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A novel and faster route for the synthesis of polyether–polycarbonate from carbon dioxide and epoxide through microwave irradiation

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Abstract—The purpose of this study was to investigate the utilization of CO_2 in order to obtain polyether–polycarbonate by the co-polymerization of epoxide with CO_2 using microwave irradiation. Double metal cyanide containing Zn with Co, Fe(II), Fe(III) and Ni has been utilized as a catalyst for the co-polymerization reaction. The effect of microwave power, catalyst amount and types of catalysts has been studied. The microwaves were found to be successful in the synthesis of polyether–polycarbonate in a shorter reaction time with higher turnover numbers than those in conventional methods.

Keywords: Microwave; polyether–polycarbonate; carbon dioxide; co-polymerization.

INTRODUCTION

Since the first reports on microwave-assisted high-speed organic synthesis by the groups of Gedye and Giguere in 1986 [1, 2], microwaves have attracted a considerable amount of interest in recent years. The rapid increase in the number of publications over the past 10 years agrees with the increased interests for this non-conventional energy source as a driving force for chemical reactions. This enabled a way to the general availability of new and reliable microwave instrumentations rather than domestic or modified microwave ovens. Several reports and reviews have been published on the utilization of microwaves in organic synthesis [3–6], such as solvent-free reactions [7, 8], cycloaddition reactions [9], synthesis of radioisotopes [10], fullerene chemistry [11], polymers [12],

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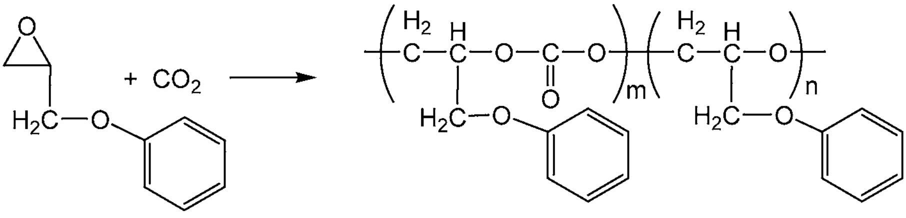
heterocyclic chemistry [13], carbohydrates [14], homogeneous and heterogeneous catalysis [15], medicinal and combinatorial chemistry [16] and green chemistry [17–19]. The main attributes of microwave-assisted organic synthesis is the dramatic acceleration of chemical reactions as consequence of the higher heating rate (5–1000-fold) compared to conventional heating. Compared to the traditional methods in organic synthesis, microwave saves the reaction time significantly along with the improvement in yields of products very often. It has been demonstrated that some transformations which were practically impossible by conventional heating methods were successfully carried out using microwave irradiations. The shorter reaction time unlocks the conceptualization for performing new ideas and its repetition to produce modified protocols for the synthetic reactions.

Utilization of carbon dioxide has become a hot trend among the scientists for effective reduction of this green house gas through the chemical reactions to generate valuable products. Being a promising step towards the sequestration of CO_2, cycloaddition or co-polymerization of CO_2 with epoxides gained more attention. In order to search for an environmentally benign counterpart of toxic phosgene as a carbonyl source, coupling of CO_2 with epoxides catalyzed by Et_2Zn/H_2O was first discovered by Inoue *et al.* [20] in 1969. To date several catalysts have been reported and reviewed for the effective utilization of CO_2 [21–23] including double metal cyanide complexes (DMC). DMC complexes were considered to be a good catalyst for the ring opening polymerization of epoxides. But lately various DMC catalysts were utilized successfully for the co-polymerization of epoxide with CO_2 by conventional methods [24–26].

The pressurized reaction in microwave was a technological challenge till the first report on the cycloaddition reaction of CO_2 with epoxides [27]. The reaction was not successful enough to produce cyclic carbonate of various epoxides with higher yields using a microwave batch reactor (MBR). In this study we have synthesized a series of Zn–M DMC, where M = Co, Fe(II), Fe(III) and Ni. The catalytic effect of these catalysts at different microwave powers on the co-polymerization of epoxide with CO_2 (Scheme 1) under microwave irradiation were investigated.



PGE
(Phenyl glycidyl ether)

(Polyether-polycarbonate)

Scheme 1. Co-polymerization of phenyl glycidyl ether (PGE) with CO_2.

EXPERIMENTAL

Materials and solvents

All materials, zinc chloride, potassium hexacyanocobaltate (III) ($K_3Co(CN)_6$), potassium ferricyanide (III) ($K_3Fe(CN)_6$), potassium ferrocyanide (II) trihydrate ($K_4Fe(CN)_6 \cdot 3\ H_2O$), potassium tetracyanonickelate (II) hydrate ($K_2Ni(CN)_4 \cdot xH_2O$), tertiary butyl alcohol, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (M_n approx. 1100) and phenyl glycidyl ether (PGE, 99%), were purchased from Aldrich and used without further purification. Carbon dioxide of 99.999% purity was used without further purification.

Catalyst synthesis and characterization

All DMC catalysts containing Zn, Co, Fe(II), Fe(III) and Ni were synthesized by the procedure reported elsewhere [28]. The morphology of the catalysts synthesized were characterized by X-ray diffraction (XRD) with RINT2000 Wide angle goniometer 185 using Cu Kα at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) analysis was done with a ESCALAB 250 induced electron emission spectrometer with Al Kα (1486.6 eV, 12 mA, 20 kV). IR spectra of the catalysts were obtained in transmission mode using React IR.

Co-polymerization of epoxide with CO_2

Co-polymerization of epoxides with CO_2 was carried out in a 50 ml Pyrex glass reactor equipped with a magnetic stirrer. A multimode microwave reactor (KMIC 2KW) containing source with continuously adjustable power from 0 to 2000 W using a 3-stub tuner operating at a frequency of 2450 MHz were utilized for the reactions. In a typical co-polymerization reaction, the required amount of dried catalyst was taken in the reactor, followed by adding desired amount of purified PGE (36.9 mmol (5 ml)) using a syringe. Then the reactor was capped by the reactor head inside the microwave cavity. The reactor was purged several times with CO_2 and then pressurized with CO_2. The reaction was started by microwave irradiation at a particular microwave power for sufficient time along with stirring. After a certain period, the pressure inside the reactor was reduced to atmosphere to terminate the co-polymerization. The product was dissolved in dichloromethane and filtered to remove the catalyst. Polymer formed was precipitated out by adding excess methanol, filtered and dried under vacuum at 60°C. The soluble portion of the product was also recovered from the solvent.

Yield of the polymer formed was obtained gravimetrically. The polymer formed is characterized by React IR for carbonate linkage, ^{1}H-NMR (Varian Gemini 2000 (300 MHz) in $CDCl_3$) for the percentage of carbonate content and gel permeation chromatography (Waters 515, using polystyrene as standard and THF as solvent) for molecular weight and polydispersity index (PDI).

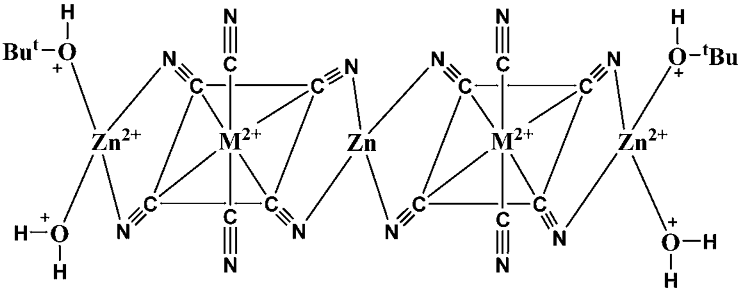


Figure 1. Tentative structure of the double metal cyanide (DMC) complex.

Table 1.
XPS analysis of DMC catalysts

Compound	Binding energy (eV)						at%	
	Zn_{2p3}	M_{2p3}	O_{1s}	N_{1s}	C_{1s}	Cl_{2p}	Zn_{2p3}	M_{2p3}
Zn^{Cl}–Co	1020.36	780.28	531.55	398.51	285.79	197.96	61.83	1.07
Zn^{Cl}–Fe(II)	1019.56	707.02	531.98	397.62	284.8	–	58.84	0.86
Zn^{Cl}–Fe(III)	1021.69	708.09	532.33	397.49	284.42	197.49	57.48	0.7
Zn^{Cl}–Ni	1020.6	854.85	532.78	399.52	286.11	201.1	65.78	1.5

RESULTS AND DISCUSSION

Catalyst characterization

The general formula of the DMC catalyst synthesized is expected to have the formula $Zn_3M(CN)_6(ZnCl_2)_x(H_2O)_yCA$, where M=Co, Fe(II), Fe(III) and Ni (Fig. 1). Even though the insolubility of catalysts restricted their thorough characterization, the surface formulation could be examined by XPS and XRD and the electronic properties by IR analysis. The results of XPS analysis of the catalysts are summarized in Table 1. The binding energy of the zinc atom of $ZnCl_2$ (1023.7 eV) is higher than all the DMC catalyst formed after complexation. The shift might be attributed from the coordination of zinc atom to the oxygen atoms of co-complexating agent (Fig. 2).

Different surface properties and alteration of the crystal structure of the catalysts synthesized could be shown by the X-ray diffraction spectra (Fig. 3). All the spectra, except Zn^{Cl}–Co DMC, exhibited broad signals (*d*-spacing of Zn^{Cl}–Co = 5.91, 5.13, 3.63, 2.56 and 2.29; Zn^{Cl}–Fe(II) = 5.42, 4.08, 3.64, 2.53 and 2.37; Zn^{Cl}–Fe(III) = 5.89, 5.12, 3.61, 2.57 and 2.3; Zn^{Cl}–Ni = 4.15, 4.08, 3.69, 3.47 and 2.52). The XRD spectra described the cubic lattice structure of the catalyst, thereby proving its amorphous morphology.

Infrared spectra of all the four DMC catalysts are depicted in Fig. 4. The ν(CN) of free CN^- is 2131.3 ($K_3Co(CN)_6$), 2046.5 ($K_4Fe(CN)_6 \cdot 3H_2O$), 2117.8 ($K_3Fe(CN)_6$) and 2125.6 ($K_2Ni(CN)_4 \cdot xH_2O$). The CN^- ion acts both as a σ-donor by donating

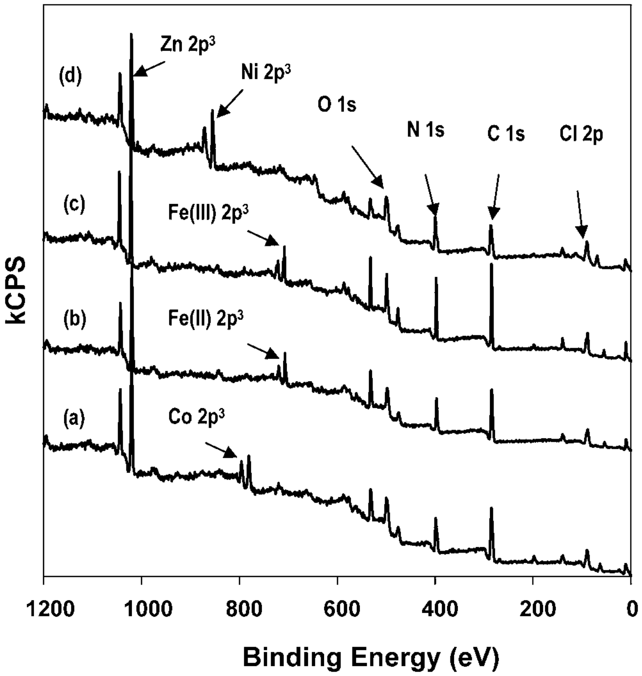


Figure 2. XPS spectra of the DMC catalysts; (a) Zn^{Cl}–Co, (b) Zn^{Cl}–Fe(II), (c) Zn^{Cl}–Fe(III) and (d) Zn^{Cl}–Ni.

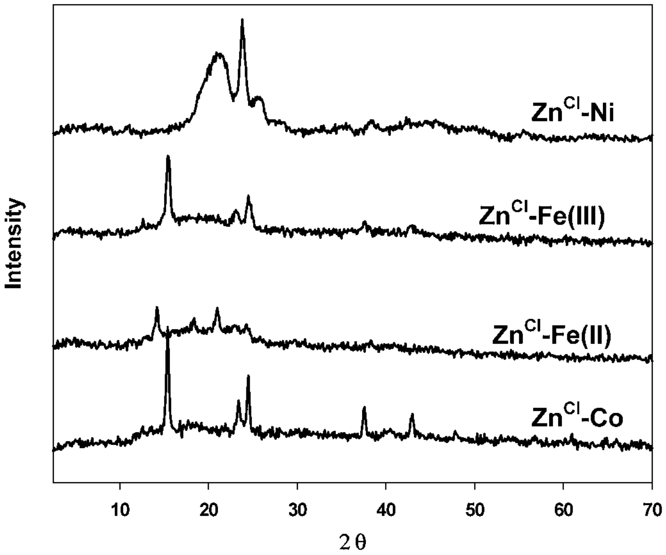


Figure 3. XRD patterns of DMC catalysts.

electrons to the corresponding metal in DMC catalysts and an electron donor by coordination to the zinc metal, which could be clarified by the higher frequency shift of ν(CN) peaks.

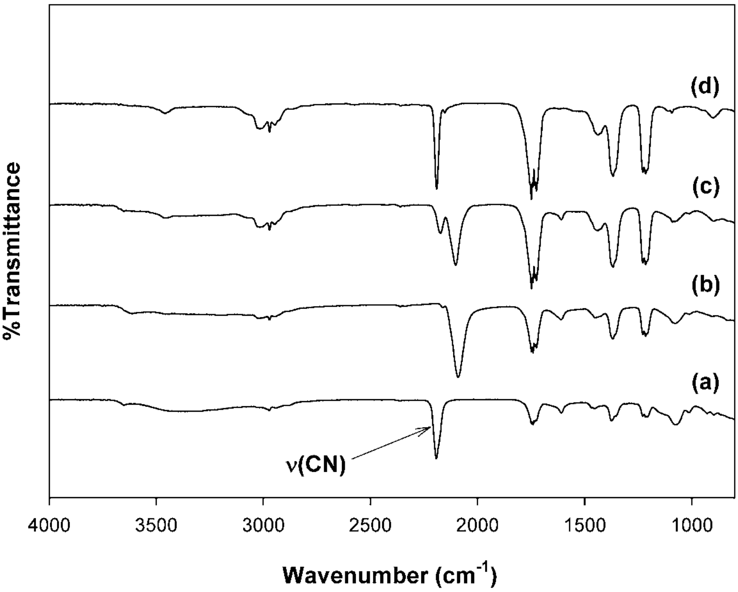


Figure 4. React IR spectra of DMC catalysts; (a) Zn^{Cl}–Co, (b) Zn^{Cl}–Fe(II), (c) Zn^{Cl}–Fe(III) and (d) Zn^{Cl}–Ni.

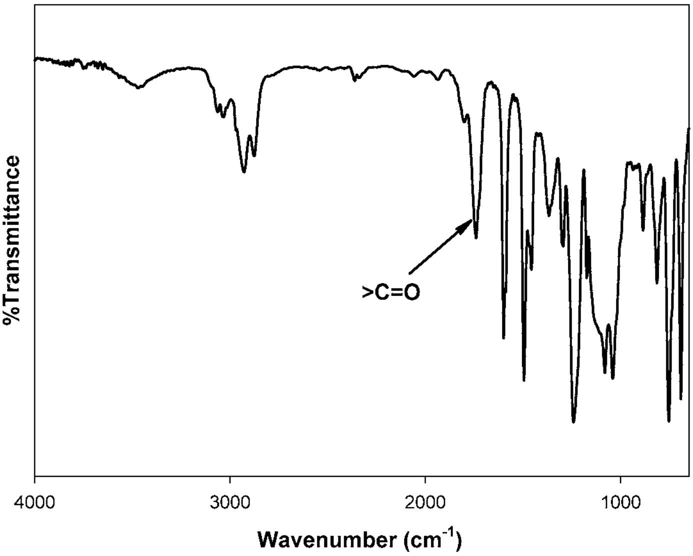


Figure 5. React IR spectrum of polyether–polycarbonate from PGE and CO_2.

Co-polymerization of epoxide with CO_2

The co-polymerization of PGE with CO_2 was carried out under the influence of microwave radiations. The reaction was found to be successful to get higher conversion upon microwave irradiation. The polymer formed was confirmed and characterized by React IR (Fig. 5) and ^{1}H-NMR, and its molecular weight and

Table 2.
Effect of microwave power on co-polymerization of PGE with CO_2

Entry	MW power (W)	Time (min)	PGE conversion[a] (mol%)	f_{CO_2}[b]	M_n[c]	PDI[c]	TOF[d]
1	100	11.5	99.8	1.5	1693	1.5	602
2	200	4.5	99.8	1.0	1983	2.1	1435
3	300	4.2	99.6	0.7	1615	1.5	1366
4	400	4.0	99.7	0.8	1461	1.4	1264
5	500	3.5	99.5	1.4	1549	1.4	1766

Polymerization conditions: PGE = 36.9 mmol, catalyst = 0.01 g Zn^{Cl}–Co, $P_{CO2}(25°C) = 140$ psi.
[a] Obtained from GC analysis.
[b] Carbonate content = ([carbonate]/([carbonate] + [ether])) × 100, determined by ^{1}H-NMR.
[c] Data from GPC.
[d] Turnover frequency = (g polymer/g catalyst)/h.

polydispersity index was obtained from GPC analysis. The co-polymerization was executed at different microwave powers ranging from 100 to 500 W. The results obtained were tabulated in Table 2. For a perfect polycarbonate formed by the incorporation of CO_2 the polymer chain should contain only carbonate linkage. But as a side reaction, the kinetically controlled homo-polymerization of PGE resulted in polyether linkages. The percentage of incorporation of CO_2 could be easily measured from the integrated ^{1}H-NMR spectrum.

Table 2 shows the effect of microwave power on the co-polymerization of PGE with carbon dioxide. On increasing the microwave power from 100 to 500 W the time of polymerization reduced considerably and the TOF value increased up to 1766, but the microwave power has negligible effect on molecular weight. In all cases the conversion of PGE is found to be above 99.5%, among that the highest conversion is obtained for 100 W microwave powers. The highest molecular weight was attained when the reaction was carried out at 200 W but the molecular weight distribution became broader than the other cases. But in all the cases the CO_2 incorporation is found to be too low. In our previous work [25], with the same Zn–Co DMC catalyst (0.02 g) we have synthesized a polycarbonate with 10% carbonate linkages at 50°C for 36 h from PGE ($M_n = 9300$, PD = 3.6 and TOF = 13) without microwave irradiation. On comparison with conventional reaction, microwave irradiation was found to be successful to give polyether–polycarbonate with higher TOF and narrow molecular weight distribution in a shorter reaction time.

Amount of catalyst has found to have remarkable influence on the polymerization reaction. Table 3 explains this trend in which, on decreasing the catalyst amount from 0.02 to 0.01 g, the molecular weight as well as the carbonate content increased. The monomer to catalyst ratio increases on decreasing the catalyst amount; thereby the number of monomers inserted to the reactive center will be higher, thus increasing the molecular weight. Comparing entry 1 in Table 2 and entry 2 in Table 3, both reactions carried out at 100 W power with 0.01 g catalyst and 140 psi CO_2 pressure, an increased reaction time increased the carbonate content

Table 3.
Effect of catalyst amount on the co-polymerization reaction

Entry	Catalyst (mg)	MW power (W)	Time (min)	PGE conversion[a] (mol%)	f_{CO_2}[b]	M_n[c]	PDI[c]	TOF[d]
1	20	100	20	100	3.85	5273	3.99	825
2	10	100	35	99.8	4.76	13471	3.98	840
3	5	100	50	94.6	4.76	12591	7.60	41

Polymerization conditions: PGE = 36.9 mmol, catalyst = Zn^{Cl}–Co, $P_{CO2}(25°C) = 140$ psi.

[a] Obtained from GC analysis.

[b] Carbonate content = ([carbonate]/([carbonate] + [ether])) × 100, determined by ^{1}H-NMR.

[c] Data from GPC.

[d] Turnover frequency = (g polymer/g catalyst)/h.

Table 4.
Effect of other DMC catalyst on the co-polymerization reaction

Entry	MW power (W)	Catalyst	Time (min)	PGE conversion[a] (mol%)	f_{CO_2}[b]	M_n[c]	PDI[c]	TOF[d]
1	200	Zn^{Cl}–Co	4.5	99.8	1.0	1983	2.1	1445
2	200	Zn^{Cl}–Fe(II)	10	44.1	–	–	–	Trace
3	200	Zn^{Cl}–Fe(III)	10	46.4	–	–	–	Trace
4	200	Zn^{Cl}–Ni	10	48.1	–	–	–	Trace

Polymerization conditions: PGE = 36.9 mmol, catalyst = 0.01 g, $P_{CO2}(25°C) = 140$ psi.

[a] Obtained from GC analysis.

[b] Carbonate content = ([carbonate]/([carbonate] + [ether])) × 100, determined by ^{1}H-NMR.

[c] Data from GPC.

[d] Turnover frequency = (g polymer/g catalyst)/h.

in polymer formed. In fact, to obtain higher carbonate there is an induction period required to activate the catalyst, otherwise a homo-polymerization will be dominant. Because of this reason longer reaction time activates the catalyst for the effective incorporation of CO_2 to give higher carbonate linkages [29].

The effect of other DMC catalyst was tested for the reaction under microwave irradiation. Among the catalyst tested Zn^{Cl}–Co DMC catalyst showed better activity towards co-polymerization than Zn^{Cl}–Fe(II), Zn^{Cl}–Fe(III) and Zn^{Cl}–Ni. The conversion of PGE for these catalysts was obtained around 44% (entries 2, 3, 4 in Table 4). Trace amount of polymer were formed even after 10 min irradiation at 200 W microwave power. This could be explained by the fact that the activity of DMC catalyst depends on the non-crystalline content [29], usually DMC catalysts with higher activity have a lower level of crystallinity. From the XRD results of the various DMC catalysts, the crystallinity decreases in the order Zn^{Cl}–Fe(II) > Zn^{Cl}–Fe(III) > Zn^{Cl}–Ni > Zn^{Cl}–Co. The amorphous Zn^{Cl}–Co DMC complex showed higher catalytic activity than others.

CONCLUSION

Microwave-induced polyether–polycarbonate synthesis from phenyl glycidyl ether and CO_2 were carried out successfully at different microwave powers ranging from 100 to 500 W using various zinc-based double metal cyanide catalyst containing Co, Fe(II), Fe(III) and Ni. Among the four DMC catalysts used, Zn^{Cl}–Co catalyst has proved to be the best. Zn^{Cl}–Co gave >95% conversion of the monomer with higher TOF (=1766). The CO_2 pressure, as well as the catalyst amount showed good agreement with the percentage of carbonate content (f_{CO_2}) and molecular weight. At lower pressures the catalyst showed more affinity towards the production of polyether than polycarbonate. The catalyst amount played a crucial role in the increment of molecular weight.

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