

## Net Spin Transfer in Polymer Depolymerization

Depolymerization plays an particularly important role in the synthesis of novel macromolecule materials form recycled monomers, but it could also be influenced by multiple factors, especially the experiment conditions which makes analysis difficult to the polymer depolymerization. Thus, it is essential to exploring and understanding the specific depolymerization process and the polymers depolymerization mechanism. Actually, polymer depolymerization mainly involves bonds breaking, the changes of physicochemical properties, formation of new functional groups and others.

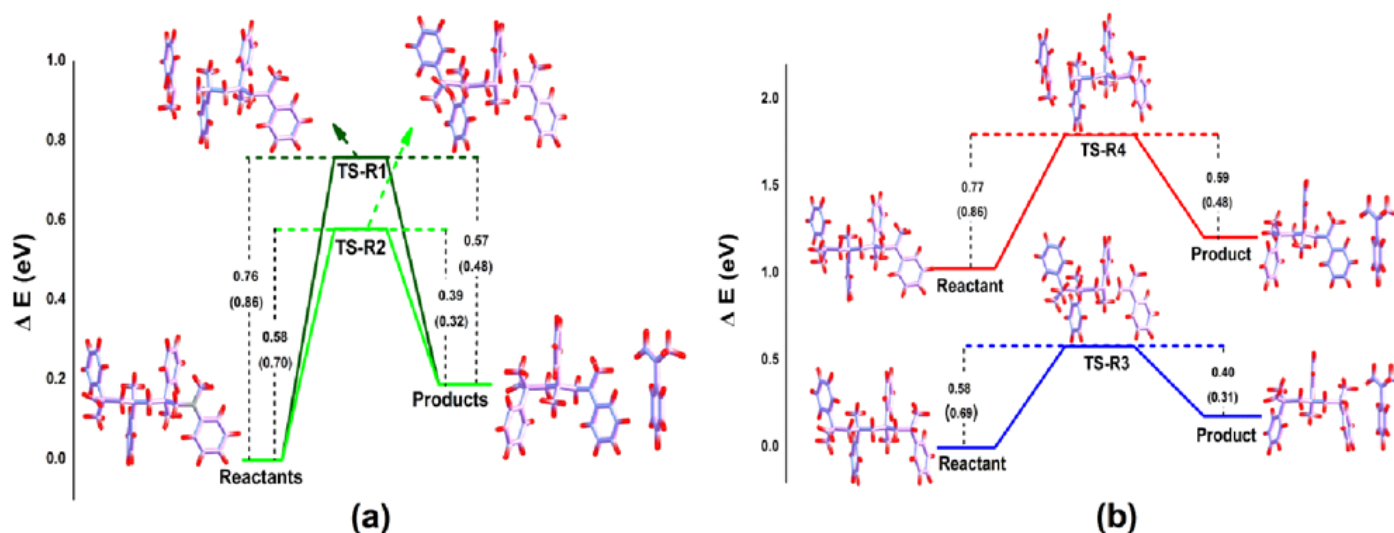


Fig. 1. The potential energy curves of four typical depolymerization reactions. (a) R1 and R2, (b) R3 and R4.

Currently, experimental techniques have been improved greatly, the geometrical information of reactants and products can be obtained by some technical methods. But unfortunately, some transition states (TSs) and intermediates are difficult to be observed directly in experiments for some polymers with many complex reaction channels. Therefore, a comprehensive theoretical study is necessary for understanding the free-radical depolymerization mechanism at atomic level.

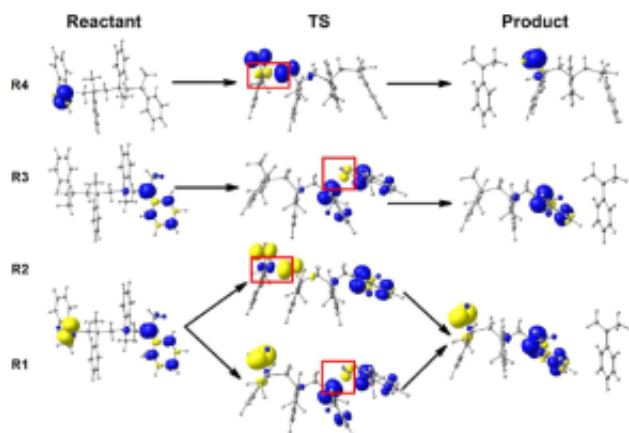


Fig. 2. The spin populations of four typical depolymerization reactions. The red squares show the sites of breaking C-C bond.

High accuracy first-principles density functional theory (DFT) calculations are focused on the four typical depolymerization reactions with chain-end scission based on a typical poly alpha-methylstyrene (PAMS) tetramer model. The calculated results show that these depolymerization reactions all need to overcome the energy barriers in the range of 0.58 to 0.77 eV, and the direct breaking of C-C bonds of the main chain near the unsaturated chain end leads to dissociation of the polymers into alpha-methylstyrene (AMS) monomers. From the potential curves of the four reactions, we find that the thermal compensation is not enough to overcome the reaction energy barrier after C-C bond breaking. Thus, depolymerization of PAMS is an endothermic reaction (see Fig 1). Importantly, the spin population also presented a unique net spin transfer process in free-radical depolymerization reactions (see Fig 2). In the reactants, the net spins are mainly distributed on the unsaturated ends. For the TSs, the net spins distributed on the dissociated monomer begin to gradually reduce. For the dissociated monomer in products, all the net spin electrons on the monomer self-coupled to form a C=C double bond, and thus the monomer has a closed-shell electronic structure; however, the net spin electrons on the surplus main chain still maintain free-radical characteristics. Hoping that the current findings could provide a theoretical basis for understanding the free-radical depolymerization mechanism and controlling the experimental operation.

## Publication

[Depolymerization of Free-Radical Polymers with Spin Migrations.](#)

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