

Review

Copolymerization of ethylene with non-vinyl polar monomers

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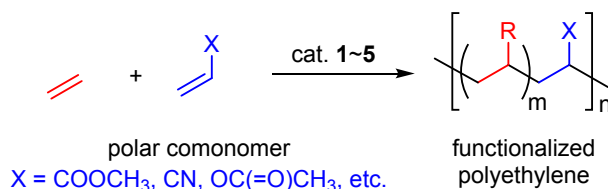
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Abstract: Introduction of functional groups on polyethylene endows it with a higher surface property and thus various catalysts have been developed for the copolymerization of ethylene with polar vinyl monomers. Aside from vinyl monomers, however, other classes of polar monomers have not found application in the copolymerization with ethylene. Here, in this short review article, our latest studies on catalyst development aiming at the use of non-vinyl polar monomers and the properties of the resulting copolymers are summarized.

Keywords: ethylene, copolymerization, polar monomer, non-vinyl monomer, transition-metal catalyst

1. Introduction

Polyethylene is an artificial resin produced in large quantities, roughly a quarter of the annual production of all plastics in the world. Since the discovery of the Ziegler catalyst, group 4 metals play a major role in polyethylene production. Owing to its non-polar nature, the surface of polyethylene lacks the adhesive ability toward other materials and thus post-polymerization functionalization is often employed to introduce polar-functional groups onto the polyethylene surface. Regarding the copolymerization of ethylene with polar monomers, monomers having oxygen or nitrogen-based functional groups would be an ideal alternative in the synthesis of functionalized polyethylenes, and examples have been hardly found until recently since group 4 metals get deactivated by functional groups. The deactivation originates from the strong coordination of polar groups to group 4 metals, usually known as hard metals. In the last two decades, group 10 metals, mostly nickel and palladium, became the metals of choice for the copolymerization of ethylene with polar monomers, thanks to their highly tolerant nature for catalyst poisoning. As polar monomers, alkyl acrylate, acrylonitrile, and vinyl acetate can be incorporated into polyethylene



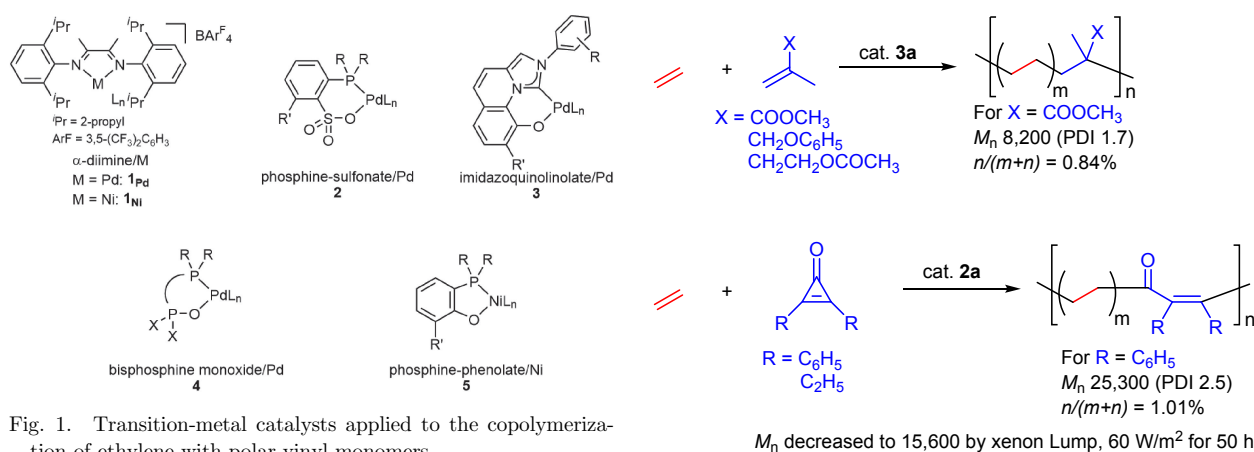
Scheme 1. (Color online) Copolymerization of ethylene with polar vinyl monomers.

(Scheme 1). The polar monomer incorporation ratio is mostly low (up to 5%–10%), in contrast to the conventional radical copolymerization which provides copolymers rich in the polar monomer content. The representative catalysts thus far reported are summarized in Fig. 1.

Historically, in 1996, Brookhart *et al.* reported the first copolymerization of ethylene with methyl acrylate catalyzed by the diamine/Pd or Ni complexes **1**.¹⁾ The obtained copolymers consist of branched structures and the esters were incorporated mostly at the chain-ends. In 2002, Drent *et al.* reported that a combination of Pd(0) precursor with *ortho*-diarylphosphinobenzene sulfonic acid (**2**) affords linear ethylene/methyl acrylate copolymers.²⁾ As the linear copolymer having a small number of polar groups can be regarded as a high-density polyethylene analog endowed with adhesive property, the reaction attracted much attention as a one-step synthesis of functionalized polyethylene. Since then, intensive efforts have been devoted to catalyst development, for such as **3** and **4**, aiming at a higher

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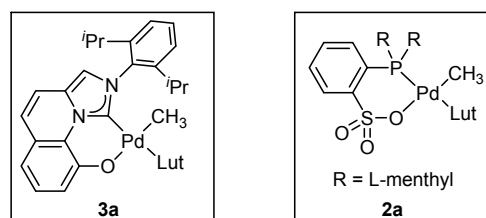
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activity and a higher molecular weight, with variable polar monomer incorporation ratios. Not only palladium but also nickel catalyst was successfully applied as was represented by the phosphinephenolate/nickel catalyst **5** developed by the researchers of MCC.³⁾ Notably, the polar monomers thus copolymerized were limited to vinyl monomers, the compounds bearing the $\text{CH}_2=\text{CH}$ -group (vinyl group), having only one substituent on the carbon-carbon double bond. In contrast, non-vinyl monomers were hardly employed for the metal-catalyzed copolymerization until recently. For further details of the metal-catalyzed copolymerization of ethylene with common vinyl polar monomers, the readers are guided to refer to many review articles published to date.⁴⁾ Here in this manuscript, the focus is on the use of non-vinyl polar monomers. In addition, the unique properties of the obtained copolymers will be discussed.

2. Disubstituted ethene comonomers

1,1-Disubstituted ethenes. It should be noted that the copolymerization is susceptible to steric hindrance around the C-C double bond of olefinic monomers. As a result, disubstituted monomers have never been applied until recently. In 2018, we reported the coordination incorporation of methyl methacrylate, a 1,1-disubstituted polar comonomer, with ethylene for the first time (Scheme 2, top).⁵⁾ We developed a new palladium complex, carbene-phenolate **3a** for this purpose. The copolymer thus obtained showed a linear structure with a molecular weight (M_n) of 8,200 (PDI 1.7) and a polar monomer incorporation ratio of 0.84%. Notably, catalyst **3a** exhibited a higher tolerance for steric demand compared to the conventional catalyst **2**. This could be explained as follows: the large aromatic ring on the



Scheme 2. (Color online) Copolymerization of ethylene with disubstituted ethene comonomers.

nitrogen of the carbene moiety of **3a** effectively prevents the polymer-chain from undesired chain-transfer reactions while enough space is provided near the metal center for monomer coordination and insertion. In addition to methyl methacrylate, 2-methyl-2-propenyl phenyl ether and 3-methyl-3-butenyl acetate were also employable as polar comonomers. We also applied the steric tolerance of **3a** to the first copolymerization of propylene with polar monomers.⁶⁾

2,3-Disubstituted cyclopropanones. When both carbons of the C-C double bond are substituted, the incorporation is even more difficult. This problem was circumvented using a monomer with a higher reactivity originating from steric strain. Cyclopropanone was copolymerized with ethylene using catalyst **2a** affording polyethylene containing α,β -unsaturated ketone units in the chain, accompanied by the ring-opening of the cyclopropane ring (Scheme 2, bottom).⁷⁾ The obtained copolymer has an M_n of 25,300 (PDI 2.5) with a polar monomer incorporation ratio of 1.01%. Since the α,β -unsaturated carbonyl moiety is known as a chromophore for UV-vis light absorption, we anticipated that oxidative cleavage of the double bond would take place by photoexcitation. Thus, upon treatment of

the copolymer with light using a xenon lamp under air, the polymer caused a decrease of M_n down to 15,600 suggesting that the conjugated enone moiety is cleavable by the photostimuli.

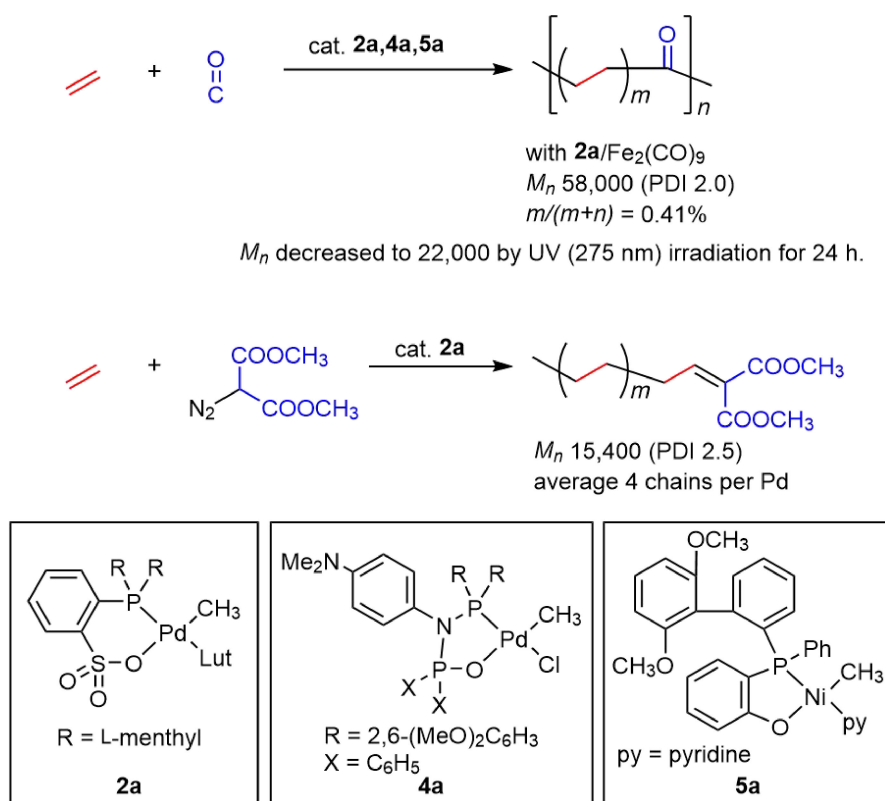
3. C1 comonomers

Carbon monoxide. In addition to C–C double bonds, the C1 unit can also be incorporated into a polyethylene chain. Carbon monoxide (CO) is a representative C1 unit. We became interested in the incorporation of a small amount of CO so that the copolymer maintains the property of high-density polyethylene but contains the carbonyl functional group in the chain. Historically, two methods were reported for the copolymerization of ethylene with CO. One is the radical copolymerization affording an ethylene-rich copolymer with branches. The other is the coordination copolymerization mediated by palladium catalysts. In the latter method, the polymerization proceeds in a completely alternating manner rather than statistical incorporation. In 2002, Drent *et al.* reported the first palladium-catalyzed synthesis of moderately non-alternating copolymers of ethylene and CO by employing a phosphine sulfonate (P/S) ligand **2** (up to 18.4 mol% extra ethylene units with 40.8 mol% CO content).⁸ Yet, the incorporated CO was located in mostly alternating structures. Aiming at the synthesis of polyethylene containing a completely isolated ketone moiety, we used metal carbonyls as a CO source expecting that the slow release from the metal carbonyls would avoid the alternating incorporation. Using $\text{Fe}_2(\text{CO})_9$, polyethylene containing a predominantly isolated ketone unit was obtained using catalyst **2a** (Scheme 3, top).⁹ The obtained copolymer contained 0.41 mol% of ketone moiety with an M_n of 58,000 (PDI 2.0). This copolymer showed similar thermal properties to polyethylene, namely, a T_m of 130 °C for the copolymer and 131 °C for polyethylene (with an M_n of 47,000). Aliphatic ketones are known to undergo photodegradation by the Norrish type 1 reaction. That is, the $n-\pi^*$ transition of the carbonyl group by UV irradiation induces the C–C bond scission at the α -position of the carbonyl group. Accordingly, we exposed the copolymer to UV light (275 nm) to detect the molecular weight decrease from M_n 58,000 to 22,000. In contrast, polyethylene did not show any degradation (M_n 47,000 was kept to 41,000). Given that the xenon lamp (covering the wavelength of sunlight) was not as effective as the 275 nm UV light for the copolymer degradation, the material may be decomposed *on-*

demand upon UV irradiation. It should be noted that during our study, new catalysts **4a** and **5a** were developed by Chen¹⁰ and Mecking¹¹ independently, for lowering the content of the alternating structure in the ethylene/CO copolymers. Mecking reported that the mechanical property, the stress–strain curves, of the ketone-containing polyethylene (0.6 mol% of CO) is also similar to that of polyethylene.

Ester-disubstituted carbene. Carbene, a divalent carbon species is another class of a C1 source for the copolymerization with ethylene. We employed a diazodiester as a carbene precursor. By the reaction of ethylene with dimethyl diazomalonate using catalyst **2a**, the carbene unit was incorporated into polyethylene but only at the chain-end (Scheme 3 bottom).¹² No in-chain incorporation was observed. It is likely that the dicarbonyl-substituted alkyl palladium species generated by the carbene insertion did not undergo further ethylene or carbene insertion. Instead, it ended up with β -hydride elimination affording the α,β -unsaturated diester chain-end. Seemingly, the two ester groups on the α -carbon prevented the species from further migratory insertion possibly due to the steric hindrance around the metal center. Spontaneously generated palladium hydride re-initiates the ethylene polymerization by the ethylene insertion to the Pd–H bond. Thus, by the chain-transfer mechanism, multiple numbers of polymers were obtained from one catalyst, four polymer chains per palladium on average (Scheme 3, bottom). The polymer with a terminal conjugated ester moiety has potential for further use as a macromonomer.

In summary, here we described the latest progress in the copolymerization of ethylene with non-vinyl polar monomers. As shown, the expansion of the comonomers applicable to the synthesis of functionalized polyethylene further pushes forward the polymer's use in more sophisticated manners. The functional groups thus introduced can be subjected to further chemical transfers. For example, chain-end functionalization with the manolate unit (Scheme 3) makes the product a good Michael acceptor, so that it can be grafted on poly nucleophiles. On-demand degradation proposed above could be another future direction. For example, the methyl methacrylate incorporation described in Scheme 2 allows facile homolytic carbon–carbon bond cleavage upon heating since it can afford a tertiary radical. Both the enone moiety (Scheme 2) and the ketone group (Scheme 3) endow the polymers with photodegradability. It may allow the use of



Scheme 3. (Color online) Copolymerization of ethylene with C1 comonomers.

polyethylene waste for recycling and or upcycling that might contribute to the mitigation of plastic waste.

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Profile

Kyoko Nozaki was born in Osaka and graduated from Kyoto University with a B.Sc. degree in 1986. She received her Ph.D. in 1991 from the same university. During her Ph.D. study, she spent a year at the University of California, Berkeley as an exchange student. Since 1991, she has been a faculty member as Instructor and then Associate Professor at Kyoto University, moved to the University of Tokyo in 2002, and has been in the current position of Professor at the University of Tokyo since 2003. Her research interest is focused on the development of homogeneous and heterogeneous catalysts for polymer synthesis and organic synthesis. Her achievements include The Award of the Society of Polymer Science, Japan (2013), Kuggie Vallee Distinguished Lecturer (2019), Chemical Society of Japan Award (2020), Distinguished Women in Chemistry or Chemical Engineering (2021), Toray Science and Technology Prize (2021), and L'Oréal-UNESCO For Women in Science International Awards (2021). She has been an International Honorary Member of the American Academy of Arts & Sciences since 2021.

