ChemComm

Dual-Site Catalysis for Sustainable Polymers to Replace Current Commodity Polymers – Carbonylative Copolymerization of Ethylene, Ethylene Oxide, and Tetrahydrofuran

Journal:	*ChemComm*
Manuscript ID	CC-COM-08-2020-005657.R3
Article Type:	Communication

COMMUNICATION

Dual-Site Catalysis for Sustainable Polymers to Replace Current Commodity Polymers – Carbonylative Copolymerization of Ethylene, Ethylene Oxide, and Tetrahydrofuran

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Yiwei Dai, Jiancheng Luo, Tianbo Liu, and Li Jia*

Zwitterionic Ni(Ⅱ)-catalyzed carbonylative copolymerization of ethylene and cyclic ethers is reported for synthesis of photolytically and hydrolytically degradable polymers. The segmented tetrapolymer products are composed of polyketone segments from alternating enchainments of CO and ethylene and poly(ether-co-ester) segments from non-alternating enchainments of CO, ethylene oxide, and tetrahydrofuran. Plastic and elastic products can be obtained via the general synthetic platform with the appropriate choice catalyst and polymerization conditions.

Plastic waste cumulated in the oceans[1] has accentuated the urgency for fundamental shifts of the polymer field toward sustainability. While efforts of recycling, composting, and incineration will reduce mismanaged wastes,[2] a fraction of them will inevitably escape into the environment. Degradable polymers can be expected to play a crucial role in minimizing the environmental hazard of plastic waste. To achieve overall sustainability, lowering carbon footprints must be considered simultaneously.[3] Naturally, any attempted solution must be commensurate with the scale of the problem. The sheer magnitude of polymer production[4] is perhaps the most challenging element in the pursuit of polymer sustainability. Commodity polymers are at the center of the issue in this regard. To begin with, the monomers of degradable polymers must be readily available at the scales and costs comparable to current commodity monomers such as ethylene and propylene.

Aliphatic polyketones[5] and polyesters[6] have each attracted considerable interests for various practical applications. As potentially degradable polymers, the ketone functionality undergoes photolysis when excited by ultraviolet lights at the end of the solar spectrum,[7] and the ester undergoes hydrolysis.[6b] Aliphatic polyketones,[8] poly(3-hydroxyalkanoate)s,[9] and polyglycolide[10] can be synthesized *via* carbonylative polymerizations of olefins, epoxides, and formaldehyde, respectively. If carbonylative copolymerization of these monomers could be realized, the resultant copolymers with aliphatic ketone and ester groups in their backbones would be degradable in a variety of environments on the surface of earth where light or water are present.[11]

Carbon monoxide (CO) is readily produced from a variety of carbon feedstocks including CO_2. Olefins can be produced from renewable sources,[12] and in particular, ethylene from bioethanol[13] or directly from CO_2.[14] These monomers, including epoxides, are available on the scales necessary for production of commodity polymers. The carbonylative polymerization route would therefore potentially satisfy all aforementioned criteria for sustainable commodity polymers.

However, olefins and the polar epoxides and aldehydes have different reactivities and so far required different catalysts for their polymerizations. We have recently shown that zwitterionic Ni(II) compounds catalyze carbonylative polymerization of cyclic ethers to give non-alternating copolymers composed of ester and ether repeat units.[15] The same type of catalysts catalyze the carbonylative polymerization of ethylene to give the alternating copolymer.[16] They display the dual reactivity because of the zwitterionic structure and the existence of both 4- and 5-coordinate acyl-Ni(Ⅱ) species[16c] in substantial amounts under conditions relevant to the polymerizations (Scheme 1). The 4-coordinate species, ***i***, allows ethylene coordination and insertion at the Ni(Ⅱ) center. The acyl site of the 5-coordinate species, ***ii***, is highly electrophilic and initiates cyclic ether enchainments. Ion-pairing at the propagating chain end allows re-establishment of the C-Ni bond in ***vii***. We report here that the dual reactivity of the zwitterionic Ni(Ⅱ) catalysts can be harnessed to synthesize tetrapolymers of CO, ethylene, ethylene oxide (EO), and tetrahydrofuran (THF). We further demonstrate that depending on the composition, the product can be either plastic to elastic.

The tetrapolymerization of CO, ethylene, EO, and THF was carried out in batch reactors at room temperature in neat mixtures of EO and THF under various CO and ethylene

---

*School of Polymer Science and Polymer engineering, The University of Akron, 170 University Avenue, Akron, Ohio 44325

Electronic Supplementary Information (ESI) available: Experimental details, ^1H-^1H COSY, additional ^1H NMR spectra, and Zimm plots. See DOI: 10.1039/x0xx00000x

Scheme 1. Mechanistic hypothesis of dual-site zwitterionic acyl-Ni(II) catalysts.

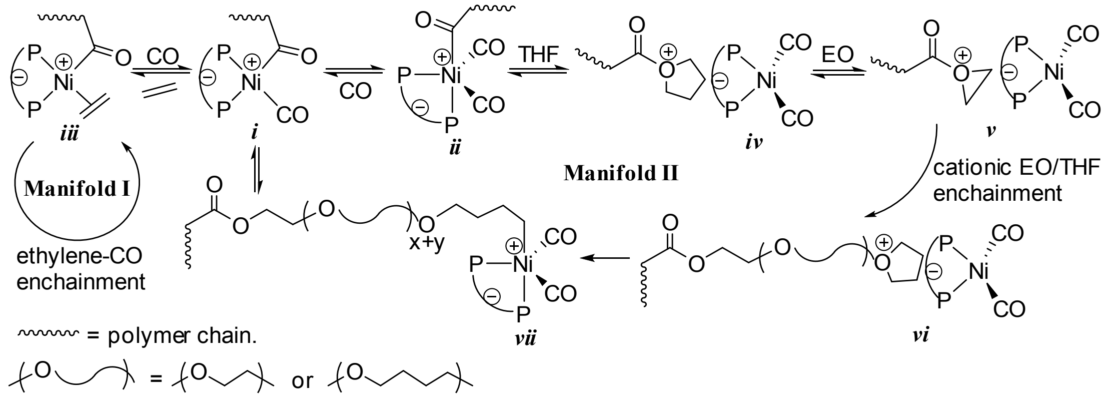
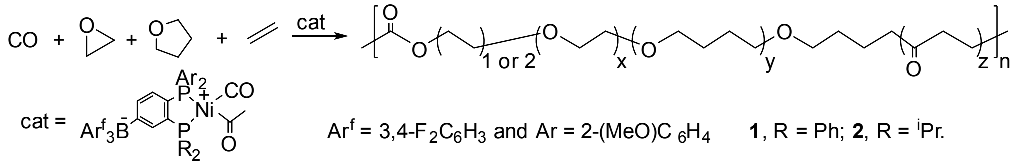


Table 1. Summary of carbonylative copolymerization of ethylene, EO, and THF.[a]



(1)

$Ar^f = 3,4\text{-}F_2C_6H_3$ and $Ar = 2\text{-}(MeO)C_6H_4$ **1**, R = Ph; **2**, R = ^{i}Pr.

entry	catalyst	ethylene (psi)	CO (psi)	EO (mL)	THF (mL)	ratio of repeat units[b] (1 : x : y : z)	M_w[c] (10^3 g/mol)	T_g[d] (°C)	T_m[d] (°C)	T_d[e] (°C)	Yield (g)
1	**1**	300	300	1	1	1 : 7.5 : 9.5 : 120	320	30	234	> 260	2.3 (0.1)
2	**2**	300	300	1	1	1 : 6.8 : 7.6 : 190	658	38	80, 226, 238	> 260	1.4 (0.2)
3	**1**	100	800	1	1	1 : 5.5 : 11 : 13	160	-	-	156	1.2 (0.1)
4	**1**	50	800	1	1	1 : 12 : 22 : 8.1	55	14	240	> 260	1.4 (0.1)
5	**2**	100	800	1	1	1 : 18 : 36 : 100	277	-	75, 189, 204	> 260	2.3 (0.1)
6	**2**	50	800	1	1	1 : 30 : 46 : 69	111	5.3	188	> 260	2.3 (0.2)
7	**1**	100	800	2	2	1 : 7.4 : 13 : 4.1	67	-	-	158	1.4 (0.0)
8[f]	**2**	100	800	1	1	1 : 16 : 33 : 140	55	29	92, 226, 236	> 260	2.3 (0.1)
9[f]	**1**	50	800	1	3	1 : 7.8 : 24 : 14	39	-	-	176	1.6 (0.0)

[a] Reaction conditions: 15 mg of catalyst in neat mixture of EO and THF at room temperature. The reaction time was 16 h. [b] Determined by ^{1}H NMR integration. The sum of the areas of the ester peaks *a* and *b* is normalized to unity as the structure of the polymer product in eq 1 indicates. The x, y, and z values have two significant figures. [c] Weight-average molecular weight determined by light scattering. [d] Glass transition and melting temperatures on the 2nd heating ramp of differential scanning calorimetry (DSC). See Supplementary Information for DSC traces. [e] Decomposition temperature on the 1st heating ramp. [f] The reaction is not stirred.

pressures in the presence of **1** or **2** (Table 1). The ^{1}H NMR spectrum of a representative product is shown in Figure 1. The peak assignments are made by comparison with the ^{1}H NMR spectra of an alternating CO-ethylene copolymer, a non-alternating CO-EO-THF terpolymer, and a tetrapolymer obtained using THF-d_8 to substitute THF. The assignments are further corroborated by ^{1}H-^{1}H COSY spectroscopy (see Supplementary Information). The product consists of ketone (peaks *g*), ester (peaks *a* and *a'*), and ether repeat units (peaks *b*, *c*, and *d*). The majority of the ester units arise from sequential CO-EO enchainments (peak *a*), and a minority from CO-THF (peak *a'*). All products in Table 1 are insoluble in and cannot be fractionated by common organic solvents including ethanol, ethers, acetone, and chloroform. Instead, they are soluble in hexafluoroisopropanol (HFIPA) or a mixture of trifluoracetic acid and chloroform, as is polyketone from CO-ethylene alternating copolymerization. The observed solubility leaves no doubt that the products are tetrapolymers composed of sizable segments of ketone repeat units from alternating CO-ethylene enchainments and segments of ester-*co*-ether units from non-alternating CO, EO, and THF enchainments, rather than physical mixtures of the two. The peaks belonging to the units at the end of or separating the two types of segments can be identified in the ^{1}H NMR spectrum. The peaks labelled as *g* at δ 2.92 and δ 2.75 ppm separated from the main ketone peak at δ 2.84 ppm are assignable to the last ethylene unit in a ketone segment before an ester-*co*-ether segment starts. Peak *f* at δ 2.62 ppm belongs to the last methylene in an ester-*co*-ether segment α to the first ketone repeat unit at the beginning of a ketone segment. Its chemical shift is different from *f* at δ 2.44 ppm, which belongs to a methylene α to an ester carbonyl rather than a ketone carbonyl, as is the case in the terpolymer of CO, EO, and THF (see Supplementary Information for comparison of the ^{1}H NMR spectra).

The compositions of the tetrapolymers can be varied by varying the initial commoner concentrations in ways consistent with the mechanistic hypothesis. Under 300 psi of ethylene and 300 psi of CO, the polymerizations catalyzed by **1** and **2** both

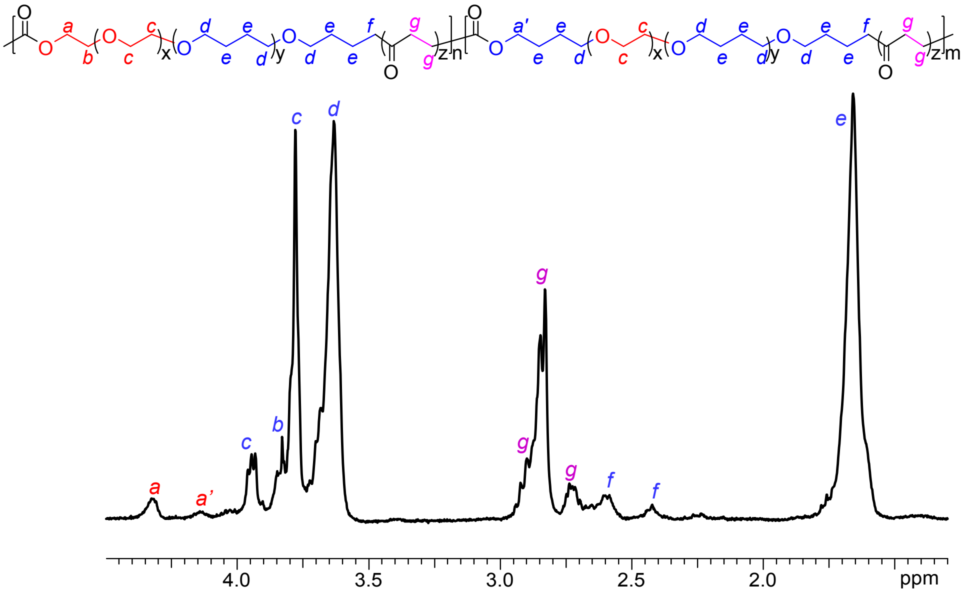


Figure 1. A representative ^{1}H NMR spectrum of the tetrapolymer product in anhydrous $CDCl_3$/TFA-d (10:1 volume ratio) along with peak assignments. The microstructures related to peaks labelled as *g* and *f* with different chemical shifts are described in the text.

give ketone as the main component and ester and ether as the minor components of the product (entries 1 and 2, Table 1). Increasing CO pressure and decreasing ethylene pressure (entries 1 vs 3 and 4 and entries 2 vs 5 and 6) increase the ester-to-ketone ratio. The ester-to-ketone ratios are higher with **1** as the catalyst than with **2** under the same conditions. The ester-to-ether ratio decreases with the above pressure changes, more dramatically for **2** than for **1**. Decreasing the catalyst concentration by doubling the initial amounts of EO and THF results in an increase in the ester-to-ketone ratio and a decrease in the ester-to-ether ratio (entries 3 vs 7).

The formation of the segmented structure is explained by the mechanistic hypothesis in Scheme 1. Turnovers in manifold ***I*** give rise to the ketone segment from alternating enchainments of CO and ethylene. Intermediates ***i*** and ***ii*** serve as the conduit between catalytic manifolds ***I*** and ***II***. Formation of an ester unit starts manifold ***II***. The ester units mostly arise from THF-promoted EO enchainment (***ii*** → ***iv*** → ***v*** → ***vi***), but the acyl-THF onium can also undergo ring-opening reaction to give an ester unit (not shown in Scheme 1), as evidenced by the small methylene peak *a′* in the ^{1}H NMR (Figure 1). The simultaneous presence of EO and THF is required for either of them to substantially participate in the polymerization, as the enchainment of one relies on the assistance of the other.[15] Following the formation of one ester unit, a few to a few tens of ether units are formed by ring-opening cationic enchainments of EO and THF. Nucleophilic addition of the Ni(0) anion to its THF-onium countercation followed by CO insertion (***vi*** → ***vii*** → ***i***) completes one catalytic cycle in manifold ***II***. The catalyst does occasionally turn over more than once in manifold ***II*** before returning to manifold ***I***, as evidenced by the presence of *f* at δ 2.44 ppm in the ^{1}H NMR (Figure 1). In other words, the catalyst does not necessarily enter manifold ***I*** when it passes through ***i***. Rather, returning to manifold ***I*** is stipulated by ethylene insertion into the acyl-Ni bond in ***iii***.

Determination of the molecular weights of the products proved challenging due to the limited solvent choices and the hydrolytic lability of the ester bond. GPC analysis gave erratic irreproducible results. The weight-average molecular weight (M_w) determined by static light scattering (SLS) decreased over time before a constant value was reached in a few days (see Supplementary Information). We suspected that hydrolysis might be responsible for the erroneous GPC and SLS results. Indeed, the decrease in M_w over time was substantially suppressed when the samples for the SLS experiments were dissolved in HFIPA dried with molecular sieves. The M_w values reported in Table 1 were determined using such anhydrous HFIPA. We were unable to find a way to determine the number average molecular weight of the products.

The factors affecting the yield of the polymerization are complex. The heterogeneous nature of the polymerization due to precipitation of the product during the reaction appears to affect the yield, as well as the molecular weight and composition of the product. For example, when the polymerization was carried out without stirring under otherwise identical conditions, the yield, molecular weight, and composition all changed appreciably (entries 3 vs 9).

The appearances of tetrapolymers range from plastic to elastic depending on the composition. The stress-strain curves of two representative samples are shown in Figure 2 to demonstrate such a wide range of viable mechanical characteristics. The samples for the tensile test were prepared by performing the polymerization without stirring so that a sheet of the product covering the bottom of the autoclave was obtained. Dumbbell specimens were cut out from these sheets. The sample having a moderate amount of ester and ether units (entry 8) has a Young's modulus of ~200 MPa similar to that of low density polyethylene.[17] When the ester and ether content are substantially increased, the sample (entry 9) bec becomes very soft with a Young's modulus of 2 MPa and displays elastic recovery after large deformation (Figure 2, inset). Apparently,

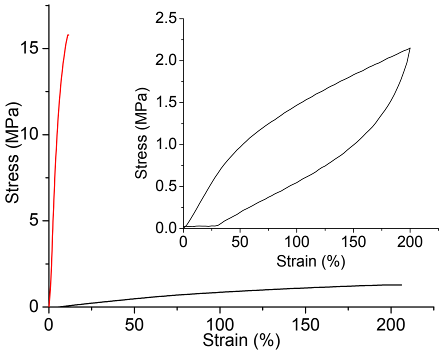


Figure 2. Stress-strain curves of plastic product from entry 8 of Table 1 (red) and elastic product from entry 9 of Table 1 (black). The inset is the stress-strain curve of a cyclic tensile test of the elastic sample. Toughness (area under the tensile curve) of the samples are 1.62 and 1.16 MJ/m^3, respectively.

the ester-*co*-ether segments in the sample are long enough to give rise to elasticity, and the crystalline ketone segments provide physical crosslinks.[18]

In summary, the dual reactivity of zwitterionic Ni(II) catalysts allows carbonylative copolymerization of two types of comonomers (*i.e.*, olefins and cyclic ethers) with dissimilar reactivities. The resultant tetrapolymers of CO, ethylene, EO, and THF have segmented structures. One type of segment is composed of ketone units from alternating enchainments of CO and ethylene, and the other is composed of esters and ether units from non-alternating enchainments of CO, EO, and THF. The tetrapolymers display mechanical properties ranging from plastic to elastic depending on the composition and presumably the lengths of the segments. In the broad scheme of sustainability, the present communication introduces a new synthetic platform for photolytically and hydrolytically degradable polymers based on abundant monomers with low-carbon footprints. The current products certainly do not have the ultimate desirable structures (for example, the ether repeat units in the plastics products should be eliminated or at least reduced) and consequently mechanically inferior to polyethylene. Ample exciting fundamental research opportunities exist to improve the catalytic efficiencies and to achieve tailored structures and properties for various commodity applications.

Conflicts of interest

The authors have no conflicts of interest to declare.

Notes and references

‡ Experimental details, ^{1}H-^{1}H COSY spectrum, additional ^{1}H NMR spectra, Zimm plots of SLS study, DSC traces are included in The Supporting Information.

§ The research is supported by grants of the National Science Foundation of USA to L.J. (CHE-1900430) and T.L. (CHE-1904397). T.L. also acknowledges support by The University of Akron.

1 J. R. Jambeck, R. Geyer, C. Wilcox, T. R. Siegler, M. Perryman, A. Andrady, R. Narayan and K. L. Law, *Science*, 2015, **347**, 768.

2 P. Dauvergne, *Global Environmental Change*, 2018, **51**, 22.

3 Y. Zhu, C. Romain and C. K. Williams, *Nature*, 2016, **540**, 354.

4 R. Geyer, J. R. Jambeck and K. L. Law, *Science advances*, 2017, **3**, e1700782.

5(a) E. Drent, W. Mul and A. Smaardijk, in *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, New York, 2002, pp. 678-703; (b) A. Sommazzi and F. Garbassi, *Prog. Polym. Sci.*, 1997, **22**, 1547.

6(a) I. Goodman, H. Mark, N. Bikales, C. Overberger and G. Menges, John Wiley & Sons, New York, 1988; (b) S. Philip, T. Keshavarz and I. Roy, *Journal of chemical technology & biotechnology: International research in process, Environmental & clean technology*, 2007, **82**, 233.

7(a) G. H. Hartley and J. Guillet, *Macromolecules*, 1968, **1**, 165; (b) A. X. Zhao and J. C. Chien, *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 2735; (c) F. Y. Xu and J. C. Chien, *Macromolecules*, 1993, **26**, 3485; (d) T. O. Morgen, M. Baur, I. Göttker-Schnetmann and S. Mecking, *Nature communications*, 2020, **11**, 1.

8(a) E. Drent and P. H. Budzelaar, *Chem. Rev.*, 1996, **96**, 663; (b) A. Sen, *Accounts of chemical research*, 1993, **26**, 303.

9(a) M. Allmendinger, R. Eberhardt, G. Luinstra and B. Rieger, *Journal of the American Chemical Society*, 2002, **124**, 5646; (b) D. Takeuchi, Y. Sakaguchi and K. Osakada, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 4530; (c) J. T. Lee and H. Alper, *Macromolecules*, 2004, **37**, 2417; (d) K. Nakano, K. Fumitaka and K. Nozaki, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 4666; (e) G. Liu and L. Jia, *J. Am. Chem. Soc.*, 2004, **126**, 14716; (f) E. W. Dunn and G. W. Coates, *J. Am. Chem. Soc.*, 2010, **132**, 11412.

10(a) E. Göktürk, A. G. Pemba and S. A. Miller, *Polymer Chemistry*, 2015, **6**, 3918; (b) Y. Reyhanoglu, E. Sahmetlioglu and E. Gokturk, *ACS Sustainable Chemistry & Engineering*, 2019, **7**, 5103; (c) M. Ragazzini, M. Modena, E. Gallinella and G. Cevidalli, *Journal of Polymer Science Part A: General Papers*, 1964, **2**, 5203.

11 K. J. Arrington, J. B. Waugh, S. C. Radzinski and J. B. Matson, *Macromolecules*, 2017, **50**, 4180.

12 V. Zacharopoulou and A. A. Lemonidou, *Catalysts*, 2018, **8**, 2.

13 S. Raju, M.-E. Moret and R. J. Klein Gebbink, *ACS Catalysis*, 2015, **5**, 281.

14(a) F. S. Roberts, K. P. Kuhl and A. Nilsson, *Angew. Chem.*, 2015, **127**, 5268; (b) F. Li, A. Thevenon, A. Rosas-Hernández, Z. Wang, Y. Li, C. M. Gabardo, A. Ozden, C. T. Dinh, J. Li and Y. Wang, *Nature*, 2020, **577**, 509.

15 Y. Dai, S. He, B. Peng, L. A. Crandall, B. R. Schrage, C. J. Ziegler and L. Jia, *Angew. Chem.*, 2018, **130**, 14307.

16(a) X. Jia, M. Zhang, F. Pan, I. Babahan, K. Ding, L. Jia, L. A. Crandall and C. J. Ziegler, *Organometallics*, 2015, **34**, 4798; (b) X. Jia, M. Zhang, M. Li, F. Pan, K. Ding, L. Jia, L. A. Crandall, J. T. Engle and C. J. Ziegler, *Organometallics*, 2017, **36**, 1122; (c) C. S. Shultz, J. M. DeSimone and M. Brookhart, *Organometallics*, 2001, **20**, 16.

17 D. James, *Wiley-Interscience, Encyclopedia of Polymer Science and Engineering.*, 1986, **6**, 429.

18 P. Dreypuss, L. Fetters and D. Hansen, *Rubber Chem. Technol.*, 1980, **53**, 728.