

Issues in Catalytic Polymerization of Polar Monomers

Dean M. Philipp, Richard P. Muller, and William A. Goddard, III.

Materials and Process Simulation Center (139-74), California Institute of Technology,
Pasadena, California, USA 91125

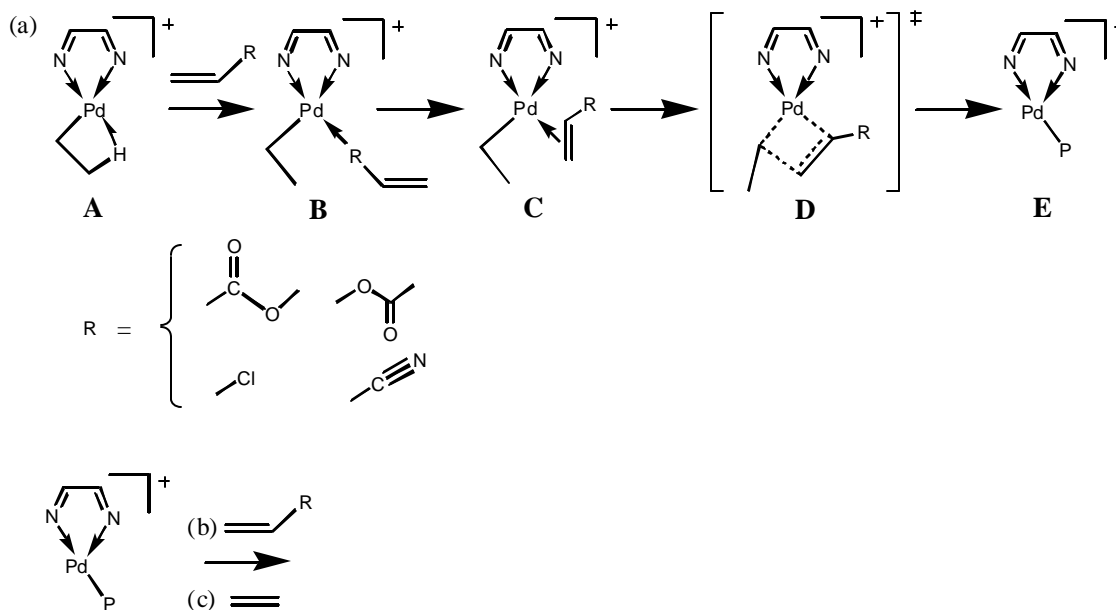
Joey Storer, Mark McAdon

The Dow Chemical Company, Midland, MI 48640

Mike Mullins

The Dow Chemical Company, Freeport, TX 77541

Taking Pd di-imine catalysts as an example, we use first principles density functional theory (B3LYP/6-31G*) to investigate the chain propagation steps for polymerization of polar monomers. We start with the complex formed from insertion of ethylene into the polymer chain and consider insertion into the Pd-C bond for each of four polar monomers: methyl acrylate, vinyl acetate, vinyl chloride, and acrylonitrile [step (a) below]. We find 2,1-insertion is favored in each case (by 3 to 5 kcal/mol), resulting in a product with a strong interaction of the polar group for the growing polymer chain with the metal. Next, we insert another unit of the same polar monomer [step (b) below] or an ethylene unit [step (c) below], except for acrylonitrile. We optimize the structures for all important intermediates and transition states using a continuum dielectric to account for solvation effects.



These studies pinpoint the critical difficulties in designing catalysts to polymerize polar monomers:

- Methyl acrylate and vinyl acetate insertions lead to products with strong interactions between the carbonyl oxygen and metal. This is consistent with experiments by Brookhart and co-workers who find that methyl acrylate incorporation is slow and limited to placement at chain branch ends. We find that barriers to subsequent insertions are even larger after vinyl acetate insertion; thus predicting that the catalyst would become trapped in this state.
- Insertion of vinyl chloride leads to a product in which the chloride prefers to dissociate onto the metal, thus poisoning the catalyst.
- Acrylonitrile forms such a strong σ -complex that no further insertions can occur.
- Polar olefins often form weaker π -complexes, and insertion barriers are often larger than for non-polar olefins.

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Selected Results

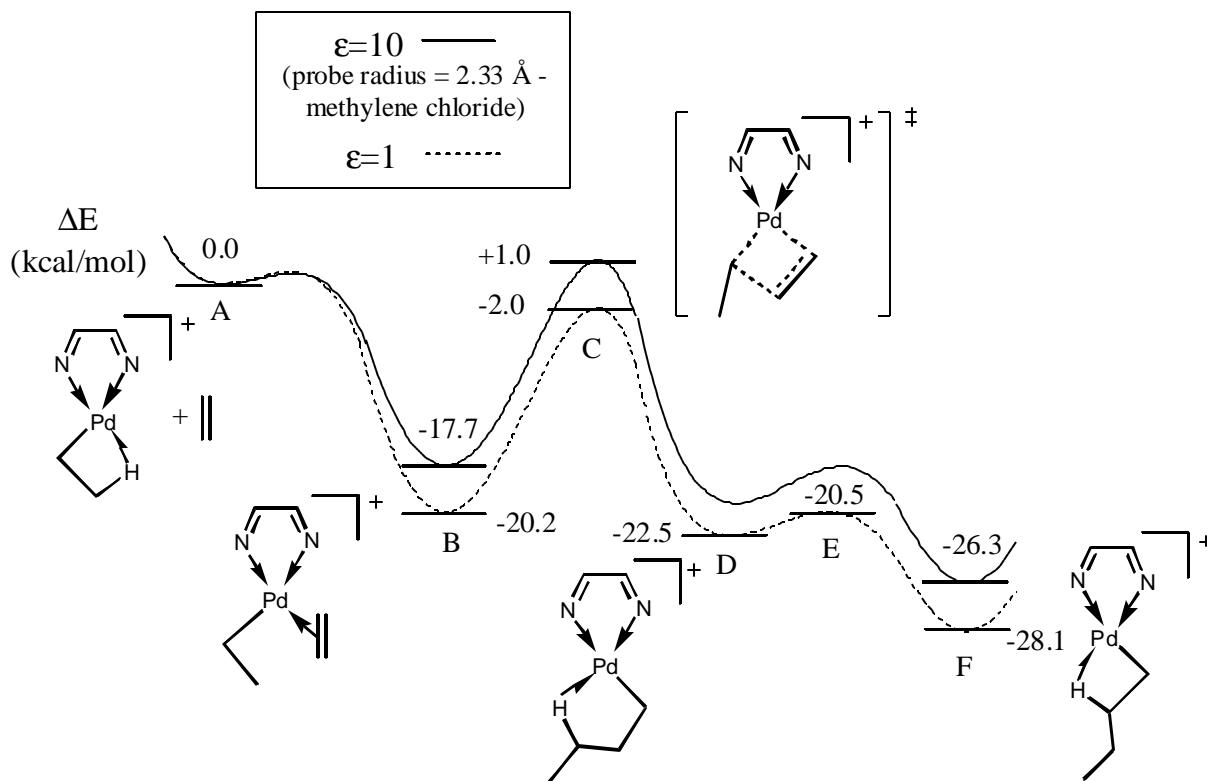


FIGURE 1. Potential energy diagrams for Pd di-imine catalyst with ethylene. The curves demonstrate insertion of an ethylene unit after a prior insertion of ethylene. The solid curve includes solvation effects while the dotted curve is for gas-phase (vacuum). These results will be used as a benchmark for comparison with the polar monomer studies.

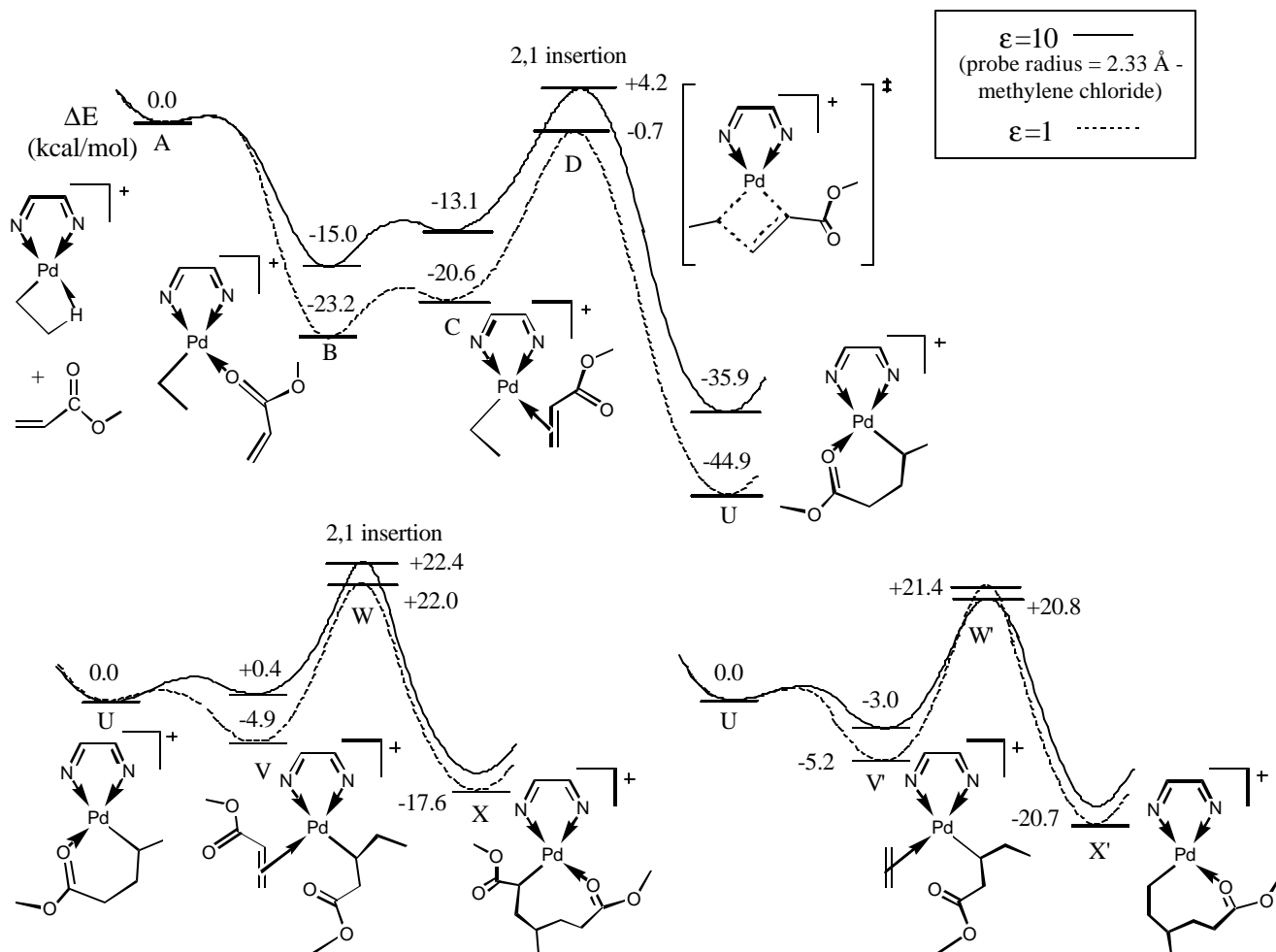


FIGURE 2. Potential energy diagrams for Pd di-imine catalyst with methyl acrylate including solvation. The top curves demonstrate insertion of a methyl acrylate unit after a prior insertion of ethylene. The bottom left curves show subsequent addition of a second methyl acrylate, while the bottom right curves show subsequent addition of ethylene. Solid curves include solvation effects (with a dielectric constant and probe radius representative of methylene chloride solvent), and dotted curves are gas-phase results. Methyl acrylate is just one of the polar monomers in this study, though the above typifies the critical challenges associated with polymerization of such polar monomers.