

Free Radical Polymerization in Ionic Liquids - Explanation of the Solvent Influence

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In general, ionic liquids (ILs) consist of a voluminous organic cation and a complex anion. The most common types of cations used in ILs are imidazolium, pyridinium ammonium and phosphonium ions. As anions the hexafluorophosphate (PF_6^-) and the tetrafluoroborate (BF_4^-) are mostly used. The excellent solubility of many different organic and inorganic compounds in ionic liquids leads to a decrease of the required amount of solvent for a reaction. ILs as solvents have an effect on the reactivity and selectivity of the applied processes as well.

The analysis of the influence of ionic liquids in polymer synthesis as an alternative for common organic solvents is still an active field of research.^[1] Using ILs as solvents for free-radical polymerizations a significant increase in polymerization rates and molecular weights can be observed. It is dependent on the used ionic liquid itself, its concentration in the reaction mixture and the reaction temperature.

In^[2] and^[3] the increase of the propagation rate coefficient k_p for the polymerization of methyl methacrylate (MMA) in [BMIM]PF₆ with increasing IL concentration in the reaction solution is described. The authors discuss that this increase may be due to charge transfer and/or complex formation between either radical or monomer and ionic liquid.

One purpose of our work is the determination of the propagation rate coefficient k_p via PLP-SEC (pulsed-laser polymerization in combination with size-exclusion chromatography for polymer analysis) for the polymerization of MMA and glycidyl methacrylate (GMA) carried out in various ionic liquids.^[4]

Furthermore we examined the analysis of the homo- and copolymerization behaviour of styrene (S) and methacrylates (MMA, GMA and 2-hydroxypropyl methacrylate (HPMA)) with acrylonitrile (AN) and maleimides.

The ionic liquids 1-ethyl-3-methylimidazolium diethylsulfate (ECOENGTM212), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆) and methanol (MeOH) are used as solvents. The homopolymerization of AN, its copolymerization with HPMA and the copolymerization of S with maleimides can be carried out in solution independent of the conversion. The other polymerizations proceed under precipitation at conversions higher than 10 %.

Our examinations show the strong influence of the temperature and of the mixing solvents on the polymerization reaction rate and the molecular weight^[5]. The extreme solvent influence of the ILs can be explained better on this basis.

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