ABSTRACT

Complexes [Rh(cycloolefin)(acac)] (cycloolefin = norborna-2,5-diene, cycloocta-1,5-diene and cyclooctatetraene) were investigated as catalysts of polymerization of monosubstituted acetylenes into stereoregular *cis-transoid* polyacetylenes. All complexes were highly active in arylacetylenes polymerizations in both coordinating and non-coordinating solvents. Selection of solvent and cycloolefin ligand of the catalyst allowed the control over polymer MW. The onset of initiation in the [Rh(cycloolefin)(acac)]/monomer systems proceeded as the proton transfer from the monomer molecule to the acac ligand under the release of acetylacetone and coordination of -C≡CR ligand to Rh(cycloolefin) moiety.

C*is-transoid* poly(phenylacetylene) and poly[(2,4-difluorophenyl)acetylene]s with required initial MW were prepared with these catalysts and submitted to the long-term ageing in which the polymers were exposed to the atmosphere and diffuse daylight either dissolved in tetrahydrofuran or in the solid state. Tightly connected processes of *cis*-to-*trans* isomerization of the polymer main-chains double bonds and oxidative degradation were found to proceed during polymers ageing in the solution. Besides, the formation of corresponding cyclotrimers accompanied the polymers ageing. However, the cyclotrimers amount was too low for explaining the degradation and isomerization of polymers in terms of intramolecular cyclization mechanism of Percec et al.

The mechanism was proposed that assumes the *cis*-to-*trans* isomerization of a particular macromolecule to be affected by a “domino effect” that results in the deep isomerization of this macromolecule. As experimentally verified, the isomerized macromolecules were enriched with unpaired electrons and thus they were significantly more prone to the oxidative degradation than the non-isomerized ones that were also present in the partly aged sample. The different degradation rates of isomerized and non-isomerized macromolecules explain the experimentally observed non-uniform distribution of these two kinds of macromolecules along the MW distribution of partly aged samples. The proposed mechanism is consistent with the experimental finding that the increase in configurational stability (resulting either from reduction of polymer MW or from a change in the covalent structure) is simultaneously accompanied by an increase in the MW stability of the polymer.