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Research Highlight

Versatile catalytic strategy for polar-functionalized, cross-linkable, self-healing, and photo-responsive polyolefins

Yanshan Gao [⇑], Tobin J. Marks [⇑]

Department of Chemistry, Northwestern University, Evanston, IL 60208-3113, USA

Polyolefins are the most widely used polymeric materials worldwide, with abundant, low cost ethylene and propylene as the principal feedstocks. The broad polyolefins applications scope is in part due to the chemical inertness/stability of the exclusively alkane C–C and C–H bond networks. However, this advantageous attribute becomes a limitation when considering other important applications requiring adhesion, toughness, surface activity, compatibility with other materials, dyeability, barrier properties, electrical conductivity for static electricity suppression, and favorable rheological properties [1–4]. While post-polymerization functionalization has been used in the past to enhance polyolefin performance [1], such modifications typically require harsh conditions, lack selectivity, and may induce side reactions such as chain scission and/or cross-linking [3]. Thus, introducing polar functional groups into polyolefins during the initial polymerization process has become an atom-economical ‘‘holy grail” and a central focus of olefin polymerization research today.

In creating polar polyolefin materials, industrially successful early transition metal catalysis has only achieved limited success, mainly due to high catalyst oxophilicity/Lewis acidity and typical polar comonomer Lewis basicity [5–7]. In contrast, late transition metal (Ni, Pd) catalysts exhibit far greater polar comonomer tolerance [1,2,8], which enables copolymerizations with a variety of polar comonomers. However, due to the relatively low polymerization activity and low product molecular weight, the real-world applications potential remains a challenge. Thus, developing new catalyst systems and polymerization methodologies, for both early and late transition metals, is a topic of intense research focus. While developing efficient catalytic systems at a low cost is a significant challenge, another important question concerns which polar polyolefins might deliver desirable performance to satisfy market/customer needs. There are only few relevant studies [9] on the wide range of polar polyolefins available via Ni/Pd catalysis [1,2,8]. Thus, performance studies of these newly developed polar polyolefins are at the initial stage and limited.

Recently, Prof. Changle Chen’s group [10] at the University of Science and Technology of China reported the efficient synthesis of ethylene + ethylidene norbornene (ENB) + 10-undecenoic acid (or the methyl ester thereof) polar terpolymers with tunable amounts of carboxylic acid and cyclic comonomer via Pd-catalyzed terpolymerization. Incisive characterization studies reveal impressive performance enhancement, including significantly altered surface properties, dynamic crosslinking, self-healing, and photo-response (Fig. 1).

Chen group [10] convincingly demonstrated the greatly expanded modularity of his polyolefins vs. the non-polar analogues by introducing –COOH and C=C double bond groups into the polyolefins. These features combined with precise control over polar comonomer and ENB comonomer content provide a powerful toolbox for achieving a range of enhanced performance beyond the reach of the corresponding non-polar polyolefins. The COOH functionality and the corresponding Fe^{3+} carboxylate complexes efficiently modulate polymer surface properties and provide active sites for dynamic crosslinking, which in turn modifies the mechanical/elastic properties and enables self-healing. In the presence of citric acid, achievable Fe^{3+}/Fe^{2+} redox chemistry offers an efficient way of recycling thermo-setting polymers. The ENB comonomer content can also efficiently modulate the crystallinity and elastic properties of the polyolefin. Moreover, the enchained ENB unit C=C double bonds enable efficient sulfur-induced vulcanization, leading to permanent cross-linking. These transformations are both versatile and modular, and thus potentially applicable to other polyolefins.

In summary, Chen group [10] reported a well-designed polymerization system illustrating how precise control of polar polyolefin microstructure through a well-developed coordination polymerization, which enables the creation of new high-performance polyolefin materials. However, it is not a trivial goal to proceed from elegant fundamental university research to commercializable polymers. This requires team efforts from academic labs, chemical companies, downstream customers, etc. Ideally, recent catalyst advances and polar polyolefin structure-performance relationship studies as described here can play an important role.

Conflict of interest

The authors declare that they have no conflict of interest.

[⇑] Corresponding authors.

E-mail addresses: yanshan@northwestern.edu (Y. Gao), t-marks@northwestern.edu (T.J. Marks).

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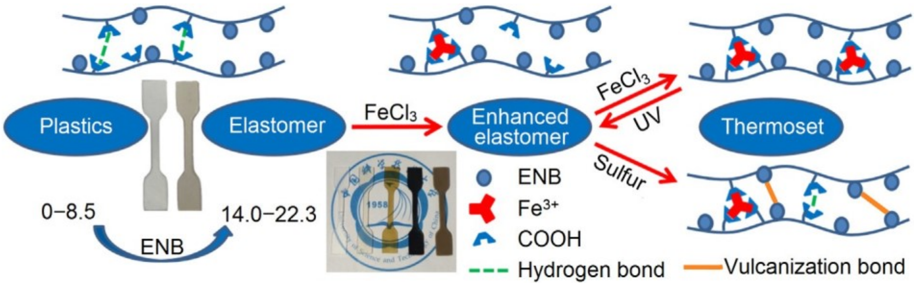

Fig. 1. Modulation of polyolefin properties through ethylidene norbornene (ENB) incorporation, hydrogen bonding, Fe^{3+}-induced crosslinking, and sulfur vulcanization. Reproduced with permission from Ref. [10]. Copyright 2019 John Wiley & Sons, Inc.

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Yanshan Gao is Research Assistant Professor at Northwestern University. He obtained his Ph.D. degree from the Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences, conducting research under the supervision of Prof. Yong Tang and Prof. Zuowei Xie (Chinese University of Hong Kong), and a B.S. degree from Shandong University. He worked with Prof. Tobin J. Marks as an SIOC Postdoctoral Fellow and a Dow Chemical Postdoctoral Fellow. His current research interests include olefin polymerization, supported organometallic catalysis, and organolanthanide catalysis.

Tobin J. Marks is Ipatieff Professor of Chemistry and of Materials Science and Engineering at Northwestern University. He holds a B.S. degree from the University of Maryland and a Ph.D. degree from Massachusetts Institute of Technology. His current research interests include olefin polymerization, supported organometallic catalysis, and organolanthanide catalysis. His current research interests include synthetic organo-f-element and early-transition metal organometallic chemistry, polymer chemistry, materials chemistry, homogeneous and heterogeneous catalysis, molecule-based photonic materials, superconductivity, metal-organic chemical vapor deposition, and biological aspects of transition metal chemistry.