

“CLICK” CHEMISTRY WITHIN LDPE

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Specialty LDPE copolymers provide some of the highest added value polyolefin applications and, in the quest to differentiate in an increasingly commoditized polyolefin environment, are of considerable interest to LDPE producers and other polyolefin players.¹ In 2015, global specialty LDPE copolymers production was estimated around 6900 kT, from those EVA (Ethylene Vinyl Acetate) accounts for nearly 90 % of it.¹ Other examples are EBA (Ethylene Butyl Acrylate), EVOH (Ethylene Vinyl Alcohol), COC (Cyclic Olefin Copolymer), MAH (Maleic Anhydride) grafted PE, ... which all have their specific properties and are used in different kind of applications. All above mentioned commercial grades are made either by in reactor functionalization, copolymerization of ethylene and a monomer, or by post-modification, grafting of a monomer onto a PE backbone. A combination of both routes would give the advantage of producing one base grade; therefore, no changes in reactor settings are required and the properties of the polymer can be tuned by post-modification reactions.

In a first step, production of the base grade, ethylene is copolymerized with a monomer bearing a triple bond e.g. propargyl methacrylate, in a high pressure reactor to form a functionalized LDPE with alkyne groups. In this investigation, it is demonstrated that certain alkyne containing comonomers do not cause runaway reactions, contrary to acetylene under high pressure conditions.² These alkyne containing comonomers do not undergo a thermal decomposition during the applied reaction conditions, serving the intended mechanism of free-radical copolymerization with ethylene at high pressures. The reactive group (C=C bond) in the alkyne containing comonomer, together with ethylene, reacts with the generated radicals and incorporates the C≡C bond in the growing polymer chain. It was found that C≡C bond does not react with the generated radicals under chosen reaction conditions and is maintained in the copolymer, obtained as branches of the main chain.

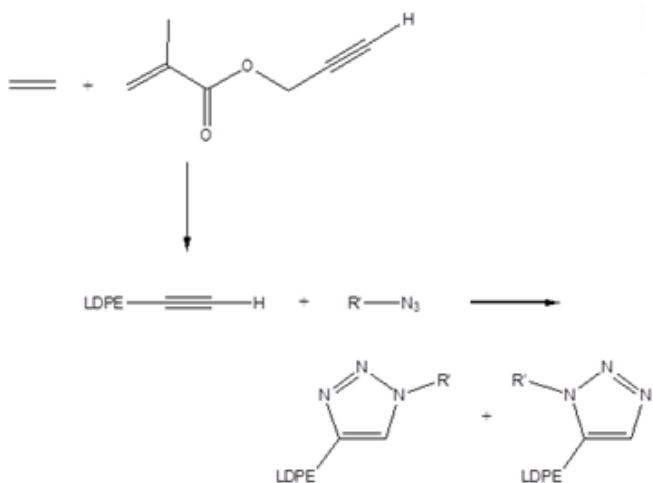


Figure 1 – Explanation of “click” chemistry within LDPE

In a second step, the alkyne groups can be used for further modification reactions with e.g. azides to undergo a Huisgen 1,3-dipolar cycloaddition to form 1,2,3-triazoles. A reaction scheme of step 1 and 2 is presented in figure 1. The functionality on the other side of the azide molecule (R') will determine the properties of the LDPE. Via this route, it is possible to synthesize e.g. LDPE functionalized with alcohol, amine, maleic anhydride groups ... without changing the reactor settings and thus avoid grade changes. The versatility of this reaction is demonstrated using azidomethyl phenyl sulfide as an azide, in various media, under different reaction conditions, in the presence and absence of a catalyst system yielding high conversions. These new type of high pressure ethylene copolymers can be used for various applications like films for packaging, consumer durables, disposable diapers, textiles, agricultural film, shrink film, medical packaging, foam, adhesive ...

References

¹ Specialty LDPE Copolymers PERP 2016S4, July 2016, NexantThinking™.

² Zhang et al.; Runaway Phenomena in Low-Density Polyethylene Autoclave Reactors, AIChE Journal, October 1996, 42, 10, 2920.