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Polyisobutylene supports—a non-polar hydrocarbon analog of PEG supports

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Abstract—Synthetic routes to terminally functionalized polyisobutylene oligomers useful as supports in synthesis and catalysis are discussed and described. Such hydrocarbon polymers serve as highly soluble non-polar analogs of well known poly(ethylene glycol) supports for synthesis and catalysis with the difference that they are separated after a reaction by an extraction with alkane solvent.

1. Introduction

The most common organic polymer support is polystyrene. In its cross-linked form with various pendant groups, this insoluble material is the organic polymer support most commonly used in biotechnology, in combinatorial chemistry, in organic synthesis, and in environmental chemistry. Many versions of this polymer with various crosslinkers or pendant groups exist and are commercially available.[1] Beginning in the 1960s, soluble polymers were examined as alternatives to insoluble polymer supports for organic chemistry.[2] Linear soluble polymers then and now are as widely available as their insoluble analogs. However, soluble polymers to this point are still used less in synthesis and catalysis. This partly reflects a perception that soluble polymer supports are harder to use or harder to separate from reaction mixtures. Recently alternative approaches using membranes or biphasic separations have developed that are leading to increasing attention being paid to such supports. Such soluble polymer supports have advantages because of the facility with which species on such supports can be characterized and modified and because groups on such supports can more faithfully mimic the chemistry of low molecular weight species.[3,4]

If one considers copolymers as well as homopolymers, there are a countless number of soluble supports that one might study. However, this paper and most work to date has focused on homopolymers lightly modified with pendant or terminal groups. The most common soluble polymer used in synthesis has been poly(ethylene glycol) (PEG), a terminally functionalized polyether.[2,5] This reflects the commercial availability of this polymer and its utility as a modifying group for drug delivery and for facilitation of drug bioavailability.[6] While PEG has historically been the most used soluble polymer, there remain many alternatives. The most contrasting alternative is polyethylene (PE)—poly(ethylene glycol) that has been stripped of its oxygens.[7] This polyolefin is perhaps the most common polymer. However, polyethylene as a support has limitations that limits its use in synthesis. First, the most useful forms of polyethylene for synthesis would be low molecular weight oligomers, which are not commercially available though they can be synthesized by several routes.[8,9] Second, there is the practical problem of polyethylene's solubility. Polyethylene oligomers that would likely be useful in synthesis are generally insoluble in any solvent below 60–70 °C. Nonetheless, PE has the virtues of the inertness of alkanes, a relatively transparent ^{1}H NMR spectrum, and synthetic versatility in end group modification.[8] This suggests that while PE might not be generally useful as a support, that other terminally functionalized polyolefins might merit more attention.

An alternative polyolefin support that we have recently begun to study is polyisobutylene (PIB).[10] PIB has the chemical inertness of polyethylene. As an oil or fuel additive, it is commercially available.[11] More usefully, unlike polyethylene, PIB and its derivatives are very soluble. As shown in this paper, vinyl terminated oligomers of polyisobutylene that are commercially available are easily modified by conventional chemistry and are viable precursors to many sorts of soluble polymeric reagents and supported ligands.

Keywords: Poly(ethylene glycol); PEG; Polyisobutylene; Polymer supported synthesis; Polymeric ligands.
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2. Results and discussion

Polyisobutylene (PIB) with vinyl groups is commercially available and is typically synthesized by cationic polymerization (Eq. 1).[12,13] It is a material that is prepared on a large scale because of its utility in adhesives and in fuel additives.[11] Our work has focused on modification of vinyl-terminated polyisobutylene. The polymer we have used here is available as a trade named product called Glissopal (M_w=1000, Dp=18 or M_w=2300, Dp=41) in tank car quantities and is predominantly vinyl terminated. A ^{1}H NMR spectrum of the starting polymeric material used here shows that the oligomer we used is predominantly terminated with a=CH_2 group (Fig. 1). While there are some internal trisubstituted alkene termini in these oligomers, the proportion of these groups is <10% and this impurity has little effect in the subsequent chemistry.

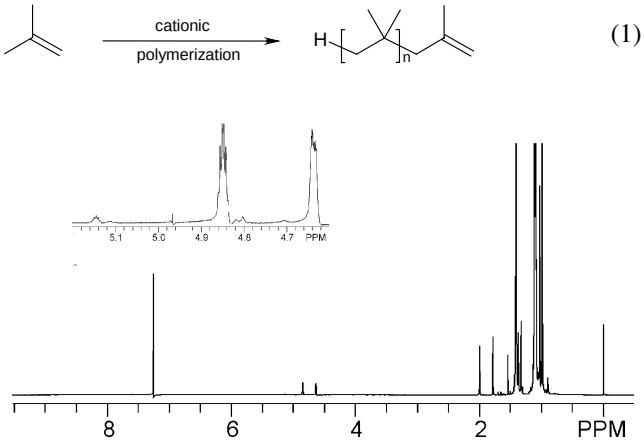

Figure 1. ^{1}H NMR spectrum of the starting vinyl-terminated polyisobutylene (**1**). The diastereomeric vinyl protons for the terminal =CH_2 group appear at δ 4.64 and δ 4.85. Some minor impurities are also present, principally an internal alkenyl group at δ 5.25.

Several strategies were used to convert the terminal double bond of **1** into functional groups useful in synthesis. Many of these strategies have precedence in earlier studies of others with PIB, PE, or PEG,[13–15] but are reiterated here to show the versatility of **1** for synthesis of useful organic functional groups. These strategies can be divided into three broad approaches—the design of functionality or the preparation of reactive intermediates at PIB termini that serve as nucleophilic sites for elaboration of the PIB, the design of functional groups or intermediates that serve as electrophilic entities for modification of PIB termini, and the incorporation of new functionality at PIB termini by concerted or catalytic reactions.

In the studies described below, the first chemical steps for synthesis for functional PIB oligomers for synthesis and catalysis involve oxidation of the terminal double bond of PIB. The simplest example of this approach involves conversion of the alkene into alcohols by hydroboration/oxidation. The resulting –CH_2OH groups can then be converted into a variety of other species as shown in Figure 2. An important feature of the chemistry in Figure 2 and of the chemistry described throughout this paper is that the terminally functionalized polyisobutylene oligomers being prepared are easily analyzed by ^{1}H NMR spectroscopy. ^{13}C NMR spectroscopy can be used as well. As is true in PEG derivatization chemistry, the ^{1}H NMR spectra of PIB derivatives is simplified by the fact that the protons of the PIB oligomers largely do not interfere with analysis of the functionality being introduced on PIB termini. In PEG chemistry, the –CH_2O– groups of the PEG backbone appear as a singlet at ca. 3.6 δ. While this peak overlaps regions of interest for some functional groups, with high field spectroscopy the PEG background signal only obscures a small portion of the useful region of the ^{1}H NMR spectrum. In PIB, the situation is even more favorable since the –CH_2–

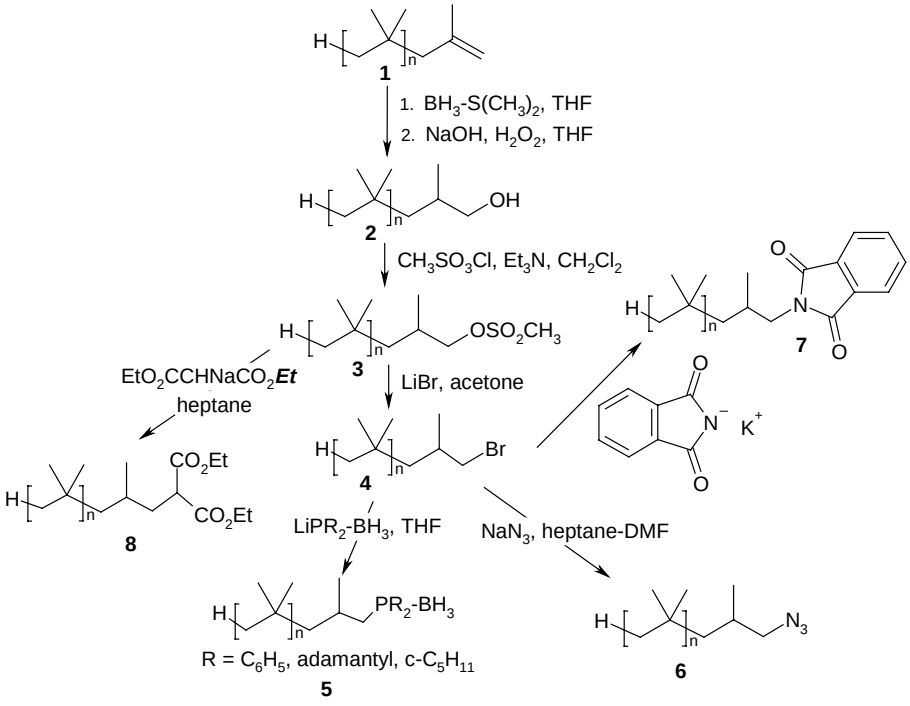

Figure 2. Examples of simple reactions that successfully introduce useful organic functional groups onto terminally functionalized polyisobutylene.