Comparison of UV degradation of high-density polyethylene-like polymers with methyl ketone side chains or in-chain ketone groups

Haobo Yuan[1], Kohei Takahashi[1], Kyoko Nozaki[1]
([1]Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-8656, Japan)
[1]Tel: +03-5841-7264, E-mail: yuanhb@g.ecc.u-tokyo.ac.jp

Polyethylene (PE) has been widely applied because of its unique mechanical properties and chemical resistance. On the other hand, its high stability (or low degradability) endowed by its non-polar all-carbon main chain makes it one of the main waste sources for white pollution. Efforts have been made to make HDPE degradable or recyclable by inserting functional groups into or on the main chain. For example, the HDPE with ester or peptide groups in main chains can be recycled by fragmentation and repolymerization.[1-2] HDPE with carboxylic acid groups can be degraded under blue light through radical process.[3]

Efforts have also been made for making ethylene/CO copolymers (poly(E/CO)) with CO contents, high in dispersion but low in amount, and with high molecular weights. Such polymers can degrade under UV light by cutting the ketone groups through Norrish reactions. Previously, our group has synthesized high density polyethylene bearing isolated in-chain carbonyls, that degrades under UV-light irradiation (Fig. 1).[4]

In this work, HDPE-like polymer with methyl ketone side chains were synthesized by copolymerization of ethylene and methyl vinyl ketone (poly(E/MVK)) and its UV degradability was compared with poly(E/CO)[4] (Fig. 1). By tracing the molecular weight by size-exclusion chromatography, Poly(E/MVK) showed higher degradation efficiency than the corresponding poly(E/CO). By an NMR study, rapid consumption of the ketone moiety via both Norrish type I and II scissions were suggested for the degradation of poly(E/MVK), while mainly type II is responsible for poly(E/CO). Such difference could be associated with preferable location of ketone group in the amorphous phase or conformationally flexible to undergo the type II reaction in poly(E/MVK). By the precise control of the ketone content of poly(E/MVK), the ones with low MVK content were found to have physical properties comparable to HDPE yet photodegradable.

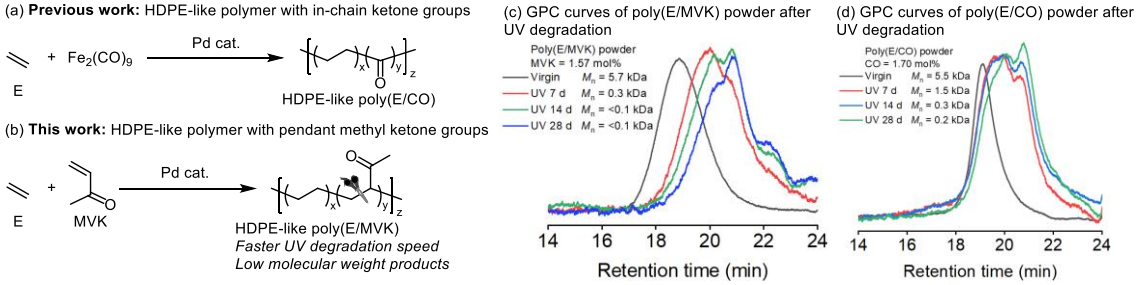

Fig. 1 HDPE-like polymers with methyl ketone side chains or in-chain ketone groups.

References

(1) Arroyave, A.; Cui, S.; Lopez, J. C.; Kocen, A. L.; LaPointe, A. M.; Delferro, M.; Coates, G. W., *J. Am. Chem. Soc.* **2022,** *144* (51), 23280-23285.
(2) Lu, Y.; Takahashi, K.; Zhou, J.; Nontarin, R.; Nakagawa, S.; Yoshie, N.; Nozaki, K., *Angew. Chem. Int. Ed. Engl.* **2024,** *63* (43), e202410849.
(3) Lu, B.; Takahashi, K.; Zhou, J.; Nakagawa, S.; Yamamoto, Y.; Katashima, T.; Yoshie, N.; Nozaki, K., *J. Am. Chem. Soc.* **2024,** *146* (28), 19599-19608.
(4) Tang, S.; Seidel, F. W.; Nozaki, K., *Angew. Chem. Int. Ed. Engl.* **2021,** *60* (51), 26506-26510.