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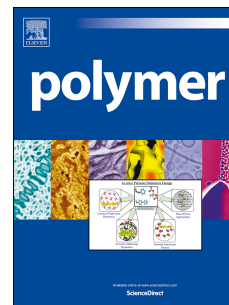
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Combining Advantages of Homogeneous Organocatalysis and Heterogeneous Catalysis with Thermosensitive Single-Chain Nanoparticles in a Representative Tetrahydropyranilation of Alcohols

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ABSTRACT: A significant scientific problem solved in this work is the development of effective polymer catalysts that allow carrying out organic reactions under homogeneous conditions with high rates and to remove catalyst from the system as a heterophase without the use of special treatment, thus combining the advantages of both homogeneous and heterogeneous catalysis. Kinetic experiments show high catalytic activity of the synthesized catalyst in homogeneous regime even at low dosage of the catalyst. Thus, it was demonstrated that tetrahydropyranilation of methanol was completed in nearly quantitative yield of the corresponding ether in 80 minutes at 60 °C with a dosage of the polymeric catalyst as low as 0.2 mol%. On the other hand anomalous decrease in the values of the effective rate constant was observed when the reaction was run at temperatures below the phase transition temperature. Kinetic data were used along with thermodynamic calculations to discuss the effect of the synthesized polymeric catalyst on the stabilization of the transition state. The high activity of the catalyst is complemented by its high sedimentation ability; thus, it usually takes a few minutes for the polymer to precipitate from the alcohol solution when cooled below the phase-transition temperature after the completion of the reaction. It was also revealed via dynamic light scattering that catalytic polymers adopt a thermodynamically stable conformation of the single-chain nanoparticles with average hydrodynamic radius in the range 2–2.5 nm.

1. Introduction

Despite the great achievements of modern chemistry, creating highly efficient and environmentally friendly catalyst systems is one of the major chemical problems. In recent years, development of the scientific foundations of polymer enzyme-like catalysis has become urgent. Investigations arising from this challenge allow one to approach the parameters of enzymatic catalysis, which are high speed and selectivity achieved under mild reaction conditions, biodegradability, and nontoxicity of catalytic systems. As a result of breakthroughs in some areas, the foremost of which are the development of polymer chemistry and organocatalysis, it has become possible to approach this problem. Folding of single-chain polymer chains in dilute solutions has gained much attention in recent years. Objects of this area of research are commonly called single-chain nanoparticles (SCNP) and interest in this field continues to grow due to the variety of applications and unique properties of SCNP, including specific catalytic abilities [1-6].

After the year 2000, investigations focusing on organocatalysis appeared and continue to expand [7-13]. Derivatives of the nitrogen containing heterocycles constitute a significant group [14] among the

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