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Nucleophilic catalysis of halide displacement from brominated poly(isobutylene-co-isoprene)

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ABSTRACT

The dynamics of halide displacement from brominated poly(isobutylene-co-isoprene)-(BIIR) by carboxylate nucleophiles are detailed and discussed in terms of a general reaction mechanism. The exomethylene allylic bromide isomer within BIIR is shown to undergo simultaneous S_N2 alkylation of Bu_4Nacetate and S_N2' rearrangement with Bu_4NBr. The latter generates a Z-BrMe isomer that is more reactive toward esterification. Hence, overall polymer modification rates are auto-accelerating, as Bu_4NBr liberated by esterification catalyzes allylic bromide rearrangement to a more reactive electrophile. This knowledge of reaction mechanisms is used to develop nucleophilic catalysis techniques involving iodide intermediates.

1. Introduction

Poly(isobutylene-co-isoprene) is an elastomeric material that is valued commercially for its oxidative stability [1], superior gas impermeability [2], and potential for use in biomedical applications [3]. Halogenation of the residual unsaturation in this elastomer yields brominated butyl rubber (BIIR), whose allylic bromide functionality reacts readily with sulfurating agents [4] and Lewis acids [5] to generate thermoset products that are suitable for a wide range of practical applications. Halogen displacement by nitrogen [6,7], phosphorus [8] and oxygen [9] nucleophiles have also been developed to prepare functional elastomers that retain the desirable characteristics of the parent material while providing increased range of use.

The esterification of BIIR is particularly attractive, given the widespread availability of functional carboxylate nucleophiles as well as mono-chelic, carboxylate-terminated polymers. These nucleophilic substitutions proceed irreversibly under solution-borne and solvent-free conditions [10], but their dynamics do not abide by simple bimolecular kinetics. This is due, in part, to the susceptibility of BIIR toward isomerization. The exomethylene allylic bromide (Exo-Br) within BIIR is a kinetically favoured bromination product that can rearrange to thermodynamically more stable bromomethyl (E,Z-BrMe) isomers (Scheme 1) [11,12]. As a result, BIIR esterification involves concurrent isomerization and bromide displacement, yielding up to three allylic esters in proportions that can vary significantly with reaction conditions.

The objective of this work was to create a general mechanism for BIIR esterification, with particular attention paid to allylic bromide isomerization, the reactivity of each allylic bromide isomer toward carboxylate nucleophiles, and the joint influence of these factors on esterification rates. Our studies began with homogeneous reactions of tetrabutylammonium carboxylate salts before advancing to more complex phase-transfer catalyzed reactions of alkali metal carboxylates. This fundamental knowledge was used to develop nucleophilic catalysis techniques for accelerating allylic halide rearrangement and substitution.

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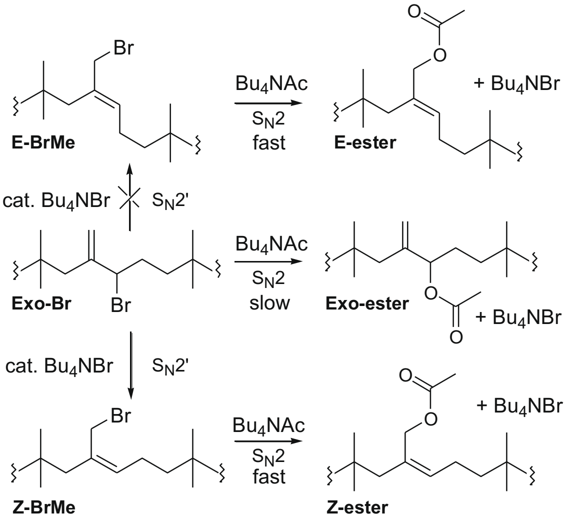

Scheme 1. General kinetic scheme for BIIR + Bu_4NAc reactions at 85 °C.

2. Experimental

2.1. Materials

Tetra-*n*-butylammonium salts of acetate, bromide and iodide (Bu_4NAc, Bu_4NBr, Bu_4NI, respectively), stearic acid and zinc stearate were used as received from Sigma–Aldrich. BIIR (BB2030, Mn ≈ 400 kg/mole; 0.15 mmole/g allylic bromide) was used as supplied by LANXESS Inc. (Sarnia, Ontario). Brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN) was prepared as previously described [8].

2.2. Iodinated 2,2,4,8,8-pentamethyl-4-nonene

A solution of BPMN (3 mg) and excess NaI (5 mg) in $CDCl_3$ (0.5 ml) was heated to 45 °C for 150 min to give the desired iodinated derivative. ^1H NMR ($CDCl_3$): δ 0.7–2.3 (m, 24H, 2*x* —$C(CH_3)_3$, 3*x* —CH_2—); E-IMe: δ 4.07 (=CH—**CH**$_2$—I, 2H, s), δ 5.83 (=**CH**—CH_2—I, 2H, s); Z-IMe: δ 3.97 (=CH—**CH**$_2$—I, 2H, s), δ 5.33 (=**CH**—CH_2—I, 2H, s).

2.3. Iodinated butyl rubber

A solution of BIIR (1 g) and Bu_4NI (5 eq, 0.51 g) in toluene (19 ml) was heated for 4 h at 85 °C. The product was isolated by precipitation from acetone, redissolved in toluene with Bu_4NI (20 eq, 2.0 g), and heated for 20 h at 85 °C. The product was recovered by precipitation from acetone and dried under vacuum at room temperature. Downfield ^1H NMR ($CDCl_3$): E—I—IIR: δ 4.08 (=CH—**CH**$_2$—I, 2H, s), δ 5.81 (=**CH**—CH_2—I, 2H, s); Z—I—IIR: δ 3.99 (=CH—**CH**$_2$—I, 2H, s), δ 5.35 (=**CH**—CH_2—I, 2H, s).

2.4. BIIR isomerization

BIIR (1 g) and the desired isomerization catalyst (0.12 g zinc stearate, 6.4 mg Bu_4NBr, 7.4 mg Bu_4NI) were dissolved in toluene (22 ml) and stirred in an oil bath at 85 °C. Samples were withdrawn at intervals, precipitated into acetone and dried under vacuum. Allylic bromide contents were quantified by ^1H NMR spectrum integration using the following signals: δ 5.01 (Exo-Br, =**CH**H, 1H, s); δ 4.11 (E-BrMe, =CH—**CH$_2$**—Br, 2H, s), δ 4.09 (Z-BrMe, =CH—**CH$_2$**—Br, 2H, s).

2.5. BIIR esterification with Bu_4NAc

BIIR (1 g), Bu_4NAc (0.06 g /1.5 eq; 0.12 g/3.0 eq) and the desired catalyst (none, 6.4 mg Bu_4NBr, 7.4 mg Bu_4NI) were dissolved in toluene (22 ml) and stirred in an oil bath at 85 °C. Samples drawn at regular intervals were precipitated into acetone, dried under vacuum, and analyzed for allylic bromide and allylic ester content by ^1H NMR analysis using the following chemical shift assignments: δ 5.01 (Exo-Br, =**CH**H 1H, s); δ 4.11 (E-BrMe, =CH—**CH$_2$**—Br, 2H, s); δ 4.09 (Z-BrMe, =CH—**CH$_2$**—Br, 2H, s); δ 5.19 (Exo-ester, =CH—CHOCOR-R, 1H, s); δ 4.52 (E-ester, =CH—**CH$_2$**—O—COR, 2H, s); δ 4.59 (Z-ester, =CH—**CH$_2$**—O—COR, 2H, s) [8].

2.6. BIIR esterification with potassium stearate

BIIR (1 g) was dissolved in xylenes (10 ml) and treated with 2A molecular sieves prior to adding KOH (54 mg), stearic acid (5.5 mg) and phase transfer catalyst (4.1 mg Bu_4NBr or 4.9 mg Bu_4NI) and heating to 85 °C in an oil bath. Samples drawn at regular intervals were precipitated into acetone, dried under vacuum, and analyzed for allylic bromide and allylic ester content by ^1H NMR analysis using the following chemical shift assignments: δ 4.51 (E-stearate, =CH—**CH$_2$**—OCO—, 2H, s), δ 4.59 (Z-stearate, =CH—**CH$_2$**—OCO—, 2H, s) [8].

3. Results and discussion

3.1. Dynamics of uncatalyzed allylic ester syntheses

Toluene solutions containing 5 wt.% BIIR and tetra-*n*-butylammonium acetate (Bu_4NAc) are homogeneous mixtures at 85 °C that react irreversibly to give the desired esters without interference from dehydrobromination and its accompanying side-reactions [13]. Fig. 1 illustrates the progress of reactions conducted at different nucleophile concentrations and/or initial allylic bromide isomer distributions. In these plots, allyl group concentrations are expressed as mmoles of functionality per gram of elastomer (mmol/g-XIIR), and Bu_4NAc concentrations are listed as molar equivalents relative to the 0.15 mmol/g of allylic bromide within the polymer.

Fig. 1a and b summarize reactions of “as received” BIIR containing a 95:0:5 ratio of Exo-Br:Z-BrMe:E-BrMe isomers. As expected for a bimolecular process, the initial rate of Exo-Br consumption generated by 3 eq of Bu_4NAc (Fig. 1b) was greater than that supported by 1.5 eq of nucleophile (Fig. 1a). However, Exo-Br consumption rates did not decline appreciably as the reactions approached 50% conversion, unlike simple bimolecular substitutions that slow as reagents are consumed. The immediate conversion of E-BrMe functionality to an equivalent amount