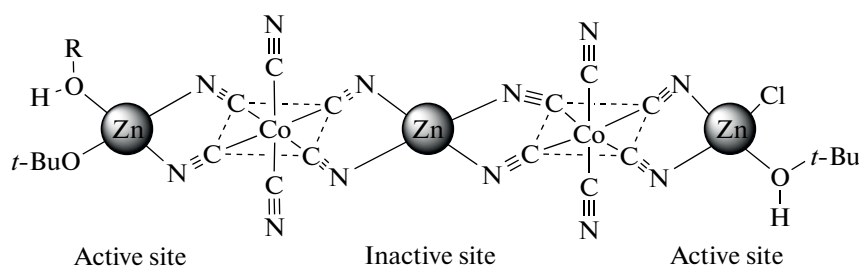
Poly(propylene oxide) (**PPO**) is a large-tonnage product, which is used in the synthesis of other widely demanded polymers, polyurethanes (**PUs**), as well as nonionic surfactants [1–3]. In industry, PPO is produced by the ring-opening polymerization (**ROP**) of propylene oxide (**PO**) in the presence of a catalyst and an initiator, or a “starter.” When polyatomic alcohols

are used as starters, the resulting PPOs are PPO polyols, which, in turn, serve as monomers in subsequent polycondensation with di- and triisocyanates in the synthesis of PUs (Scheme 1).

The KOH-catalyzed anionic polymerization of PO is commonly used in industry, but it suffers from a number of drawbacks [1]. For the synthesis of PPO with properties required for special-purpose applications double metal cyanide (**DMC**) catalysts are



Scheme 1.



Scheme 2.

employed. These are hybrid (organic-inorganic) materials with the composition described by the formula



where  $\text{Mt} = \text{Zn}$ ,  $\text{Fe(II)}$ ,  $\text{Ni(II)}$ , etc.;  $\text{Mt}' = \text{Co(III)}$ ,  $\text{Fe(II)}$ ,  $\text{Fe(III)}$ , etc.;  $\text{MtX}_d$  is the salt of metal  $\text{Mt}$  used in synthesis; and  $x$ ,  $y$ , and  $z$  depend on the method of catalyst synthesis [4]. Zinc-cobalt ( $\text{Mt} = \text{Zn}$ ,  $\text{Mt}' = \text{Co(III)}$ ) catalysts prepared from  $\text{ZnCl}_2$  and  $\text{K}_3[\text{Co}(\text{CN})_6]$  are the most accessible and active. The “attribute” of highly active DMC catalysts is *tert*-butanol (**TB**) and coligands, which are usually oligomeric polyethers. In contrast to  $\text{KOH}$ -catalyzed anionic polymerization,  $\text{Zn-Co}$  DMC catalysts are highly efficient. They allow for the synthesis of PPO polyols with much higher molecular weights which contain an order of magnitude lower number of unsaturated groups and have higher hydroxyl values. The DMC-catalyzed polymerization of PO with extremely low loadings reaching 25 ppm [1, 3] does not need catalyst regeneration but its disadvantages are sensitivity of the catalytic system to moisture present in reagents and formation of the so-called “high molecular weight tails” [3].

DMC catalysts are highly amorphous, which complicates their phase analysis by powder X-ray diffraction, and quantum-chemical simulation attempts are still strongly limited [5, 6]. Meanwhile, some authors believe that the crystalline structure of  $\text{Zn}_3[\text{Co}(\text{CN})_6]_2$  forms the basis of the materials and zinc cations from  $\text{ZnCl}_2$  are coordinated to nitrogen atoms of CN groups *on periphery*, also carrying ligands in the form of chloride (or  $\text{OH}^-$ ) and TB, coligand, or water molecules [7] (Scheme 2). Anions  $[\text{Co}(\text{CN})_6]^{3-}$  are not labile, while the mechanism of catalysis is inherently associated with the lability of  $\text{Zn-O}$  and  $\text{Zn-Cl}$  bonds; therefore, such peripheral zinc atoms are considered to be active sites. At the same time, anions  $[\text{Co}(\text{CN})_6]^{3-}$  provide the necessary mesoporosity of the material [8] and inevitably tune the Lewis acidity of  $\text{Zn}^{2+}$ , contributing to the activity of these materials. It is known that polymerization mediated by DMC catalysts is accompanied by destruction of the material matrix (fragmentation) [9]; however, structural trans-

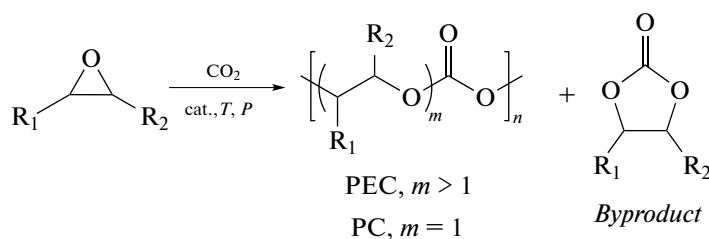
formations have not been studied in detail. Furthermore, structure of a catalyst can change not only in the course of synthesis but also during pre-activation, including its heating together with a starter at 80–150°C in vacuum (<200 mmHg) prior to monomer addition [10]. Comparatively recently it has been shown [11] that under these conditions TB-containing DMC materials undergo the unusual reaction of ligand decomposition



As a result, they may contain  $\text{Zn-OH}$  fragments, the presence of which make them similar to the zinc-containing fragment of carbonic anhydrase [12].

For a long time these catalysts have been available only in the patent literature relevant to the synthesis of PPO polyols, and academic publications devoted to them began to emerge only in the 2000s, which largely coincided with the interest of scientific community in the allied process—the copolymerization of epoxides and carbon dioxide  $\text{CO}_2$  (ring-opening copolymerization, **ROCOP**). Epoxide/ $\text{CO}_2$  ROCOP is very attractive for research, on the one hand, in terms of fixation of atmospheric  $\text{CO}_2$ , an accessible C1-monomer, to combat global warming, and, on the other hand, from the point of view of obtaining poly(ether carbonates) (**PEC**) as biodegradable polymers [13]. This process became the second most important application of the considered catalysts. This was followed by the use of DMC catalysts in other processes, primarily copolymerizations involving epoxides, as well as hydroamination of alkenes and alkynes [14, 15], transesterification of triglycerides [16–22] and carbonates [23–25], polycondensation between glycerol and succinic acid [26–28], condensation reactions [29–34], and others [35–38].

The DMC-catalyzed copolymerization of epoxides and  $\text{CO}_2$  is the subject of several reviews (e.g., [39–43]). However, they concern individual aspects and suffer from a lack of comprehensive analysis of publications on the subject, including the most recent ones. The goal of this review is to systemize data on the application of DMC catalysts in the synthesis of polymer materials other than PPO polyols. The DMC-catalyzed ROCOP of epoxide/C1 comonomers ( $\text{CO}_2$ ,



Scheme 3.

CS<sub>2</sub>, COS) and epoxide/cyclic anhydride, as well as multicomponent copolymerization reactions of epoxide/cyclic anhydride/CO<sub>2</sub> and epoxide/ $\epsilon$ -caprolactone/CO<sub>2</sub>, are described. Results on the application of multicomponent catalytic systems based on DMC materials in the mentioned processes are presented. Great attention is given to chemo- and regioselectivity issues and mechanistic aspects of DMC-catalyzed ROCOP of epoxide/CO<sub>2</sub>.

#### DMC-CATALYZED COPOLYMERIZATION REACTIONS WITH PARTICIPATION OF EPOXIDES AND C1 COMONOMERS (CO<sub>2</sub>, CS<sub>2</sub>, COS)

##### *Copolymerization of Epoxides with CO<sub>2</sub>. General Characteristic*

In contrast to homogeneous metal-complex catalysts, for example, Co(III) and Cr(III) salen complexes affording aliphatic polycarbonates (PC), this copolymerization on DMC catalysts yields PEC [40].

Similar to the homopolymerization of PO, when polyatomic alcohol or polybasic acid is used as a starter, reaction products are corresponding PEC polyols. PEC polyols demonstrate good flexibility and oxidative and hydrolytic stability and, alongside PPO polyols, are of interest as monomers for the synthesis of PUs. Byproducts are cyclic carbonates (Scheme 3) that which are also valuable as electrolytes for Li-ion batteries [44, 45] and components of modern hydrocarbon processing technologies [46, 47]. In addition to the PEC selectivity of copolymerization, an important characteristic of PEC is the degree of insertion of CO<sub>2</sub> (the content of carbonate units)  $F_{CO_2}$  determined as the fraction of carbonate units from the total number of units in a copolymer (carbonate + ether). Achievement of high  $F_{CO_2}$  values, which in the limit are 100%, as for PCs (alternating copolymers), is necessary not only in terms of the effective use of CO<sub>2</sub>. With an increase in  $F_{CO_2}$ , the content of primary OH groups in PECs increases, which positively affects their reactivity in the synthesis of PUs [48]. At the same time, just the presence of ether fragments imparts to PECs physicochemical properties that advantageously distinguish them from PCs [49].

As in the homopolymerization of PO, the initiators (starters) of PO/CO<sub>2</sub> copolymerization are most often oligomers based on propylene glycol and glycerol but, for example, paraform [50] and phenols [51, 52] can also be employed. Well coordinating amines able to chelate Zn<sup>2+</sup> ions (diethanolamine, diethylenetriamine, etc.), urea, and low molecular weight carboxylic acids (formic, acetic, and butyric) serve as process inhibitors [53]. Some aliphatic dicarboxylic acids [54, 55] and aromatic polybasic acids [56–58] were successfully used in the copolymerization of epoxides and CO<sub>2</sub>; the strength of acids affected the catalytic system. It was found that weak acids ( $pK_{a1}$  4.43–4.72) act as initiators, whereas strong acids ( $pK_{a1}$  1.87–4.2) act as chain initiation-transfer agents, that is, initiate the cationic ROP of epoxide, and in situ formed PPO polyol initiates copolymerization.

The focus of research is the copolymerization of PO and CO<sub>2</sub> [49, 57, 59–70]. Some papers concern effect of the method of preparing DMC materials on their catalytic properties in this process. The ratio of inorganic precursors in the synthesis of DMC materials and its relation to catalytic properties were investigated in only one paper [59]. The highest catalyst activity and PEC selectivity were reached in the case of the maximum excess of ZnCl<sub>2</sub> (in this case 8 mol per mol of K<sub>3</sub>[Co(CN)<sub>6</sub>]), which in general correlates with the behavior of DMC catalysts in PO homopolymerization [71]. However, the catalysts reported in [59] were inefficient in the synthesis of PEC because of a low  $F_{CO_2}$  value (~7%); therefore, features observed for them cannot be extended to other DMC catalysts. I. Kim et al. studied effect of the nature of halides ZnX<sub>2</sub> (X = Cl, Br, or I) on the properties of DMC materials synthesized using TB and poly(tetramethylene ether) glycol (PTMEG) as coligands [61]. Catalysts prepared from ZnBr<sub>2</sub> were the best in terms of the  $F_{CO_2}$  (36%) and polydispersity  $\bar{D}$  (~1.0) of copolymers. The authors of [62] described the mechanochemical synthesis of TB-containing DMC catalysts using polyethers as coligands: poly(ethylene glycol), poly(propylene glycol), and PTMEG. These catalysts showed moderate activity but afforded PEC with high  $M_n = 61 \times 10^3$ , narrow MWD ( $\bar{D} = 1.46$ ), and the degree of insertion of CO<sub>2</sub> 36–43% that was somewhat

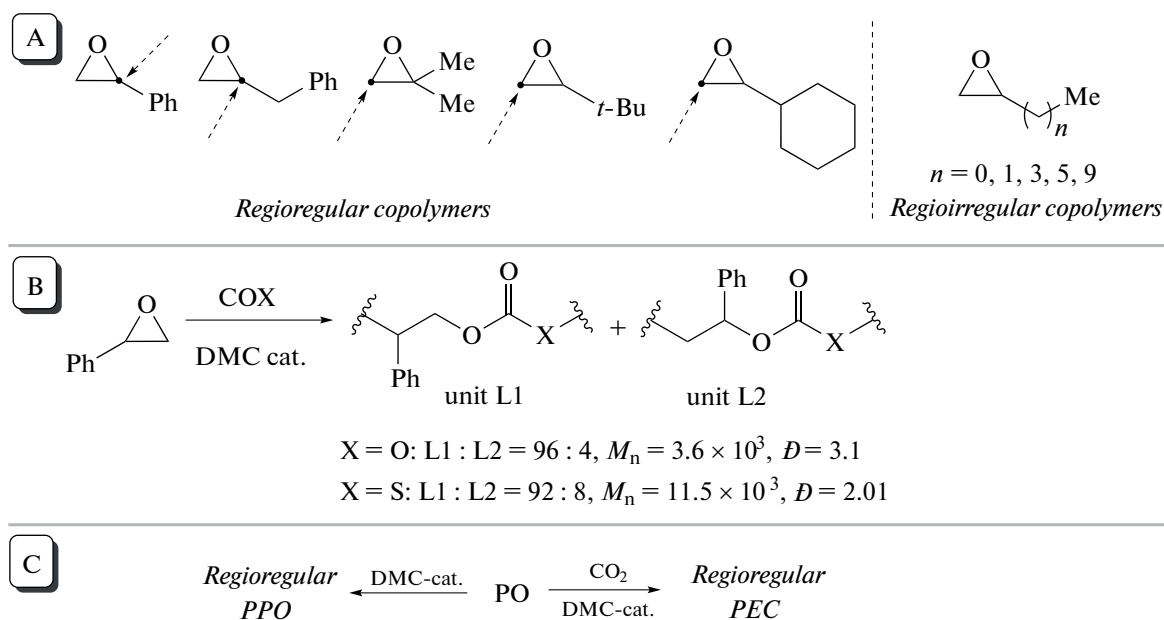
higher than that for the DMC catalyst prepared by traditional synthesis (32%). Effect of the nature of a ligand, as an alternative to TB, in the mechanochemical synthesis of DMC catalysts was previously examined in [72], but the samples reported there did not rank above TB/polyether-containing materials in their catalytic behavior. DMC catalysts based on alkyl nitriles as ligands were superior to traditional TB-containing catalysts in PO/CO<sub>2</sub> ROCOP in activity, and the highest activity was exhibited by materials based on acetonitrile (turnover frequency 475 h<sup>-1</sup>) [73]. The copolymerization of PO on a highly crystalline DMC catalyst was carried out; it was characterized by a high PEC selectivity (>95%) and the degree of insertion of CO<sub>2</sub> was 39% [67].

Some papers deal with the effect of other factors on the DMC-catalyzed copolymerization of PO/CO<sub>2</sub>. For example, a high PEC selectivity (<3% of cyclic carbonate) was exhibited by the DMC catalyst supported on titania [74]. The observed selectivity was attributed by the authors to the suppression of “back-biting” (see below) because of the facilitated adsorption of PO on the TiO<sub>2</sub> support as a Lewis acid (the probability of chain growth increases). To increase molecular weight and degree of insertion of CO<sub>2</sub> it was proposed to use ultrasound; despite the positive effect, the resulting copolymers had high  $\bar{D}$  values (2.0–3.5) and the rate of the process at the chosen temperature (60°C) increased insignificantly [64]. Low-temperature PO/CO<sub>2</sub> copolymerization carried out at 40–80°C yielded PEC with selectivity up to 94% and high  $M_n$  and  $F_{CO_2}$ , up to  $36.5 \times 10^3$  and 75%, respectively [65]. To date, the study [58], in which 1,2,4,5-benzenetetracarboxylic acid acted as a starter, is the record for the achieved degree of insertion of CO<sub>2</sub> (up to 96%) and the values of  $\bar{D}$  (up to 1.08). The synthesis and study of the properties of PUs obtained from PO-based PEC polyols were described in [60, 68, 70, 75].

Along with the copolymerization of PO, the copolymerization of cyclohexene oxide (CHO) has been actively studied [61, 63, 76–84]. The above-mentioned TB/PTMEG-containing DMC materials based on halides ZnX<sub>2</sub> (X = Cl, Br, or I) were also tested in the CHO/CO<sub>2</sub> ROCOP [61]. The highest  $F_{CO_2}$  (53%) was achieved for PEC in the case of the catalyst based on ZnCl<sub>2</sub>, whereas the sample derived from ZnBr<sub>2</sub> was superior to it in activity, yielding the copolymer with a lower  $\bar{D}$  and a slightly smaller  $F_{CO_2}$  = 51%. Yi et al. [76] investigated catalysts prepared by the reverse emulsion method; they showed higher  $F_{CO_2}$  (58%) and activity commensurate with the sample synthesized by the traditional method. Dharman et al. employed microwave heating in the copolymerization of CHO at a low pressure (9.7 bar); as a result, the induction period decreased (<30 min) and the synthesized polymer had  $M_n$  =  $14.5 \times 10^3$  ( $\bar{D}$  = 1.5)

and contained 75% of carbonate units [78]. Supporting of a nanolamellar DMC catalyst [65] on silica gel increased its activity in CHO/CO<sub>2</sub> copolymerization: productivity attained 7.5 kg PEC/g of catalyst (100°C, 3.8 MPa) and turnover frequency was 3815 h<sup>-1</sup> [81]. However, in a later work of the same authors it was found that the preliminary heat treatment of the catalyst at 210°C without supporting on SiO<sub>2</sub> is even more promising: in this case synthesis affords an almost alternating copolymer with  $F_{CO_2}$  = 97% and the catalyst productivity is 8400 g PEC/g of Zn (4.0 MPa, 80°C, 5 h) [84]. When using 4-vinylcyclohexene oxide as a comonomer, along with CHO and CO<sub>2</sub>, copolymers that can be post-modified via the thiol-ene reaction, are produced [85].

The copolymerization of the PO-CHO mixture with CO<sub>2</sub> [86] makes it possible to produce copolymers with physicochemical characteristics (e.g., the glass transition temperature  $T_g$ ) different from those of PO and CHO homopolymers, and by changing the PO : CHO ratio copolymers with desired properties can be synthesized. PECs can be endowed with desired properties using other epoxides as monomers, and the presence of additional functional groups in a monomer opens ways for the post-modification of the resulting copolymers. Among monomers tested in the reactions with CO<sub>2</sub> are styrene oxide [87–90], ethylene oxide [91, 92], epichlorohydrin [93], glycidyl acrylate [94], phenyl glycidyl ether [95], and others [89, 90, 96–98]. X.-H. Zhang et al. studied effect of the structure of epoxide on the characteristics of the process and revealed that bulky substituents, such as 2,2-dimethyl, *tert*-butyl, cyclohexyl, decyl, and benzyl, contribute to an increase in the degree of insertion of CO<sub>2</sub>, which may be almost quantitative (>99%) [89]. Regioregular copolymerization is observed in the case of styrene oxide and benzyl oxirane, wherein opening of the epoxide cycle occurs via a methyne carbon atom, while regioregular copolymerization, in which ring opening proceeds via the methylene carbon atom (Scheme 4A; the preferred direction of ring opening is shown by arrows) is typical for isobutylene oxide. Styrene oxide is inclined to form regioirregular polymers; therefore, the attained high regioselectivity equal to 96% (Scheme 4B) is an unexpected outcome, indicating that regioregularity is determined by electronic rather than steric effects [88, 89]. PO and epoxides with linear alkyl substituents form regioirregular copolymers under similar conditions [89]. Similar to anionic catalysts, the polymerization of PO on DMC catalysts is regioselective and yields exclusively PPO with head-to-tail units [53, 99]. Accordingly, the fundamental difference of the DMC-catalyzed ROCOP of PO/CO<sub>2</sub> from the ROP of PO is the absence of regioselectivity of the process (Scheme 4C). The PEC selectivity of epichlorohydrin/CO<sub>2</sub> copolymerization is 89–95% and exceeds that in the case of homoge-



Scheme 4.

neous catalysis with the Co(III) salen complex and  $F_{\text{CO}_2}$  is as high as 71% [93].

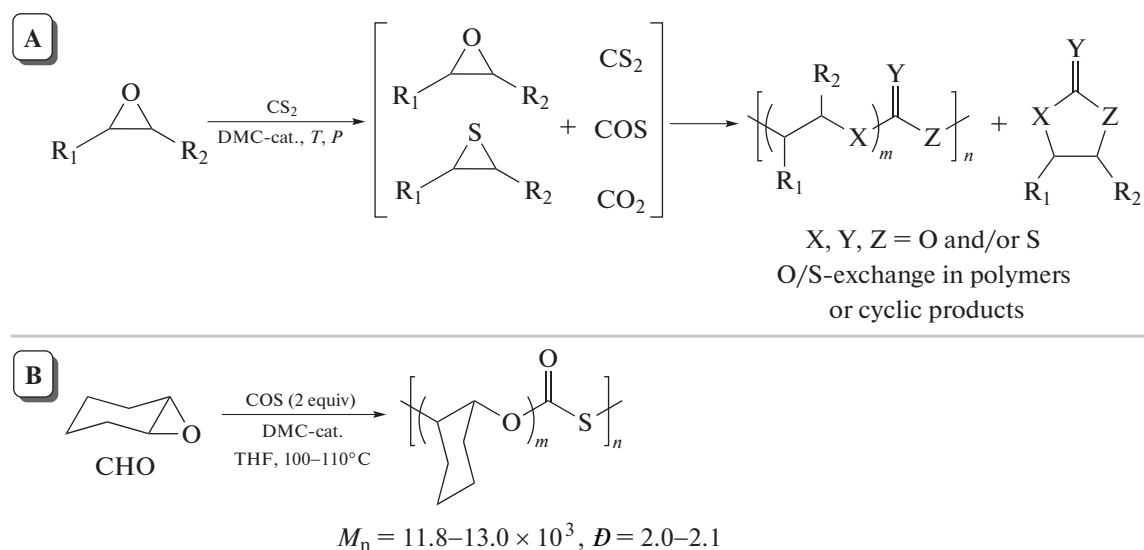
In the synthesis of PEC a notable place is held by nontraditional DMC materials, as well binary catalytic systems and composite catalysts containing DMC materials. Varghese et al. [101] synthesized a catalyst with the composition  $[\text{ZnCl}_2]_2[\text{HCo}(\text{CN})_6] \cdot \text{CH}_3\text{OH}$  via the exchange reaction between  $\text{ZnCl}_2$  and  $\text{H}_3[\text{Co}(\text{CN})_6]$  in a methanol solution. This complex compound is not a hybrid material but is allied to DMC catalysts. The catalytic properties of this compound in the synthesis of PEC from PO were much better than those of DMC catalysts with TB as a single ligand. A catalyst based on  $\text{H}_3[\text{Co}(\text{CN})_6]$  and zinc 2-ethyl hexanoate  $\text{Zn}(\text{Oct})_2$  was prepared in a similar manner [102]. Zinc–chromium materials based on  $\text{Zn}_3[\text{Cr}(\text{CN})_6]_2$ ,  $\text{ZnCl}_2$ , and TB and obtained by mechanochemical synthesis, showed good activity and efficiency in the PO/ $\text{CO}_2$  copolymerization, affording PEC with  $M_n = 68.6 \times 10^3$  and  $\mathcal{D} = 1.68$  (70°C, 4 MPa, 24 h) [103]. L.B. Lu et al. [104] synthesized multimetal catalysts, in which precursors were a mixture of  $\text{ZnCl}_2$  and  $\text{NiCl}_2$  with various ratio of salts and one of Co(III), Fe(II), or Fe(III) cyano complexes, but they showed a fairly low activity in PO/ $\text{CO}_2$  ROCOP.

The authors of [63] tested nontraditional Zn–Ni catalysts based on  $\text{Zn}[\text{Ni}(\text{CN})_4]$  and  $\text{ZnCl}_2$ , which were prepared using various organic ligands, such as TB, 1,2-dimethoxyethane (glym), 2-methoxyethanol, 1-methoxy-2-propanol, ethylene glycol, and propylene glycol, in the PO/ $\text{CO}_2$  copolymerization. The nature of organic ligands influenced catalytic activity, and in this respect glym was the best ligand, but it had

almost no effect of the composition of copolymers ( $F_{\text{CO}_2} \sim 60\%$ ). G. Penche et al. investigated DMC materials prepared from tetracyanonickelates  $\text{Mt}[\text{Ni}(\text{CN})_4]$ ,  $\text{MtCl}_2$ , and TB, where Mt = Ni, Co, Fe, and Mn [105]. Even though these catalysts possessed almost 100% selectivity, they were seriously inferior to Zn–Co materials in activity and efficiency and produced PEC with low  $M_n = (11.0\text{--}36.5) \times 10^3$  and  $F_{\text{CO}_2} = 13\text{--}42\%$  and wide MWD ( $\mathcal{D} = 2.5\text{--}5.0$ ). TB/PTMEG-containing Co–Ni materials, as well as Zn–Ni materials, exhibited the best efficiency and demonstrated moderate catalytic properties [106]. At the same time, the reaction mediated by Zn–Ni materials synthesized by mechanochemical synthesis afforded PEC with  $M_n = 10.3 \times 10^3$ ,  $\mathcal{D} = 1.45$ , and high  $F_{\text{CO}_2} = 84\%$  [107]. In [108], a number of Zn–Mt catalysts were prepared from  $\text{ZnCl}_2$ , TB, and  $\text{K}_x[\text{Mt}(\text{CN})_y]$ , where Mt = Cr(III), Ni(II), Mo(IV), Mn(III), Fe(II), and Cd(II), as well as Zn–Co catalysts, which were synthesized using complexes  $\text{K}_3[\text{Co}(\text{CN})_5\text{X}]$ , where X = Cl, Br, I,  $\text{NO}_2$ , or  $\text{N}_3$ , instead of  $\text{K}_3[\text{Co}(\text{CN})_6]$ . These catalysts allowed for the synthesis of an almost alternating copolymer of PO and  $\text{CO}_2$ .

A small addition (molar ratio 1 : 10) of the DMC material to zinc glutarate, which is a heterogeneous catalyst of PO/ $\text{CO}_2$  copolymerization yielding the corresponding PC, leads to the synergistic effect on activity: productivity increases from 134 to 508 g of copolymer/g of catalyst for pure zinc glutarate and the composite, respectively, while the  $F_{\text{CO}_2}$  of the copolymer decreases slightly, from  $\sim 100$  to 98% [109]. At the





Scheme 5.

same time, a small additive of zinc glutarate to the DMC material (mass ratio 1 : 10) also improves the properties of DMC catalysts: productivity increases from 1334 to 1689 g of PEC/g of catalyst and  $F_{CO_2}$  of corresponding PEC increases from 23 to 47% [110]. A binary catalytic system including the RET (rare-earth ternary) complex was also tested. Composite RET/DMC (RET =  $(CCl_3CO_2)_3Y$ -glycerol- $ZnEt_2$ ) was more active than the RET complex or DMC catalyst separately; PECs synthesized on this composite were characterized by high  $M_n$  values,  $93 \times 10^3$  or  $114 \times 10^3$ , depending on conditions, but had high  $D$  values, 3.16 or 4.64, respectively [111]. The binary system DMC/Co(III) salen complex was described in CHO/ $CO_2$  copolymerization in two papers [112, 113], among which the reaction in supercritical  $CO_2$  stands out: a copolymer containing up to 99% of carbonate units was synthesized [113]. It should be noted that the method of synthesizing DMC materials and zinc glutarate, as well as the method of preparing composites based on them, should theoretically influence the properties of the above heterogeneous catalytic systems, but no detailed studies on this issue have been carried out so far.

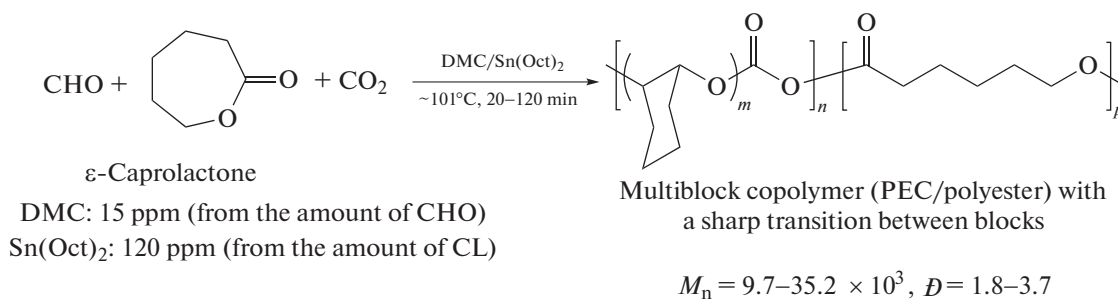
As follows from the foregoing, the relationship between the nature of DMC materials and their catalytic properties in the ROCOP of epoxides and  $CO_2$  is complex and hardly predictable. Generally, the process under consideration is implemented under fairly severe conditions and the resulting PECs are characterized by low  $M_n$  ( $(10-40) \times 10^3$ ) and high  $D$  ( $>1.5$ ). The values of  $F_{CO_2}$  for these polymers depend on the nature of epoxide, and, at present, for PO it is rarely above 40%, whereas for CHO they are much higher and are usually at least 75%. The drawback of the

DMC-catalyzed copolymerization of epoxide/ $CO_2$  on the way to scaling is a low productivity of a semi-continuous process, which in the case of PO is as low as  $0.1 \text{ kg}^{-1} \text{ L}^{-1} \text{ h}^{-1}$  [68]. A continuous process having an order of magnitude higher productivity ( $1.5 \text{ kg}^{-1} \text{ L}^{-1} \text{ h}^{-1}$ ) has the potential in this respect [69] but its possibilities have not been fully explored. A great potential is also offered by binary and multicomponent catalytic systems containing DMC materials that would combine positive properties of individual catalysts.

#### Copolymerization of Epoxides with $CS_2$ or $COS$

The scientific community is looking for routes for the chemical utilization of  $CS_2$  and  $COS$  and, therefore, regards them as C1 comonomers to produce hardly accessible sulfur-containing polymers. As in the case of homogeneous metal-complex catalysis [114], the specific feature of DMC-catalyzed copolymerization of epoxide/ $CS_2$  is that O/S-exchange reactions occur to provide mixtures of sulfur-containing polymers of complex composition and cyclic thiocarbonates. In the presence of a catalyst  $CS_2$  converts into a mixture of  $CS_2$ ,  $COS$ , and  $CO_2$  and epoxide may be partially converted into episulfide. The main products of cross reactions are polymers containing mostly mono- and dithiocarbonate, carbonate, ether and thioether units, and byproducts are cyclic mono-, di-, and trithiocarbonates (Scheme 5A).

For example, in the case of PO/ $CS_2$  cyclic thiocarbonates make up less than 15 wt % of all reaction products, which suggests a high selectivity for the copolymer. The molecular weight and  $D$  for the products of PO/ $CS_2$  copolymerization depend on temperature, relative amounts of comonomers, and catalyst loadings; they are in the range of  $(1.2-5.4) \times 10^3$  and 1.24-



Scheme 6.

3.50, respectively. Temperature  $100^\circ\text{C}$ ,  $[\text{CS}_2] : [\text{PO}] = 1.5-2.0$ , and catalyst loading  $3.2 \times 10^{-4}$  g/g of comonomers are optimal conditions for this process [116]. A similar picture is observed for the DMC-catalyzed copolymerization of CHO/ $\text{CS}_2$ , although this process has not been studied quantitatively and in detail [115].

The copolymerization of CHO and COS [115] affords copolymers belonging the class of poly(ether monothiocarbonates) (Scheme 5B). The  $M_n$  of these copolymers is  $(6.5-25.0) \times 10^3$  at  $D = 1.6-2.1$ , the catalyst productivity is 970 g of polymer/g of catalyst (turnover frequency  $97 \text{ h}^{-1}$ ) over 5 h at a CHO conversion of 95%. O/S exchange reactions are considerably suppressed when synthesis is carried out in THF at  $100-110^\circ\text{C}$ ; as a result, macromolecules contain up to 90% of monothiocarbonate, 2% of carbonate, and 8% of ether units. The resulting polymers has high  $T_g$  values, good thermal stability, and high refractive indexes (1.705); they can potentially be used for creating optical materials.

As in the case of reaction with  $\text{CO}_2$  (see above), the copolymerization of styrene oxide and COS [100] proceeds with a high regioselectivity: epoxide opens via the carbon atom bonded to the phenyl group (Scheme 4B). The DMC catalyst is significantly inferior to the binary catalytic system Cr(III) salen complex/bis(triphenylphosphine)iminium chloride in activity and copolymer characteristics ( $M_n$ ,  $D$ ), but in the latter case the regioselectivity of the reaction is different ( $L1 : L2 = 11 : 89$ ).

#### *Multicomponent Copolymerizations with Participation of Epoxides and $\text{CO}_2$*

In order to search for novel materials with unique properties multicomponent DMC-catalyzed ROCOPs with the use of various comonomers, along with epoxides and  $\text{CO}_2$ , have been studied. Cyclic anhydrides [103, 117-121],  $\epsilon$ -caprolactone [122], and *DL*-lactide [123] are used as comonomers. The introduction of polar ester units into polymer chains with the help of these comonomers leads to increase in the viscosity and  $T_g$  of polymers and causes a change in

their molecular weight characteristics. In addition to regulating physicochemical properties, maleic anhydride [117, 119] and itaconic anhydride [117, 118] units containing double carbon-carbon bonds potentially offer the possibility of UV- or redox-initiated curing of materials. Along with PO [118, 120, 121, 123], a mixture PO/allyl glycidyl ether [119, 124] or 1,2-epoxydecane [117] is used as an epoxy component. The use of the catalytic system DMC/ $\text{Sn(Oct)}_2$  ( $\text{Sn(Oct)}_2 = \text{tin(II) 2-ethyl hexanoate}$ ) in the reaction of CHO,  $\epsilon$ -caprolactone, and  $\text{CO}_2$  allows for the synthesis of the multiblock copolymer PEC/polyester [122].

Copolymerization of this system carried out in the presence of the DMC catalyst produced PEC, while in the presence of  $\text{Sn(Oct)}_2$  polycaprolactone was formed. However, in the presence of both catalysts terpolymerization occurred, which was distinguished by the one-pot one-step synthesis of multiblock copolymer with a sharp transition from one block to another. The degree of insertion of  $\text{CO}_2$  was up to 15% at  $[\text{CHO}] : [\epsilon\text{-caprolactone}] = 1 : 1$ .

Another example is the tercopolymerization of PO,  $\text{CO}_2$ , and trimellitic anhydride carried out using the catalytic system based on the composite material zinc glutarate/RET/DMC (RET =  $(\text{CCl}_3\text{CO}_2)_3\text{Y-glycerol-ZnEt}_2$ ) [125]. This catalytic system demonstrates the synergistic effect, exerting a considerable impact on the rate and selectivity of the process and the properties of the terpolymer. The most optimal is the system zinc glutarate/RET/DMC (1 : 1 : 10), which affords an almost alternating tercopolymer with a productivity of up to 66 g of copolymer/g of catalyst. The tercopolymer is characterized by  $M_n = 30.7 \times 10^3$  and  $D = 2.96$  and has excellent thermal stability.

#### *Mechanistic Aspects of Epoxide/ $\text{CO}_2$ Copolymerization*

Like for the homopolymerization of PO, the mechanism of the copolymerization of epoxides and  $\text{CO}_2$  is not completely clear, which leaves room for speculations [81, 109, 125-128]. So far, it has been generally accepted that the active sites of these materials are individual zinc atoms, although, for example,

for zinc glutarate and other carboxylates it has been established that the active site is composed of two closely spaced zinc atoms, one of which activates epoxide and another one is the source of nucleophilic alkoxide [129]. The key point for these catalysts is the molecular structure: based on calculation data it has been predicted that the “ideal” length of contacts Zn–Zn for carboxylates is within 4.3–5.0 Å, which explains a low activity of zinc succinate compared with higher homologs (zinc glutarate and others) [130]. The calculated length of contacts Zn–Zn for the model  $Zn_2[Co(CN)_6]Cl$  phase is 4.4 Å [5], and it meets this requirement, suggesting that the cooperative action of two zinc atoms is also realized in DMC catalysts [126]. In any case, issues of the ligand environment of zinc atom(s) and how it fits different qualitative and quantitative compositions of the materials still remain unclear.

If there is no initiator, active sites are zinc atoms connected to OR (R = H, *t*-Bu), while in the presence of an initiator they arise from dormant sites similarly to homopolymerization (then R = initiator alkyl) [131]. Interaction between active sites of the catalyst may occur via two pathways: initially with epoxide (Scheme 7A) or initially with CO<sub>2</sub> (Scheme 7B). In the first case fragment Zn–OCH(Me)CH<sub>2</sub>OR is formed, and at some step of polymerization the insertion of CO<sub>2</sub> will proceed to form carbonate intermediate **X**. In the second case fragment Zn–OC(O)R arises which upon interaction with epoxide will afford alkoxide intermediate **Y**. Then in both cases stages will repeat; as a result, PEC is formed but with different terminal groups, OCH(Me)CH<sub>2</sub>OR or OC(O)R. It is also generally accepted that Zn–OC(O)R should not react with CO<sub>2</sub>, since this reaction is unfavorable energetically [132]. Evidently, the reason for the above regioselectivity of PO/CO<sub>2</sub> ROCOP is different nature of zinc intermediates: epoxide regioselectively inserts into alkoxide Zn–OCH(Me)CH<sub>2</sub>OR, the only type of intermediate in PO ROP, while into carboxylate Zn–OC(O)R, which is less nucleophilic, it inserts nonregioselectively.

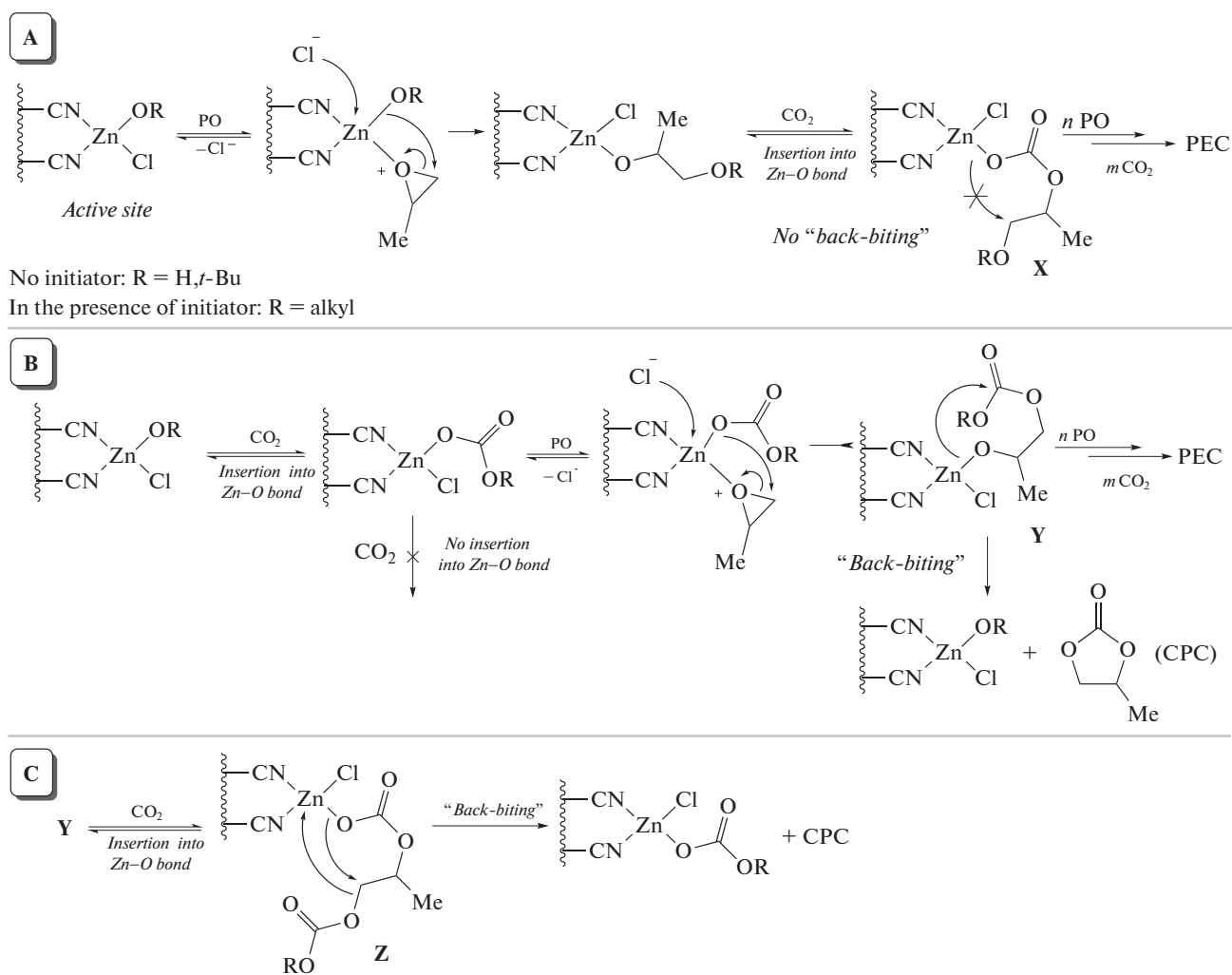
Note that for intermediate of type **Y** the intramolecular attack of alkoxide Zn–O via the carbonate fragment (back-biting) is possible, in which the regeneration of the active site occurs and cyclic carbonate is formed (in this case, propylene carbonate **CPC**; Scheme 7B). For intermediate of type **X**, in which zinc is connected to the carbonate fragment, similar attack is hardly possible (RO<sup>−</sup> is a poor nucleofuge under conditions of the S<sub>N</sub>2-reaction). However, if one more carbonate fragment is inserted into intermediate **Y**, then for the resulting carbonate intermediate **Z** back-biting will be possible (Scheme 7C). Theoretically back-biting attack can occur at any stage of polymerization but the necessary condition is the alternation of ester and carbonate fragments. Despite a higher thermodynamic stability of CPC compared with PC,

$E_a$  for the back-biting stage is higher than that for the stages of chain propagation, as evidenced by an increase in the yield of CPC with increasing temperature [126]. A similar situation is observed in the case of homogeneous catalysis, for example, for the binuclear zinc complex: quantum-chemical calculations predict that back-biting has a higher  $E_a$  than the stages of propoxylation or CO<sub>2</sub> insertion [133].

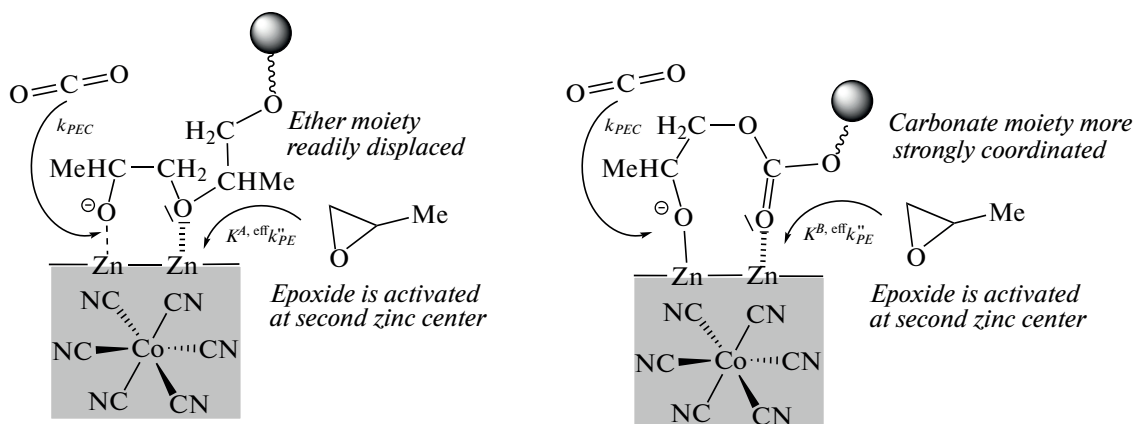
X.-K. Sun et al. made an attempt to ascertain the mechanism of copolymerization of CHO and CO<sub>2</sub> using kinetic studies and mass spectrometry of reaction mixtures [84]. The main conclusion of this work is that fragments Zn–OR (R = H, *t*-Bu) act as initiators, and at the early stages of the process they tend to react with epoxide molecules producing homopolymer fragments rather than with CO<sub>2</sub> to yield a random copolymer. Quantum-chemical calculations of average energies for the adsorption of CHO and CO<sub>2</sub> on the face (001) of the model DMC crystal confirm that copolymerization is predominantly initiated due to the coordination of epoxide to the active site (Scheme 7A) [134]. The formation of epoxide homopolymer can be explained within the concept that the active site is composed of two neighboring zinc atoms and the resulting different coordination of the penultimate unit of the growing chain [135]. It is known that the ether fragment (Fig. 1A) is less strongly bonded to zinc than to the carbonate group (Fig. 1B); therefore, the next epoxide molecule is more easily coordinated and activated via the zinc atom bonded to the ether fragment and inserted into the chain. This leads to the appearance of oligoether blocks of average length. According to statistical Monte Carlo calculations based on the kinetic data for the reaction of PO and CO<sub>2</sub>, these oligoether sequences should predominantly contain three–four PO units [135, 136].

It appears that the mechanism of the CO<sub>2</sub> insertion stage is similar to that realized in the case of the zinc-containing fragment of carbonic anhydrase catalyzing the transformation of CO<sub>2</sub> and H<sub>2</sub>O into HCO<sub>3</sub><sup>−</sup> [12]. Carbonic anhydrase can be regarded as an analog of DMC catalysts: a zinc atom is bonded to three nitrogen atoms of imidazole rings (in histidine residues) and a water molecule. Under the action of active portions of the peptide chain Zn–OH<sub>2</sub><sup>+</sup> is deprotonated to form Zn–OH and interaction with CO<sub>2</sub> proceeds via a four-membered transition state with participation of atoms of Zn–O and C=O bonds. Similarity between carbonic anhydrase and DMC catalysts also manifests itself in O/S-exchange reactions, since it converts CS<sub>2</sub> into COS and COS into CO<sub>2</sub> [137]. Note that individual zinc hydroxide-hexacyanocobaltate(III)  $Zn_2[Co(CN)_6]OH$  exhibits a lower activity than DMC materials containing glym as a ligand [138].

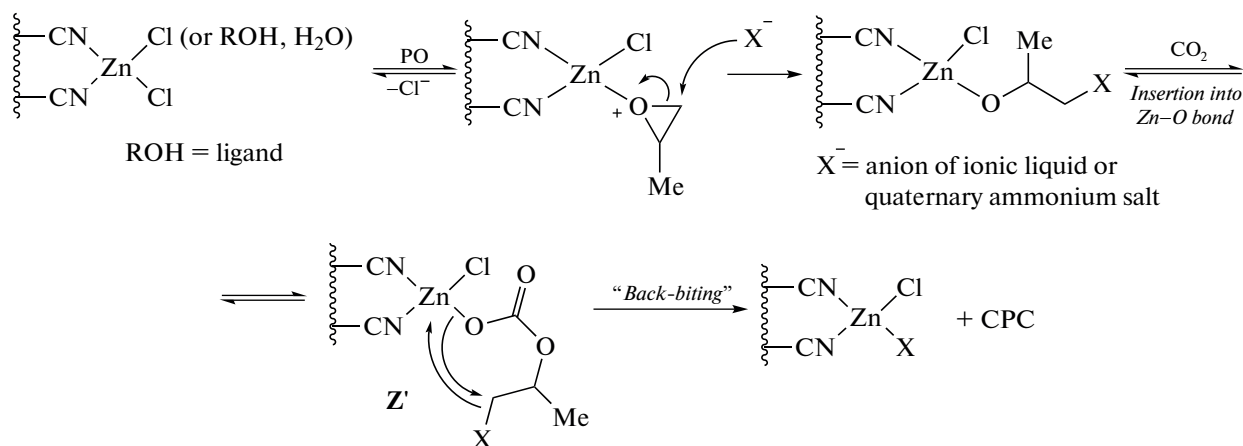
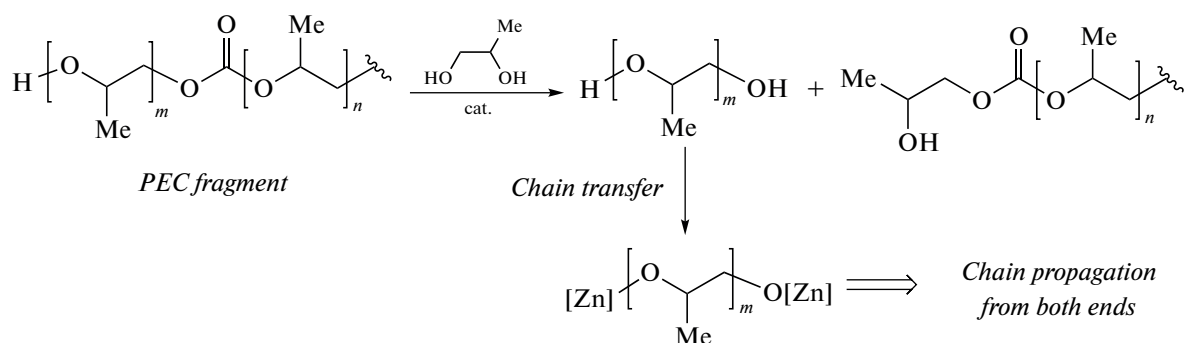




Scheme 7.

A: Terminal alkoxide ( $t \geq 2$ )B: Terminal carbonatealkoxide ( $t = 1$ )

**Fig. 1.** The proposed schematic coordination of a growing polymer chain in the case of penultimate (A) alkoxide or (B) carbonate unit which explains difference in the rates of insertion of a subsequent PO molecule ([135], copyright © 2020 American Chemical Society). Color figure is available in the electronic version.

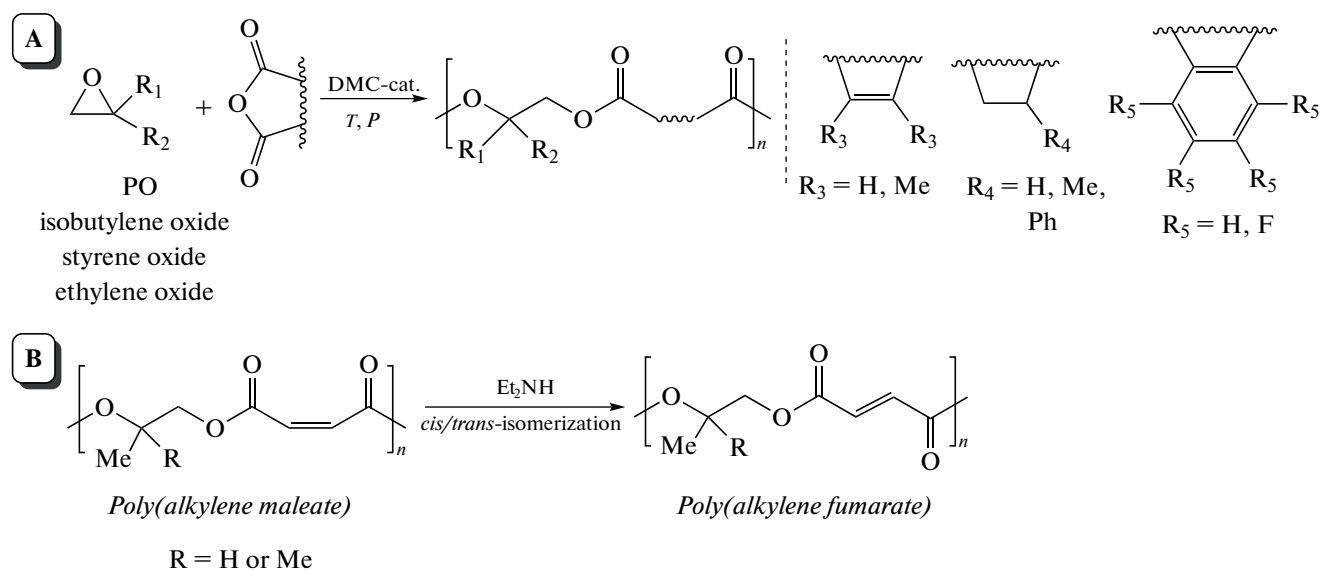


In the absence of a starter, copolymerization can lead to bimodal MWD, for which the side transesterification reaction is responsible [133]. In the presence of traced moisture epoxide hydrolyzes to form diol (in the case of PO, propylene glycol), which can transesterify polymer chains via carbonate units. As a consequence, macromolecules containing OH groups at both ends are formed which are capable of simultaneous growth from both ends.

Although DMC materials efficiently catalyze the copolymerization of epoxides and CO<sub>2</sub>, the additives of ionic liquids or quaternary ammonium salts can change selectivity of the catalytic system, making cycloaddition the main process. In the case of Zn–Co DMC catalysts, the use of cetyltrimethylammonium bromide gives an almost quantitative yield of cyclic carbonates for a number of epoxides [139], but for CHO the yield is as low as 46% [140]. The use of Bu<sub>4</sub>NCl as an additive is also accompanied by the formation of cyclic carbonates with a yield above 95% and for CHO it attains 75% [141]. Zn–Fe(III) catalysts with TB and polyethers (poly(ethylene glycol), poly(propylene glycol), PTMEG) as coligands, which are prepared by mechanochemical synthesis, demon-

strate a very high selectivity in the cycloaddition of PO and CO<sub>2</sub>—the yield of CPC is up to 98% even in the absence of ionic liquids or quaternary ammonium salts [62, 142]. One of the applications of DMC-catalyzed cycloaddition of epoxide/CO<sub>2</sub> is the synthesis of novel polymer materials [143–145].

The role of ionic liquids and quaternary ammonium salts is yet insufficiently studied, but the authors [139, 140] proposed the feasible mechanism for their action. A salt anion (usually halide) may nucleophilically attack the coordinated epoxide, thereby initiating the reaction. Upon further insertion CO<sub>2</sub> can form carbonate intermediate Z', which experiencing back-biting (halide anion is a good nucleofuge), leads to the formation of cyclic carbonate. Thus, the role of an ionic liquid or a quaternary ammonium salt is based on the ability of halides to act both as a nucleophile and a leaving group. It appears that an important difference of the cycloaddition process from the ROP of epoxides and the ROCOP of epoxide/CO<sub>2</sub> is the absence of fragmentation of catalyst particles, which confirms the possibility of its regeneration without reduction in efficiency for at least five cycles [139]. Moreover, it cannot be ruled out that ionic liquids or



Scheme 10.

quaternary ammonium salts somehow contribute to the diffusion of  $\text{CO}_2$  into the reaction mixture, enhancing the probability of its insertion and formation of intermediate  $Z'$ .

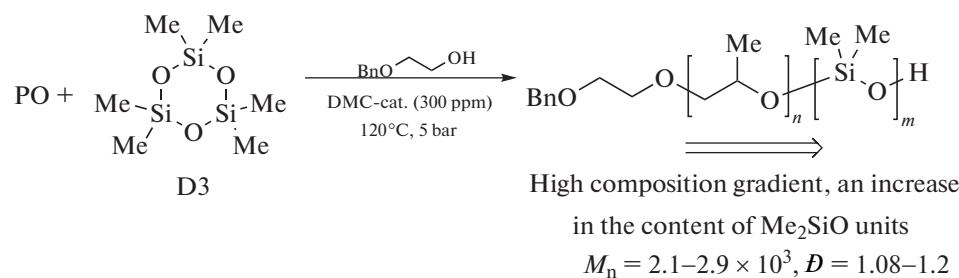
#### OTHER DMC-CATALYZED RING-OPENING (CO)POLYMERIZATION REACTIONS

Along with the copolymerizations of epoxides with  $\text{CO}_2$  and allied reactions considered above, the ROP of functionalized epoxide monomers, such as epichlorohydrin [146, 147] and glycidol [148, 149], and the ROCOP of PO with other epoxides or other comonomers have been studied. Particularly attractive is the copolymerization of ethylene oxide and PO—the two largest tonnage epoxides. Polyether polyols produced from these comonomers possess not only the required surfactant properties but also reactivity in the subsequent synthesis of PUs, since a part of macromolecules contains terminal primary OH groups [150, 151]. The properties of PPO can be modified via the copolymerization of PO with CHO [152], glycidol [153], or methyl glycidyl ether [154]. Despite a higher activity of PO in DMC-catalyzed polymerization compared with other epoxides, the ROCOP of PO/glycidol yields hyperbranched polyethers with a high degree of branching (72%), which indicates a considerable conversion of glycidol [153], and the copolymerization of PO/methyl glycidyl ether affords almost ideally alternating copolymers [154]. The introduction of methyl glycidyl ether units into the hydrophobic chain of PPO enhances the hydrophilicity of macromolecules, and polyols based on these copolymers can be considered an alternative to polyols based on PO/ethylene oxide copolymers in the synthesis of soft PU foams. The DMC-catalyzed polymerization of epichlorohydrin

affords a regioregular polymer containing more than 99% of head-to-tail units [147].

A very promising direction is the copolymerization of epoxides with cyclic anhydrides to afford polyesters (Scheme 10A). These copolymers demonstrate the clusteroluminescence phenomenon and are referred to as clusteroluminogens [155, 156]. Currently, traditional organic luminophores are compounds or polymers with long  $\pi$ -conjugated aromatic structures and fine-tuned luminescent properties. However, these materials often have poor solubility and high toxicity and their industrial production is considerably limited because of a high cost of precursors and complex multistep synthesis [155]. In contrast to aromatic conjugated polymers, the considered polyesters have no conjugation chains and are characterized by biocompatibility, processability, and biodegradability. The luminescent properties of such polyesters are primarily affected by the balance between the flexibility and rigidity of macromolecules, which depends on the nature of substituents in epoxide and the structure of anhydride. PO is the main epoxide monomer in the studied reactions, and maleic anhydride [103, 155, 157–160], succinic anhydride and its derivatives [156, 158, 159], phthalic anhydride [155, 158, 159], and others [155] are used as anhydrides. Furthermore, epoxides, such as isobutylene oxide [161] and styrene oxide and ethylene oxide [156], have been studied in this copolymerization.

In the presence of acid catalysts isobutylene oxide easily isomerizes into isobutyraldehyde and can be involved in condensation with one more isobutylene oxide molecule to produce cyclic acetal, isobutylal; therefore, in the presence of metal-complex cationic catalysts and organocatalysts, the ROCOP of isobutylene oxide/anhydride is associated with low yields of



Scheme 11.

target copolymers [161]. It is unusual that under the conditions of DMC-catalyzed copolymerization of isobutylene oxide/anhydride products are almost alternating copolymers (by more than 99%) with the regioregular structure (>90% of head-to-tail units) and  $M_n$  up to  $42.3 \times 10^3$ . For copolymers based on PO and styrene oxide no data are available on the regioselectivity of a similar process. As opposed to PO/ $\text{CO}_2$  copolymers, the copolymers of PO with methyl- or phenylsuccinic anhydride are characterized by a low content of polyether fragments: the content of polyester is 90–91%, which suggests almost alternating copolymers [156]. The ROCOP of ethylene oxide/methylsuccinic anhydride naturally yields an almost alternating copolymer [156], since it is known that the DMC-catalyzed homopolymerization of ethylene oxide does not take place [3].

Moreover, the quantitative *cis/trans*-isomerization of poly(alkylene maleates), maleic anhydride copolymers, into poly(alkylene fumarates) was realized and was accompanied by the qualitative change in the properties of polymers [161, 162] (Scheme 10B). In the case of poly(propylene maleate)—the PO/maleic anhydride copolymer—this isomerization converts it into biodegradable poly(propylene fumarate) [162], and for the isobutylene oxide/maleic anhydride copolymer physicochemical properties are considerably improved due to an increase in the melting temperature from 72 to 153°C [161].

It is worth mentioning the unusual copolymerization of PO and hexamethylcyclotrisiloxane (**D3**) [163] affording random copolymers with a high composition gradient: at the beginning ether groups predominate, while siloxane units prevail at the end.

The introduction of siloxane fragments improves the hydrophobicity and imparts high flexibility to polymer chains: at the content of  $\text{Me}_2\text{SiO}$  units 46 mol %, the water contact angle increases by 14° and  $T_g$  decreases from –67 to –95°C compared with individual PPO.

There is interest in DMC catalysts in relation to the polymerization of  $\epsilon$ -caprolactone. Liu et al. reported [164] that for the effective DMC-catalyzed ROP of  $\epsilon$ -caprolactone ~1% PO additives are needed. However, this apparently simply means that the process

requires an OH-containing initiator. The successful polymerization of  $\epsilon$ -caprolactone in the presence of a starter was carried out by the team headed by Kim [73, 165], who used both traditional TB-containing catalysts and catalysts containing acetoacetic ester or alkyl nitrile as ligands. The resulting polycaprolactones were characterized by molecular weights 950–10 100 and  $D = 1.10\text{--}1.87$ , and the use of various initiators, such as poly(propylene glycol), ethylene glycol, propylene glycol, glycerol, and sorbite, led to the production of corresponding polyols with different number of OH terminal groups controlling the properties of polymers [165]. As an application based on these polyols the synthesis of PU elastomers was implemented. In addition, the copolymerization of  $\epsilon$ -caprolactone and glycidol yielding hyperbranched polyols was realized. Catalysts with alkyl nitriles as ligands showed much higher activity than the TB-containing catalyst. The highest activity was exhibited by catalysts based on isobutyronitrile (turnover frequency 83  $\text{h}^{-1}$ ), which produced polycaprolactones with molecular weights 1000–9800 and  $D = 1.1\text{--}1.5$  [73].

## PROSPECTS AND NEW DIRECTIONS

Undoubtedly, DMC catalysts are a unique tool for creating novel macromolecular compounds from cyclic monomers. This is supported by a large body of the synthesized (co)polymers; however, most papers concern only their thermal properties. It can be expected that the intensive research of physicochemical characteristics (mechanical properties, structural-phase transformations, and degradation behavior) of these polymers will follow in the near future and understanding of the fundamental structure–property relationship, as applied of the already synthesized (co)polymers, will give further impetus to targeted synthesis in this area.

As opposed to the synthesis of PPO, in which the advantage of zinc–cobalt DMC catalysts is undeniable, nontraditional DMC catalysts also have a potential in other (co)polymerization processes with the participation of cyclic monomers. Some of them are ahead of Zn–Co materials in certain properties but are inferior to them in others. Probably, polymerization

processes different in nature require the choice of DMC catalysts optimal for them; therefore, further synthesis of novel nontraditional DMC materials will continue. Furthermore, catalytic systems based on mixtures of Zn–Co and nontraditional DMC catalysts could theoretically combine the positive properties of individual components and demonstrate the synergistic effect, but these works are still few in number.

There is good prospect for the synthesis of multi-block copolymers of various architecture. In this regard, multicomponent catalytic systems based on DMC catalysts are of value since they would allow for the one-pot synthesis of novel copolymers. It also seems that the scope of comonomers studied in DMC-catalyzed copolymerizations will be expanded, for example, due to lactides and cyclosiloxanes. It is these comonomers that should be the focus of new research works.

The intriguing direction is the DMC-catalyzed ROCOP of epoxide/cyclic anhydride, the products of which unconjugated polyesters, demonstrate clusteroluminescence. Research in this area has just begun, and the key issue concerns the effect of the nature of DMC catalysts and comonomers on the structure and microstructure and, eventually, luminescent properties of these polyesters.

Inevitably there will be works related to the scaling and research of technological aspects of DMC-catalyzed processes, primarily the production of PEC and multicomponent ROCOP involving epoxides and CO<sub>2</sub>. These processes necessitate intensification and modification in terms of productivity and selectivity, as well as CO<sub>2</sub> conversion. Addressing these issues is likely to require further investigations of composite catalysts based on DMC materials.

## CONCLUSIONS

As is evident from the forgoing, the unique properties of DMC catalysts are manifested not only in the homopolymerization of PO but also in (co)polymerization reactions involving epoxides and other cyclic monomers. The current focus of research is on the DMC-catalyzed copolymerization of epoxides with CO<sub>2</sub> or cyclic anhydrides and multicomponent reactions. The study of similar processes necessarily addresses issues of chemo- and regioselectivity of reactions. Due to the addition of ionic liquids or other homo- or heterogeneous catalysts in the ROCOP of epoxides and CO<sub>2</sub> DMC catalysts can be tuned for the selective synthesis of PEC, PC, or cyclic carbonates. Although new and new knowledge is emerging, the mechanism of the catalytic action of DMC materials is not entirely clear so far. It appears that the decisive role is played by L<sub>3</sub>Zn–OH fragments; their presence makes DMC materials developed by Man similar to carbonic anhydrase—a highly efficient catalyst created by Nature. High expectations in resolving these issues

are placed on quantum-chemical simulations. In our opinion, promising are multicomponent catalytic systems based on DMC catalysts, which would combine positive properties of individual components and allow for the synthesis of polymer materials of the future.

## FUNDING

This work was supported by the Russian Science Foundation (project 21-73-30010).

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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*Translated by T. Soboleva*

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