Zamknięcie przewodu doktorskiego

Thesis title:

Influence of σ and μ complexing agents on microstructure of polybutadiene obtained via anionic polymerization

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Abstract:

Synthetic rubber is a material which exhibits viscoelastic properties. Polybutadiene, polyisoprene and their copolymers with styrene may be regarded as the main representatives of this group. They are produced on massive scale to obtain rubber compounds with very different and specific physical and chemical properties. Macroscopic properties of a polymer or rubber are strongly related to the composition and distribution of isomeric structures in the polymer chain (microstructure) and which cannot be changed without breaking the chemical bonds. The main microstructural effects of the polymer which has to be considered are: stereoregularity (tacticity), regioregularity (head-tail, head-head isomerism) and geometric isomerism (*cis*, *trans* isomerism), and additionally, in case of copolymers, the content and distribution of monomers along the polymer chain.

During this research, under unified reaction conditions, series of anionic polymerizations of butadiene in the presence of polar modifiers were performed. This enabled to systematize the knowledge on the influence of the structure and concentration of Lewis base and Lewis acid polar modifiers, forming σ, μ, σ+μ and σ-μ complexes with polymer living center, on reaction kinetics and polybutadiene chain microstructure. Determination of butadiene isomeric structures content and distribution was performed on the basis of infrared spectroscopy (ATR-FT-IR) as well as ^{1}H and ^{13}C NMR nuclear magnetic resonance data. Additionally, enthalpy of polar modifier interaction with n-butyllithium ($\Delta H_{MOD/BuLi}$) as well as butadiene polymerization enthalpy (ΔH_{BD}) were related to the mechanistic aspect of anionic polymerization of butadiene which determines the content and distribution of butadiene isomeric structures in the polymer chain.

It was determined that the content and distribution of butadiene isomeric structures in the polymer chain very strongly depended on chemical structure and concentration of polar modifier applied as well as on the complex type formed with the polymer living center. It was found that polar modifiers forming the same type of complex exhibited similar tendency to influence on polybutadiene microstructure, nevertheless all of them lead to products exhibiting different and distinctive composition of isomeric structures. Measurements of polar modifier enthalpy interaction with n-butyllithium enabled to observe relation between $\Delta H_{MOD/BuLi}$ and the formation of 1,2 units and with butadiene polymerization enthalpy while the polymerization reaction kinetics measurements allowed to link polymerization rate constant with *cis* and *trans*-1,4 units. Additionally, essential impact of the chain structure on viscoelastic properties was presented.

The research showed the clear influence of the individual parameters of anionic polymerization and its polar modifiers on the possibility to control the structure and properties of polybutadiene and the polymerization process, which enables to synthesize tailor-made rubber products. The results were published in the international polymer journals.