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New Routes To Ester and Acid Functionalized Polyethylene

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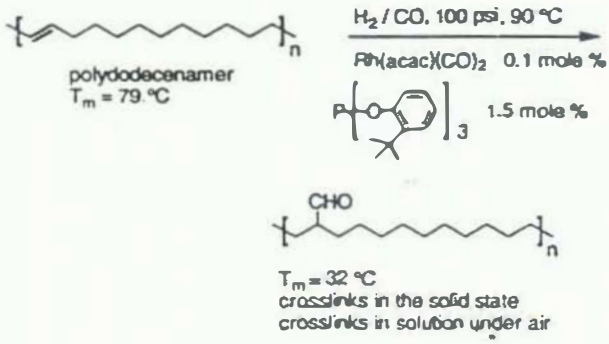
Introduction

The direct free radical copolymerization of ethylene with polar monomers such as methyl acrylate, methyl methacrylate, and acrylic acid requires extremely high pressures.[1] This paper describes three alternative routes to ester and acid functionalized polyethylene that do not require high pressure:

1. Hydroformylation/oxidation of an unsaturated ROMP polymer
2. ROMP / hydrogenation of ester functionalized cycloolefins
3. Palladium catalyzed copolymerization of ethylene and methyl acrylate

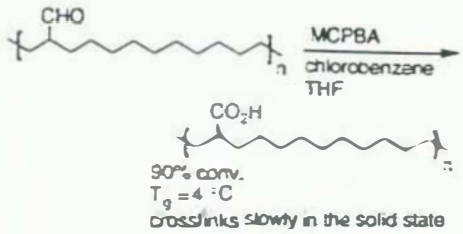
Hydroformylation/Oxidation of An Unsaturated Polymer

The catalytic hydroformylation of polypentenamer (the ring-opened metathesis polymer of cyclopentene) has been reported to occur with up to 50% conversion of the double bonds using $RhH(CO)(PPh_3)_3$.[2] We chose the ring-opened metathesis polymer of cyclododecene for hydroformylation studies because it is easily prepared, and because the spacing of the olefin groups makes intramolecular condensation reactions of the poly-aldehyde unlikely. Complete conversion of the double bonds without formation of gel was obtained using a Rh catalyst and a hindered phosphite ligand:



This catalyst is known to be particularly effective for the hydroformylation of internal olefins.[3] The poly(aldehyde) was somewhat unstable. Reaction solutions in toluene were homogeneous, and freshly precipitated polymer redissolved readily in toluene or THF. However, the polymer slowly formed insoluble gel in both dilute solution and the solid state probably due to interchain condensation reactions of the aldehyde groups.

Dilute solutions of the poly(aldehyde) were partially oxidized to the acid by stirring under oxygen at room temperature (30% conversion in 3 days); however, gel formation due to crosslinking also occurred. Higher conversion of the poly(aldehyde) to the poly(acid) without gel formation was achieved using an excess of meta-chloroperbenzoic acid in solution:

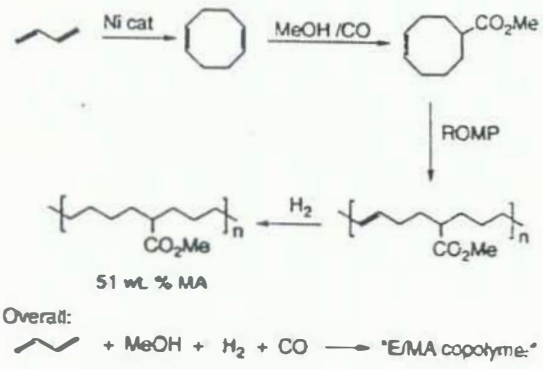


The poly(acid) was soluble in THF. It slowly formed an insoluble gel when stored as a solid. This may be due to reactions of the poly-acid itself, or to crosslinking of the residual aldehyde.

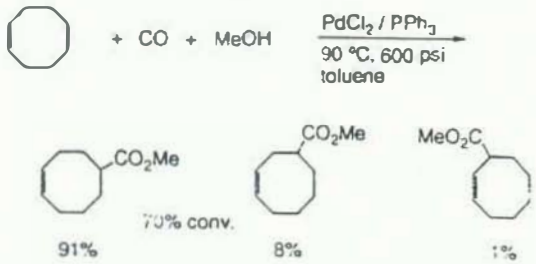
Ring-Opening Metathesis Polymerization (ROMP) / Hydrogenation Cycloolefins

An alternative method for the preparation of an ester-functionalized polyethylene is ROMP of an ester-functionalized cycloolefin followed by reduction of the double bonds. An overall scheme for the conversion of butadiene, methanol, hydrogen, and carbon monoxide into the equivalent of an ethylene/methyl acrylate copolymer is shown in Scheme 1.

Scheme 1. Metathesis Route to an "E/MA Copolymer"

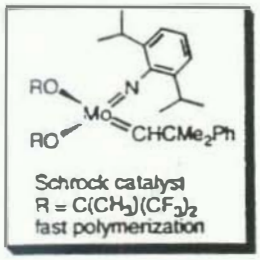


The desired 5-carbomethoxycyclooctene monomer for the ROMP step was prepared by Pd catalyzed carbomethoxylation of 1,5-cyclooctadiene:

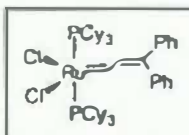


Within a narrow range of temperature and reaction time, reasonable conversions were obtained to give mixtures that were primarily 5-carbomethoxycyclooctene.

The ester functionalized cyclooctene polymerized readily with either the Schrock Mo catalyst or the Grubbs Ru catalyst.



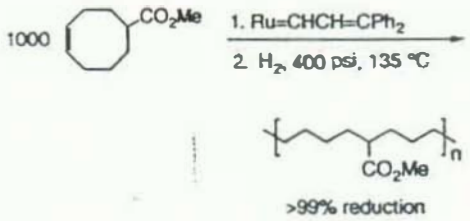
Schrock catalyst
R = $C(CH_3)(CF_3)_2$
fast polymerization



Grubbs catalyst
moderate rate, high productivity
tolerant of protic impurities

Other examples of Ru-catalyzed ROMP of functionalized cyclooctenes have recently been reported.[4,5]

The best method that we have found for the catalytic reduction of the polymer double bonds is the addition of hydrogen to a completed Ru-catalyzed polymerization. This is a particularly attractive method since the hydrogenation step can be run with no additional catalyst, and without work-up of the intermediate unsaturated polymer.



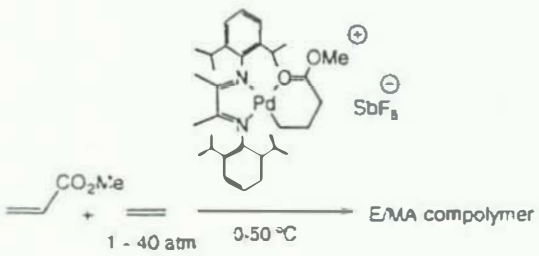
>99% reduction

The hydrogenation of the Ru alkylidene complex probably generates $RuHCl(P(cyclohexyl)_3)_2$, a very active hydrogenation catalyst.

Similar polymers with even higher levels of ester functionality were prepared from ROMP and hydrogenation of 4-carbomethoxycyclopentene.

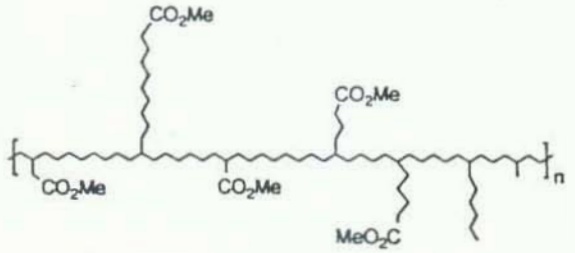
Palladium Catalyzed Copolymerization of Ethylene and Methyl Acrylate

A new class of α-diimine catalysts of Pd catalyzes the direct copolymerization of ethylene and methyl acrylate under mild conditions:[6]



On the basis of dual detection gpc (RI/UV) and solvent fractionation experiments, the products appear to be true random copolymers. The reaction works well in a variety of solvents including hexane, chloroform, toluene, and methyl acrylate. By varying reaction conditions, copolymers containing from 1-68 wt. % methyl acrylate were prepared.

Extensive NMR characterization of the copolymers revealed a highly unusual branched microstructure. They contain ester-ended branches, hydrocarbon-ended branches, and ester groups attached directly to the backbone.



If the in-chain acrylate is counted as a branch, then the overall branching level in these copolymers ranges from about 100 - 200 branches per 1000 methylene carbons. Samples prepared at higher pressure have a greater fraction of ester groups attached to the main backbone (i.e. in-chain acrylate). The copolymers are all amorphous at room temperature with Tg's from -48 to -71 °C. Samples with lower total branching levels have a small amount of low temperature crystallinity with broad melting points at about -40 °C.

The effect of various reaction parameters on the ethylene / methyl acrylate copolymerization was studied. Diluting the MA concentration with solvent increased reaction rate, copolymer molecular weight and catalyst productivity, but at the expense of methyl acrylate content. Increasing the ethylene pressure gave higher reaction rate, molecular weight and catalyst productivity, with concomitant reduction in MA content. Increasing the temperature lead to higher MA incorporation and lower molecular weight. Catalyst productivity was reduced at higher temperature. There was an inverse relationship between methyl acrylate incorporation and molecular weight. There was also a strong inverse relationship between methyl acrylate content and catalyst productivity.

Acknowledgments

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