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Functionalization of living polyisobutylene: Preference for reduction over electrophilic addition

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ABSTRACT

Polyisobutylene was synthesized using 2-chloro-2,4,4-trimethylpentane (TMPCl) as an initiator and $TiCl_4$ as a coinitiator. After taking a base sample, the living cation was reacted with 5 equivalents of (4-vinylphenyl)dimethylsilane (VPDMSi). It was observed that the cation preferred reduction by hydride elimination from VPDMSi compared to electrophilic addition of even a single vinyl group. It was postulated that the reduction of the cation in presence of strong Lewis acid such as $TiCl_4$ occurs readily before addition of cation to vinyl group. Thus saturated polyisobutylene was obtained with a terminal hydrogen group instead of chlorine group which is produced by conventional cationic polymerization.

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1. Introduction

One of the most common monomers which can only be polymerized using cationic polymerization is isobutylene (IB). Polyisobutylene (PIB) and butyl rubber have found many applications in fields such as tire tubes, inner liners in tubeless tires, electrical insulators, adhesives, sealants, additives, gaskets, moisture barriers, gloves and polymeric coatings on coronary stents [1–3]. These applications are the result of the many interesting physical and chemical properties of these polymers such as high resistance to heat, chemicals, excellent gas barrier properties, dielectric properties, high damping ability, resistance to moisture, ozone, and UV. Functionalization of PIB is an important step that alters its properties. Many successful attempts have been made to synthesize functional PIB by post polymerization treatment. One method among the many post polymerization functionalization methods involved the use of silyl hydride functional compounds as hydride donors under cationic polymerization conditions [4–6]. Against this background it was of interest to us to investigate the reaction of silyl hydride functional compounds such as (4-vinylphenyl) dimethyl silane (VPDMSi) with living PIB cations. The stability of the silyl hydride functional group of VPDMSi under anionic polymerization conditions has already been established [7,8].

One of the earliest examples of hydride transfer from a hydrosilane to a carbenium ion dates back to 1947 [9]. It was found that *n*-hexyl chloride and *n*-pentyl chloride were converted to their respective alkanes when reacted with triethylsilane in the presence of $AlCl_3$ as a Lewis acid. Later, many examples of hydride transfer were reported which focused on kinetics, thermodynamics and stereochemistry of the reaction between carbenium ions and hydrosilanes [10–13]. The reactivity of hydrosilanes towards hydride transfer depends on their substituents. The order of reactivity shows the following trend [14]:

$$Et_3SiH > nOct_3SiH > Et_2SiH_2 > Ph_2SiH_2 > Ph_3SiH > PhSiH_3$$

Triethylsilane was found to be a better hydride donor compared to other hydrosilanes because of the presence of electron donating ethyl groups and the smaller size of ethyl groups as compared to phenyl groups. At very low

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temperature (−70 °C) the relative rate of hydride transfer towards bis(*p*-anisyl)carbenium ion was found to show the following order [15]:

	$HSiMe_2Ph>$	$HSiMe_3>$	$HSiMePh_2>$	$HSiPh_3$
Relative rate	18.0	7.70	2.71	1

This result was important in our case since VPDMSi resembles the structure of $HSiMe_2Ph$ and it was shown by the authors [15] that the substituent on the phenyl ring had little effect on the rate of hydride transfer. VPDMSi has previously been polymerized via anionic polymerization showing the stability of the –SiH bond under anionic polymerization conditions [8]. The stability of the –SiH head group under cationic conditions had been demonstrated in presence of a Lewis acid such as trimethylaluminum by Kennedy and coworkers [16,17].

In this research the reactivity of the polyisobutyl carbenium ion (PIBC) towards electrophilic addition to a vinyl group versus the competitive reaction with a silyl hydride group was compared. It was found that PIBC exclusively underwent hydride transfer as opposed to any addition to VPDMSi.

2. Experimental

2.1. Materials

4-Chlorostyrene (98%, Synquest lab, Inc. Alachua, Florida, USA) was used to synthesize VPDMSi as described in previous literature [8]. Dimethylchlorosilane (98%, Aldrich), titanium chloride (99.9%, Aldrich), 2,4,4-trimethyl-1-pentene (99%, Aldrich), 2,6-di-*tert*-butylpyridine (DtBP, 97%, TCI America) and N,N-dimethylacetamide (DMA, 99.5%, Aldrich) were used as received. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was synthesized according to previous literature [18,19]. Methylcyclohexane (99%, Aldrich) was stirred over calcium hydride and distilled prior to use. Isobutylene (IB) and methyl chloride (ExxonMobile) were dried by passing through a column of $CaCl_2$/BaO before collecting in a measuring cylinder at −70 °C.

2.2. Procedures

A MBraun glovebox (purged with nitrogen) was used for carrying out polymerizations. Experiments were conducted when the moisture and oxygen level dropped below 5 ppm. All the glassware was dried for 12 h at 130 °C in an oven before transferring into the glovebox. In a typical experiment, first 200 mL of methylcyclohexane and 130 mL of methyl chloride were added to a three-necked flask kept at −70 °C. Isobutylene (12 g, 214 mmol), 2-chloro-2,4,4-trimethylpentane (2.0 g, 13 mmol), dimethylacetamide (0.6 g, 7 mmol) and 2,6-di-*tert*-butylpyridine (0.5 g, 3 mmol) were added first to the flask at −70 °C. The reaction was started after addition of precooled titanium tetrachloride dissolved in a methylcyclohexane (6 mL) and methyl chloride (4 mL) mixture. After 60 min, half of the sample was taken aside and quenched with 10 mL of precooled (−70 °C) methanol (with 10% NaOH wt/vol). To the rest of the solution, (4-vinylphenyl)dimethylsilane (5.4 g, 33 mmol) was added which changed the color of the solution to dark red (that of red kidney beans). After 30 min, 10 mL of precooled methanol (10% NaOH wt/vol) was added to the solution.

Both the parts (PIBCl, 4.79 g, 98%) and reacted polymer (PIBVPDS, 6.96 g, 98%) were precipitated into methanol. The dissolution (in dichloromethane) and precipitation (in methanol) cycle was repeated four times. The precipitated polymers were dried under vacuum for 72 h.

2.3. Size Exclusion Chromatography (SEC)

SEC measurements were recorded using Waters 515 HPLC pump coupled with Wyatt OPTILAB DSP Interferometric Refractometer, Wyatt DAWN EOS multi-angle light scattering detector, Wyatt ViscoStar viscometer attached to six Styragel® columns (HR0.5, HR1, HR3, HR5, and HR6). Tetrahydrofuran (THF) continuously distilled off CaH_2 at a flow rate of 1 mL/min was used as a mobile phase at 35 °C. Astra software (Wyatt technology) was used for analyzing the results. Sample concentration was between 1.73 and 1.74 mg/mL for both the samples with a dn/dc of 0.108 (mL/g).

2.4. Nuclear Magnetic Resonance (NMR)

NMR spectra were recorded using Varian Mercury 500 NMR spectrometer. For measuring ^1H NMR ~20 mg of sample was dissolved in 1.0 mL of deuterated chloroform. For a typical ^{13}C NMR ~150 mg of sample was dissolved in 1.0 mL deuterated chloroform. Peaks at 7.27 ppm and 77.00 were used as internal references for ^1H and ^{13}C NMR, respectively. Samples were run for 64 scans (5 s relaxation delay) and 2000 scans (10 s relaxation delay) for ^1H and ^{13}C NMR, respectively.

3. Results and discussion

After polymerizing IB, a base sample of polyisobutylene (PIBCl) was taken and the remaining solution was treated with a precooled solution of (4-vinylphenyl)dimethylsilane. The treated polymer (PIBVPDS) was quenched with a precooled solution of methanol. Both the polymers PIBCl and PIBVPDS were dried under vacuum for 3 days and analyzed by SEC (coupled with refractive index, viscometer, and light scattering detectors). The SEC chromatograms (RI detector response and light scattering detector response) of PIBCl and PIBVPDS as a function of elution volume are shown in Fig. 1.

The molecular weight data (M_n, M_w and M_w/M_n) of PIBCl and PIBVPDS are summarized in Table 1. As seen from Table 1 and Fig. 1, there is no significant difference between the molecular weights and distributions of PIBCl and PIBVPDS.

The ^1H NMR spectrum of PIBCl is shown in Fig. 2. The peaks are assigned to PIBCl chains based on the reported literature as shown in the inset of Fig. 2. The resonances of the terminal $–CH_3$ and $–CH_2$ groups as well as $–CH_3$ head groups were observed at δ 1.70, 1.98, and 1.01 ppm respectively [5,20–22]. The M_n of PIBCl was calculated by taking

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