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Molecular engineering of organic reagents and catalysts using soluble polymers

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Abstract

The separation of the final product of a reaction from byproducts, catalysts, or excess reagents is a process common to all synthetic procedures. Various methods to facilitate such separations continue to receive increasing attention as avenues to refine synthetic protocols. This review discusses recent developments in one of these areas, the use of soluble polymers as supports for organic synthesis and catalysis. The general purpose of such work is to combine the principal beneficial features of heterogeneous and homogeneous systems to achieve facile product/catalyst recovery without the polymer affecting the chemistry of known solution-phase processes. The work described here demonstrates that it is often possible to engineer a desired solubility profile, phase behavior, reactivity/selectivity profile, and other beneficial properties into a synthetic reagent or catalyst system by an appropriate choice of soluble polymer support and recovery scheme. In this review, emphasis is given to research published within the last two years. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Soluble polymer supports; Organic synthesis; Catalysis; Review

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1. Introduction

In parallel to the historical Copper, Bronze, and Iron ages, the term 'Polymer age' describes the modern world's current reliance on synthetic macromolecules as one of its most widely utilized construction materials. This epoch had its origins in the first half of the 20th century and owes its success to the basic research in synthesis and theory by eminent chemists like Staudinger, Zeigler, Natta, Carothers, Marvel and Flory, among many others. At this time, synthetic macromolecules are commonly viewed as end-use products. That is, much of the current research in polymer chemistry and engineering is driven by the search for polymers with specific physical and chemical properties. More recently, the biological, optical, electrochemical, and magnetic properties of polymers have received increasing attention. Regardless, the focus of this work has been particular societal and economic demands. The end result is that many modern necessities and conveniences, from trash bags to polymer liquid crystalline displays, depend on the incredible design flexibility offered by synthetic macromolecules.

Other polymer research over the past thirty years discussed below has had a different focus. This other area of research has focused on polymers not as final products, but as tools in synthesis and catalysis. The basic idea of this research is to use the macromolecular properties of a polymer, in combination with known solution-phase chemistry, to facilitate a separation or purification process. This theme originated with the pioneering work of Merrifield on solid-phase peptide synthesis, work subsequently recognized with the 1984 Nobel Prize in Chemistry. This work has now evolved to the point where two of the three main classes of biopolymers, peptides and polynucleic acids, are now routinely synthesized using solid-phase supports. Recent work suggests that oligosaccharides, too, are amenable to this sort of polymer-supported synthesis [1].

The success of the Merrifield approach to biopolymer synthesis subsequently led to a vast area of research developed around the use of insoluble, crosslinked polymers, most commonly divinylbenzene-crosslinked polystyrene, as supports for organic reagents and catalysts [2,3]. The primary advantage of these 'heterogenized' organic systems is the ease of product/catalyst/spent reagent separation. In such solid-phase synthesis, a simple filtration and washing of the polymer beads is sufficient to isolate the polymer-bound product. Cleavage of the product from the resin can then furnish, without further purification, high purity product. Likewise, the use of a catalyst or reagent bound to a crosslinked polymer support allows for facile catalyst recycling and reuse or simple product purification. Several recent reviews discuss these issues in detail [2–12].

Insoluble polymer supports have advantages. They have some disadvantages too. Ironically, the characteristic that lends them their greatest advantage, their complete insolubility, is also the origin