Synthesis of Ester Derivatives of Brominated Poly(isobutylene-*co*-isoprene): Solvent-Free Phase Transfer Catalysis

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ABSTRACT: The principles of phase transfer catalysis (PTC) are adapted to facilitate solvent-free nucleophlic substitution reactions of brominated poly(isobutylene-*co*-isoprene) (BIIR). Catalytic amounts of tetraalkylammonium halides are shown to activate alkali metal carboxylate salts to generate ester derivatives in moderate to high yields without incurring complications associated with ammonium carboxylate salt instability and BIIR dehydrobromination. The structures of a range of new aliphatic and aromatic allylic esters are characterized unambiguously through comparisons with products derived from brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN), which serves as a model for the reactive functionality found within BIIR. The dynamics of the intrinsic substitution process are examined along with factors that affect the rate and selectivity of phase-partitioned, solvent-free PTC systems.

Introduction

The chemical modification of halogenated polymers by nucleophilic substitution is a robust means of synthesizing functional derivatives that cannot be prepared through standard polymerization methods. Substitutions involving charged nucleophiles have benefited from the development of phase transfer catalysis (PTC) techniques that activate alkali metal carboxylate salts using small amounts of quaternary ammonium halides and thereby facilitate the preparation of ester derivatives from stable and inexpensive reagents.[1] To date, these reactions have been performed exclusively on polymer solutions,[2,3] but it is highly desirable to operate under solvent-free conditions using conventional polymer processing equipment to produce derivatives without the need for polymer isolation and/or purification operations.

Our studies of the reactions of brominated poly(isobutylene-*co*-isoprene), or BIIR, with uncharged nucleophiles[4,5] have demonstrated the propensity of the 1−2% of allylic bromide functionality within this polymer to undergo bromide displacement under solvent-free conditions. However, analogous reactions involving alkanethiols required strong organic bases to deprotonate the substrate and render the thiolate nucleophile soluble in the elastomer phase.[6] In the case of the carboxylate nucleophiles of present interest (Scheme 1), substrate acidity is not a concern. Rather, it is our desire to employ alkali metal carboxylates and solvent-free conditions that presents challenges, given the limited solubility and nucleophilicity of these salts within the nonpolar medium provided by a BIIR matrix.

This report describes the adaptation of PTC techniques for the synthesis of new allylic ester derivatives from BIIR and alkali metal carboxylate salts in the absence of solvent. The substitution products are characterized unambiguously through comparisons to products derived from brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN), which serves as a model of the allylic bromide functionality within BIIR.[7] Concerns regarding the stability of the starting materials, the intermediate ammonium carboxylate salts, and the resulting allylic ester products are addressed prior to defining the relationships between reaction conditions and the dynamics of solution-based and solvent-free substitution reactions.

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Experimental Section

Materials. Brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN, **1**) was prepared as described previously.[7] The following reagents were used as received from Sigma-Aldrich (Oakville, Ontario): tetrabutylammonium hydroxide (1 M in methanol), tetrabutylammonium bromide (98%), trioctylmethylammonium chloride (Aliquat 336, 95%), tributylamine (98%), *tert*-butylacetic acid (98%), stearic acid (98%), benzoic acid (98%), 4-(dimethylamino)benzoic acid (98%), anthracene-9-carboxylic acid (98%), linoleic acid (99%), and potassium hydroxide (99%). BIIR (BB2030, M_n = 410 000, polydispersity = 1.5) contained 0.19 mmol/g of allylic bromide functionality and was used as supplied by LANXESS Inc. (Sarnia, Ontario). Tetrabutylammonium and potassium carboxylate salts were prepared from their corresponding carboxylic acids by neutralization with the appropriate hydroxide base.

(3,3-Dimethylbutyl)-2-(2,2-dimethylpropyl)prop-2-enyl 3,3-Dimethylbutanoate (3a) and (*E*/*Z*)-6,6-Dimethyl-2-(2,2-dimethylpropyl)hept-2-enyl 3,3-Dimethylbutanoate (3b, 3c). BPMN (0.022 g, 0.081 mmol), tetrabutylammonium *tert*-butyl acetate (0.043 g, 0.120 mmol), and dodecane (0.4 mL) were sealed in a 1 mL Wheaton vial and heated to 100 °C for 1 h. The product was purified by column chromatography (silica, hexanes eluent) and isolated in vacuo to yield a yellow oil, **3**. It was possible to isolate the exomethylene isomer **3a** by chromatography using silica gel and mixtures of solvents (hexanes:acetone:diethyl ether). FT-IR analysis: 1734 cm^{-1} (C═O); MS analysis: required mass for $C_{20}H_{38}O_2$ is 310.5 *m*/*e*; found 311.4 *m*/*e* $[M + H]^+$ (CI+) and 333.21 *m*/*e* $[M + Na]^+$ (ESI+). ^1H NMR ($CDCl_3$) **3a**: δ 5.18 (dd, 1H, −CHOC(O)−), 5.09 (s, 1.04H, ═CH_2), 4,86 (s, 1.06, ═CH_2), 2.20 (dd, 2.1H, −CH_2−), 1.92 (dd, 2.2H, −CH_2−), 1.56 (m, 2.5H, −CH_2−), 0.6−1.3 (m, 33.2H, 2 × −$C(CH_3)_3$, 1 × −CH_2−). **3b,c**: ^1H NMR ($CDCl_3$): δ 4.48 (s, 1H, −$CH_2OC(O)$−), 5.55 (t, 0.5H, ═C−H), 4.55 (s, 0.19H, −$CH_2OC(O)$−), 5.39 (t, 0.08H, ═C−H), 0.6−2.3 (m, 59.4H, 2 × −$C(CH_3)_3$, 4 × −CH_2−). NOESY ^1H NMR: **3b**: *E*-isomer; **3c**: *Z*-isomer.

(3,3-Dimethylbutyl)-2-(2,2-dimethylpropyl)prop-2-enyl Stearate (4a) and (*E*/*Z*)-6,6-Dimethyl-2-(2,2-dimethylpropyl)hept-2-

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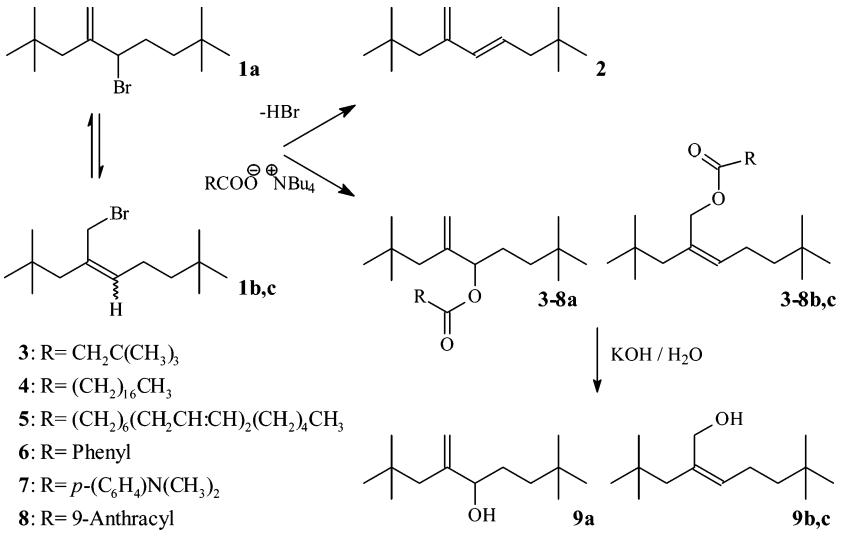
Scheme 1



enyl Stearate(4b, 4c). BPMN (0.044 g, 0.163 mmol), tetrabutylammonium stearate (0.085 g, 0.162 mmol), and dodecane (0.4 mL) were sealed in a 1 mL Wheaton vial and heated to 100 °C for 1 h. The product was purified by column chromatography (silica, hexanes eluent) and isolated in vacuo to yield a yellow oil, **4**. FT-IR analysis: 1734 cm^{-1} (C═O). MS analysis: required mass for $C_{32}H_{62}O_2$ is 478.83 *m/e*; found 478.5 *m/e* (EI+) and 479.5 *m/e* $[M + H]^+$ (CI+). ^1H NMR ($CDCl_3$) **4**: δ 0.6−2.4 (m, 108.2H, 3 × −$C(CH_3)_3$, 19 × −CH_2−), 4.4−5.6 (m, 3.3H, 1 × −CHOC(O)−, 2 × ═CH_2, 2 × −CH_2OC(O)−, 2 × ═C−H); **4a**: δ 5.17 (dd, −CHOC(O)−), 5.07 (s, ═CH_2), 4.84 (s, ═CH_2); **4b**: δ 4.49 (s, −CH_2OC(O)−), 5.52 (t, ═C−H); **4c**: δ 4.56 (s, −CH_2OC(O)−), 5.39 (t, ═C−H).

(3,3-Dimethylbutyl)-2-(2,2-dimethylpropyl)prop-2-enyl Linoleate (5a) and (*E*/*Z*)-6,6-Dimethyl-2-(2,2-dimethylpropyl)hept-2-enyl Linoleate (5b, 5c). BPMN (0.044 g, 0.163 mmol), linoleic acid (0.08 mL, 0.257 mmol), KOH (0.02 g, 0.35 mmol), Aliquat 336 (0.05 mL, 0.1 mmol), and toluene (1 mL) were transferred to a round-bottom flask and heated to 70 °C for 3 h. The product was purified by column chromatography (silica, hexanes eluent) and isolated in vacuo to yield a yellow oil, **5**. FT-IR analysis: 1734 cm^{-1} (C═O). MS analysis: required mass for $C_{32}H_{58}O_2$ is 474.4437 *m/e*; found 474.4427 *m/e* (TOF MS EI+).

^1H NMR ($CDCl_3$) **5**: δ 0.6−2.8 (m, 123.3H, 3 × −$C(CH_3)_3$, 15 × −CH_2−), 4.4−5.6 (m, 7.98H, 1 × −CHOC(O)−, 2 × ═CH_2, 2 × −CH_2OC(O)−, 6 × ═C−H); **5a**: δ 5.17 (dd, −CHOC(O)−), 5.08 (s, ═CH_2), 4.84 (s, ═CH_2); **5b**: δ 4.48 (s, −CH_2OC(O)−), 5.52 (t, H−C═); **5c**: δ 4.51 (s, −CH_2OC(O)−), 5.40 (t, H−C═).

1-(3,3-Dimethylbutyl)-2-(2,2-dimethylpropyl)prop-2-enyl Benzoate (6a) and (*E*/*Z*)-6,6-Dimethyl-2-(2,2-dimethylpropyl)hept-2-enyl Benzoate (6b, 6c). BPMN (0.022 g, 0.081 mmol), tetrabutylammonium benzoate (0.040 g, 0.110 mmol), and toluene (0.4 mL) were sealed a 1 mL Wheaton vial and heated to 95 °C with agitation for 90 min. The dark yellow product was diluted with hexanes then charged to a silica column. Nonpolar components were eluted with hexanes, while **6** was isolated by a subsequent elution with dichloromethane and drying in vacuo. High-resolution MS analysis: required for $C_{21}H_{32}O_2$ *m/e* 316.2402; found *m/e* 316.2394. FT-IR analysis: 1723 cm^{-1} (C═O); 1265 cm^{-1} (C−O−C). ^1H NMR ($CDCl_3$): **6**: δ 0.6−2.2 (m, 105H, 2 × −$C(CH_3)_3$, 3 × −CH_2−), 4.6−5.7 (m, 9.8H, 1 × −CHOC(O)−, 2 × ═CH_2, 2 × −CH_2OC(O)−, 2 × ═C−H), 7.4−8.2 (m, 15.6H, 5 × ═CH−); **6a**: δ 5.43 (dd, −CHOC(O)−), 5.18 (s, ═CH_2), 4.89 (s, ═CH_2). **6b**: δ 4.75 (s, −CH_2OC(O)−), 5.64 (t, ═C−H). **6c**: δ 4.82 (s, −CH_2OC(O)−), 5.46 (t, ═C−H).

1-(3,3-Dimethylbutyl)-2-(2,2-dimethylpropyl)prop-2-enyl 4-(Dimethylamino)benzoate (6a) and (*E*/*Z*)-6,6-Dimethyl-2-(2,2-dimethylpropyl)hept-2-enyl *p*-(Dimethylamino)benzoate (7b, 7c). BPMN (0.011 g, 0.040 mmol), tetrabutylammonium 4-(dimethylamino)benzoate (0.020 g, 0.120 mmol), and dodecane (0.4 mL) were sealed in a 1 mL Wheaton vial and heated to 100 °C for 1 h. The dark yellow/brown mixture was diluted with hexanes then charged to a silica column. Nonpolar components were eluted with hexanes, while **7** was isolated by a subsequent elution with dichloromethane and drying in vacuo. High-resolution MS analysis: required for $C_{24}H_{39}NO_2$ *m/e* 359.2824; found *m/e* 359.2837. FT-IR analysis: 1704 cm^{-1} (C═O); 1365, 1278, 1183, and 1106 cm^{-1} (C−O−C stretching vibrations of a para-substituted benzene ring). ^1H NMR ($CDCl_3$) **7**: δ 0.6−2.2 (m, 130H, 2 × −$C(CH_3)_3$, 3 × −CH_2−), 3.01 (s, 20.4H, 2 × NCH_3), 4.6−5.7 (m, 8.98H, 1 × −CHOC(O)−, 2 × ═CH_2, 2 × −CH_2OC(O)−, 2 × ═C−H), 6.5−8.0 (m, 13.5H, 4 × ═CH−); **7a**: δ 5.38 (dd, −CHOC(O)−), 5.17 (s, ═CH_2), 4,85 (s, ═CH_2). Found for 7b: δ 4.76 (s, −CH_2-OC(O)−), 5.42 (t, ═C−H). Found for **7c**: δ 4.68 (s, −CH_2OC-(O)−), 5.70 (t, ═C−H).

(3,3-Dimethylbutyl)-2-(2,2-dimethylpropyl)prop-2-enyl 9-Anthracenate (8a) and (*E*/*Z*)-6,6-Dimethyl-2-(2,2-dimethylpropyl)-hept-2-enyl 9-Anthracenate (8b, 8c). BPMN (0.044 g, 0.163 mmol), tetrabutylammonium anthracene-9-carboxylate (0.1 g, 0.2 mmol), and toluene (0.4 mL) were transferred to a round-bottom flask and heated to 80 °C for 1 h. The product was purified by column chromatography (alumina, hexanes eluent) and isolated in vacuo to yield a yellow oil, **8**. FT-IR analysis: 1721 cm^{-1} (C═O). MS analysis: required mass for $C_{29}H_{36}O_2$ is 416.2725 *m/e*; found 416.2715 *m/e* (TOF MS EI+). ^1H NMR ($CDCl_3$) **8**: δ 0.7−2.3 (m, 46.2H, 2 × −$C(CH_3)_3$, 3 × −CH_2−), 4.9−5.9 (m, 4.78H, 1 × −CHOC(O)−, 2 × ═CH_2, 2 × −CH_2OC(O)−, 2 × ═C−H), 7.4−8.6 (m, 14.06H, 9 × ═CH−); **8a**: δ 5.81 (dd, −CHOC(O)−), 5.27 (s, ═CH_2), 5.01 (s, ═CH_2). **8b**: δ 5.13 (s, −CH_2OC(O)−), 5.52 (t, ═C−H). **8c**: 5.06 (s, −CH_2OC(O)−), 5.81 (t, ═C−H).

1-(3,3-Dimethylbutyl)-2-(2,2-dimethylpropyl)prop-2-enyl Alcohol and (*E*/*Z*)-6,6-Dimethyl-2-(2,2-dimethylpropyl)hept-2-enyl Alcohol (9). To a 1 mL Wheaton vial containing xylene (0.4 mL) were added potassium hydroxide (0.0045 g, 0.08 mmol) and 18-crown-6 (0.021 g, 0.08 mmol). This mixture was stirred for 10 min prior to the addition of BPMN (0.028 g, 0.098 mmol) and kept at 100 °C for 1 h. The dark reaction mixture was diluted with hexanes and fractionated by column chromatography (alumina) into two components. The first component was eluted with hexanes and the second with diethyl ether. The more polar fraction contained the desired substitution product, **9**. FT-IR analysis: 3440 cm^{-1} (OH). ^1H NMR ($CDCl_3$) **9**: δ 0.7−2.2 (m, 42.1H, 2 × −$C(CH_3)_3$, 3 × −CH_2−), 4.0−5.6 (m, 3.8H, 1 × −C*H*-OH, 2 × ═CH_2, 2 × −C*H*$_2$−OH, 2 × ═C−H); **9a**: δ 3.97 (dd, −C*H*−OH), 4.86 (s, ═CH_2), 5.18 (s, ═CH_2); **9b**: δ 4.03 (s, −C*H*$_2$−OH), 5.52 (t, ═C−H); **9c**: δ 4.12 (s, −C*H*$_2$−OH), 5.31 (t, ═C−H).

Tetrabutylammonium *tert*-Butyl Acetate (TBA*t*BuAc). To a round-bottom flask containing 1 M solution of tetrabutylammonium

hydroxide in MeOH (10 mL, 10 mmol) was added *tert*-butyl acetic acid (1.3 g, 10 mmol). This mixture was stirred vigorously for 10 min, after which the solvent was evaporated and the residue was dried under high vacuum for 3 days. FT-IR analysis: 1564 and 1394 cm^{-1} ($RC(O)O^-$). ^1H NMR ($CDCl_3$) analysis: δ 3.38 (m, 8H, $-N^+CH_2-$), δ 1.65 (m, 8H, $-N^+CH_2CH_2-$), δ 1.44 (m, 8H, $-N^+CH_2CH_2CH_2-$), δ 0.90 (t, 12H, $-CH_3$), δ 2.10 (s, 2H, $-OC(O)CH_2-$), δ 1.03 (s, 9H, $-CH_3$).

Isolation and Characterization of *n*-Butyl *tert*-Butyl Acetate. The product of the thermal degradation of TBA*t*BuAc was diluted in hexanes and passed through a column (silica, hexanes eluent). The solvent was evaporated, and the residue containing *n*-butyl *tert*-butyl acetate was dried in vacuo. MS analysis: required mass for $C_{10}H_{20}O_2$ is 172.146 *m*/*e*; found 172.144 *m*/*e* (TOF MS EI+). ^1H NMR ($CDCl_3$) analysis: δ 4.05 (t, 2H, $-C(O)OCH_2-$), δ 1.65 (m, 2H, $-C(O)OCH_2CH_2-$), δ 1.42 (m, 2H, $-C(O)OCH_2CH_2CH_2-$), δ 0.90 (t, 3H, $-C(O)OCH_2CH_2CH_2CH_3$), δ 2.20 (s, 2H, $-OC(O)CH_2-$), δ 1.03 (s, 9H, $-CH_3$).

Solid-State BIIR Reactions. BIIR (40 g) was loaded into a Haake Polylab R600 internal batch mixer equipped with Banbury blades and operating at 140 °C and 60 rpm unless otherwise stated. The polymer was preheated for 1 min prior to the addition of the desired amount of alkali metal carboxylate. A phase transfer agent was added immediately after incorporation of the salt (30−40 s). Samples were taken at different reaction times in order to conduct spectroscopic analyses. The integration of ^1H NMR spectra of unpurified samples provided the relative concentrations of the following products: δ = 5.02 ppm (analogous to **1a**, 1H, s), δ = 4.00−4.10 ppm (analogous to **1b**,**1c**, 2H, s), and δ = 5.96−5.90 ppm (analogous to **2**, 2H, d). For allylic esters **3**−**8**: δ = 4.60−4.44 ppm (analogous to **3**−**5b**, **3**−**5c**, 2H, s), δ = 5.15−5.08 ppm (analogous to **3**−**5a**, 1H, s), δ = 4.85−4.70 ppm (analogous to **6**−**7b**,**6**−**7c**, 2H, s), δ = 5.27 ppm (analogous to **8a**, 1H, s), and δ = 5.11 ppm (analogous to **8b**, 2H, s). Signals of structure analogous to **8c** overlap with other signals and are difficult to quantify. When purification of the product was required, the material (1 g) was dissolved in hexanes (20 mL) and precipitated in acetone (100 mL) to yield colorless products that were completely soluble in chloroform and other appropriate solvents for BIIR.

Solution Reactions of BIIR. Toluene (10 mL), BIIR (0.4 g), and the desired amount of TBA*t*BuAc (0.029 or 0.120 g) were mixed at room temperature and subsequently heated to 85 ± 1 °C for 2 h. Aliquots (~0.5 mL) withdrawn at specific time intervals were added immediately to acetone to isolate the polymeric reaction product, which was dried under vacuum and characterized by monitored by ^1H NMR spectroscopy, as described above.

Analysis. NMR spectra were recorded in $CDCl_3$ on a Bruker AM400 instrument with chemical shifts (δ) reported relative to tetramethylsilane in ppm. ^1H NMR assignments were verified by 2D COSY analyses. Fourier transform infrared spectra were acquired from solvent-cast films using a Niclolet Avatar ESP 360 instrument at a resolution of 4 cm^{-1}. Low-resolution mass spectrometry was carried out using a Fisons VG Quattro triple-quadrupole mass spectrometer using chemical ionization (i-C_4H_{10}) or a Waters/Micromass ZQ single-quadrupole mass spectrometer using electrospray ionization. A Waters/Micromass GC-T TOF mass spectrometer operating in electron impact mode was used to conduct high-resolution mass spectroscopy analysis. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to study the thermal stability of the reagents. For DSC, aluminum crucibles containing the samples (5−10 mg) were subjected to heating−cooling cycles (at 10 °C/min) in a DSCQ100 apparatus (TA Instruments) with nitrogen purge. Some reagents were also heated nonisothermally (at 10 °C/min) in a TGAQ500 apparatus from TA Instruments.

Results and Discussion

Structure and Stability of Allylic Substitution Products. The allylic esters generated by reactions of carboxylate nucleophiles with BIIR are comprised of exomethylene derivatives analogous to **3**−**8a** as well as *E*,*Z*-endomethylene isomers analogous to **3**−**8b,c** (Scheme 1). Figure 1 illustrates the full range of products derived from *tert*-butyl acetate (*t*-BuAc) derivatizations of BIIR. The ^1H NMR spectrum acquired for the polymeric reaction product correlates well with that of the corresponding model allylic ester **3**, and similar agreement was observed for all the aliphatic and aromatic esters (**5**−**8**) and the allylic alcohol (**9**) produced in this work. The spectrum of the polymer derivative also reveals evidence of a stearate ester byproduct, which results from the activation of calcium stearate that is added during BIIR manufacturing to serve as an anticoagulation agent and material stabilizer. Its yield was generally less than 10% for aliphatic carboxylate nucleophiles but reached levels approaching 40% when aromatic carboxylates were employed. Byproduct yields, as well as the distribution of allylic ester isomers, are sensitive to the nature and concentration of reagents, and this subject is revisited below in the context of the influence of reaction conditions on the rate and selectivity of the substitution process.

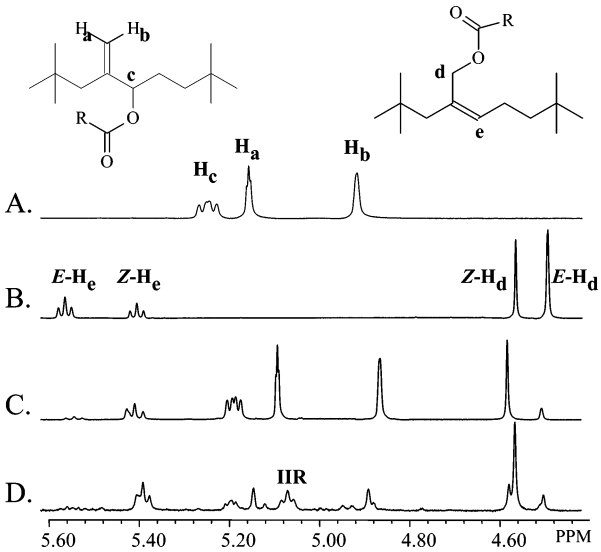
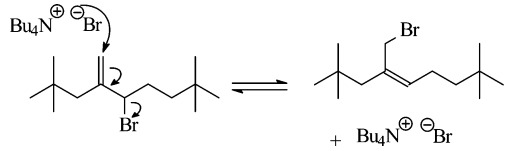


Figure 1. Downfield region of the ^1H NMR spectra ($CDCl_3$) of (A) **3a**, (B) **3b,c**, **(**C) **4**, and (D) the ester derivative of BIIR as a mixture of exomethylene and *E*/*Z*-endo isomers. IIR = unhalogenated isoprene mers.

The *t*BuAc-derived allylic esters analogous to **3** were stable with respect to isomerization and hydrolysis under typical reaction and processing conditions. The exomethylene allylic ester **3a** produced none of its corresponding *E*,*Z*-endo isomers when heated for prolonged periods to 95 °C either in isolation or in the presence of excess tetrabutylammonium carboxylate salt. Therefore, the *E*,*Z*-endo isomers analogous to **3bc** must be direct products of allylic bromide (**1**) substitution and not rearrangement products of exo allylic ester (**3a**). We further note that the polymeric analogue of **3** was stable with respect to hydrolysis, yielding only 10% of an allylic alcohol analogous to **9** when heated in xylenes to 90 °C for 4 h under basic conditions.[8]

BIIR and PTC Reagent Stability. The conditions needed to sustain PTC transformations of BIIR are considerably more severe than those commonly required for reactions of small molecules. As a result, the susceptibility of BIIR to allylic bromide rearrangement and HBr elimination is a potential concern (Scheme 1), as is the stability of the tetrabutylammonium bromide (TBAB) and carboxylate salts that support the majority of our PTC studies. Two distinct sets of reaction conditions have been examined in this work: toluene solutions at 85 °C and solvent-free conditions at 140 °C.

Scheme 2



The exomethylene allylic bromide analogous to **1a** is a kinetically favored product of butyl rubber halogenation, whose rearrangement leads to the more thermodynamically stable (*E*,*Z*)-endo isomers (**1b,c**; Scheme 1).[7,9] No change in the initial 90:10 ratio of exo:endo allylic bromide isomers was observed after maintaining a toluene solution of BIIR at 85 °C for prolonged periods. However, heating the material to 140 °C for 30 min under solvent-free conditions dehydrobrominated 21% of allylic bromide to conjugated diene (**2**) and changed the exo:endo isomer ratio to 48:52. Therefore, high-temperature BIIR substitutions may be affected by competing isomerizations and eliminations of the targeted allylic bromide functionality.

We discovered that the rate of allylic bromide isomerization is sensitive to TBAB. Although no change in the ratio of **1a** to **1b,c** was incurred upon heating BIIR to 85 °C in toluene for 2 h in the absence of TBAB, the presence of 1 equiv relative to allylic bromide produced a 25:75 ratio of **1a** to **1b,c** under equivalent reaction conditions. Similar behavior was observed in solvent-free experiments. When just 0.09 equiv of TBAB was mixed with BIIR at 140 °C, the initial isomerization rate increased 27% over the solvent-free baseline experiment described above. It is likely that that nucleophilic displacement from **1a** by free bromide underlies this accelerated isomerization rate. Whereas a direct S_N2 displacement from **1a** by bromide would have no apparent effect, an S_N2' mechanism would produce the observed rearrangement (Scheme 2). Given the widespread use of these salts as phase transfer catalysts, this heightened isomerization rate may be of practical importance to the dynamics of BIIR derivatizations.

Since alkali metal halides and carboxylates are thermally inert,[10] our studies of nucleophile stability focused on their corresponding tetrabutylammonium salts. ^{1}H NMR analysis of TBAB solutions in toluene revealed no evidence of decomposition after heating to 85 °C for 2 h. Similarly, the heating of pure TBAB to 140 °C for 1 h produced on only trace amounts of *n*-butyl bromide and tertiary amine,[11] and TGA analysis of TBAB revealed a decomposition temperature of 190 °C, which is in good agreement with the literature.[12−14]

Whereas TBAB degradation is of little concern in this work, the limited information pertaining to quaternary ammonium carboxylate salts suggests that these materials can be unstable above 120 °C.[15,16] After heating a toluene solution of tetrabutylammonium *tert*-butyl acetate (TBA*t*BuAc) to 85 °C for 2 h, we observed 50% conversion of the salt to butylamine and the corresponding aliphatic ester.[17] Heightened instability was observed at 140 °C under solvent-free conditions, with 44% of the salt undergoing decomposition within 15 min and 70% degradation occurring after 30 min. Similar results were obtained when TBA*t*BuAc was incorporated within an unreactive polyisobutylene matrix, which suggests that ammonium carboxylate instability may adversely affect BIIR derivatizations if substitution rates do not exceed that of ammonium carboxylate decomposition.

Homogeneous Substitutions. Single-phase BIIR reactions were conducted in toluene at 85 °C using a soluble ammonium carboxylate salt to gain insight into the intrinsic dependence of substitution rates and products on nucleophile concentrations.

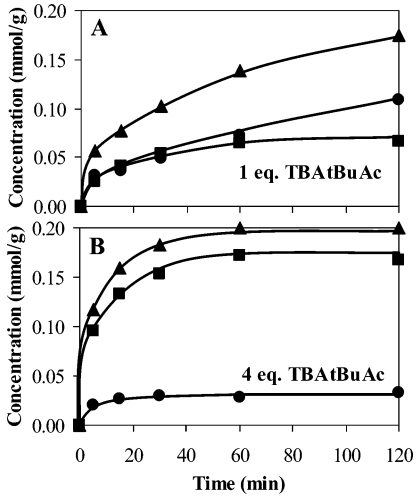


Figure 2. Dynamics BIIR/TBA*t*BuAc reactions in toluene (85 °C; ▲, total allylic ester; ■, exo-ester; ●, endo-esters): (A) 1 equiv of TBA*t*BuAc; (B) 4 equiv of TBA*t*BuAc.

Although these solvent-borne reaction conditions are not ideal from the standpoint of reaction economy, the information gained from these baseline experiments, coupled with our knowledge of reagent stability, facilitates the analysis of the more complex solvent-free PTC reactions that are examined in this report.

The data presented in Figure 2 demonstrate that ester derivatives can be prepared from BIIR and TBA*t*BuAc despite the mild instability of the carboxylate salt at the reaction conditions employed. High yields were achieved irrespective of the nucleophile concentration; stearate esters comprised less than 10% of the products, and the conjugated dienes derived from BIIR dehydrobromination were present in negligible quantities. The data also reveal the inherent bimolecular nature of the BIIR substitution process, since allylic ester formation was accelerated by an increase in the amount of TBA*t*BuAc from 1 to 4 equiv.

The reaction dynamics presented in Figure 2 not only reveal the responsiveness of the substitution rate to TBA*t*BuAc concentrations but also demonstrate the pronounced sensitivity of the allylic ester product distribution. Four equivalents of TBA*t*BuAc relative to allylic bromide dramatically increased the proportion of the exomethylene allylic ester analogous to **3a** at the expense of its endomethylene isomeric forms (**3b,c**). Furthermore, residual allylic bromide remained exclusively of the exo form (**1a**), and no evidence of endo isomers analogous to **1b,c** was apparent throughout the reaction.

Insight into the effect of allylic bromide structure on the substitution rate is gained from the plots presented in Figure 3. These data were acquired under identical reaction conditions and differ only in the distribution of allylic bromide isomers within the BIIR starting material. The data clearly illustrate the superior reactivity of the endo isomeric forms, which yielded quantitative conversion to endo allylic esters (**3b,c**) within 10 min. By comparison, the exo allylic bromide (**1a**) required 120 min to reach this level, and it yielded a high proportion of exo allylic ester analogous to **3a**.

We suggest that ester formation proceeds predominately through S_N2 displacements that convert the exo allylic bromide into its corresponding exo products (**1a** to **3a**) and the endo allylic bromides into their corresponding allylic esters (**1b,c** into **3b,c**). Since BIIR is stable to rearrangement in toluene at 85 °C in the absence of TBAB, one would expect to obtain only the exomethylene allylic ester **3a**, were it not for the generation of TBAB as a substitution byproduct. It appears, therefore, that

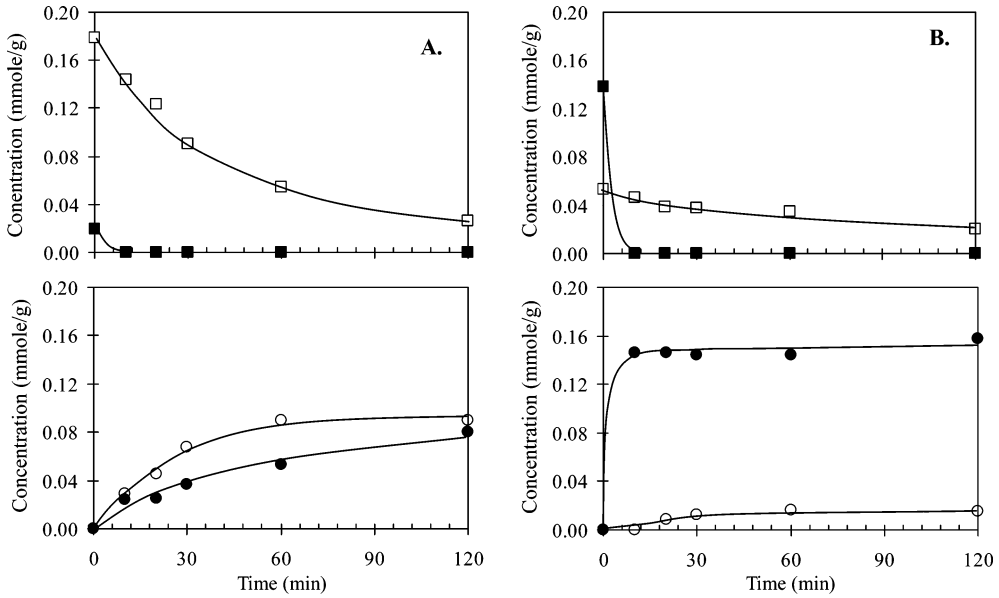


Figure 3. Influence of allyic bromide structure on BIIR/TBA*t*BuAc reactions (toluene; 85 °C; 1 equiv of TBA*t*BuAc; □, exo-bromide; ■, endo-bromides; ○, exo-ester; ●, endo-esters): (A) BIIR as received; (B) isomerized BIIR.

carboxylate and bromide are competing nucleophiles, with the former reacting mainly through an S_N2 mechanism, while the latter reacts to some degree via an S_N2' mechanism (Scheme 2).

Solvent-Free Substitutions. The chemical modification of polymers under solvent-free conditions differs from solvent-borne reactions in several respects. While a heightened concentration of allylic bromide functionality may be expected to improve the kinetics of a bimolecular substitution, the solubility of other reagents can be greatly reduced in a polymeric medium. Furthermore, high viscosities can adversely affect the efficiency of mixing in multiphase reactions, and the limited diffusivity of allylic bromide and nucleophile may detract from the intrinsic reactivity of these functional groups. Therefore, the adaptation of PTC principles to solvent-free media presents several challenges, and a detailed study of the dynamics of such processes must consider many more factors than comparable examinations of solvent-borne reactions. We have explored three solvent-free reactions of BIIR. The first utilized TBA*t*BuAc, while the second and third reactions involved the activation of K*t*BuAc using differing levels of TBAB as a phase transfer agent.

Whereas K*t*BuAc alone did not engage BIIR in nucleophilic substitutions under any circumstances, its corresponding Bu_4N^+ salt provided good reaction rates and exceptional selectivity under solvent-free conditions. Figure 4a presents the dynamics of a substitution process employing 3.5 equiv of TBA*t*BuAc relative to allylic bromide functionality. In light of the demonstrated instability of TBA*t*BuAc at 140 °C, this positive outcome is somewhat surprising and suggests that BIIR substitution proceeds more rapidly than salt decomposition, such that excess ammonium carboxylate can provide the desired allylic ester in good yield. In fact, the final product contained no dehydrobromination product, and the proportion of stearate ester byproduct was less than 10%.

The temperatures required to support solvent-free reactions were more forcing than those needed for comparable toluene-borne substitutions. Since allylic bromide rearrangement is accelerated at high temperature, the solvent-free system was expected to generate a higher proportion of endo substitution products (**3b,c**) than the low-temperature solution reactions

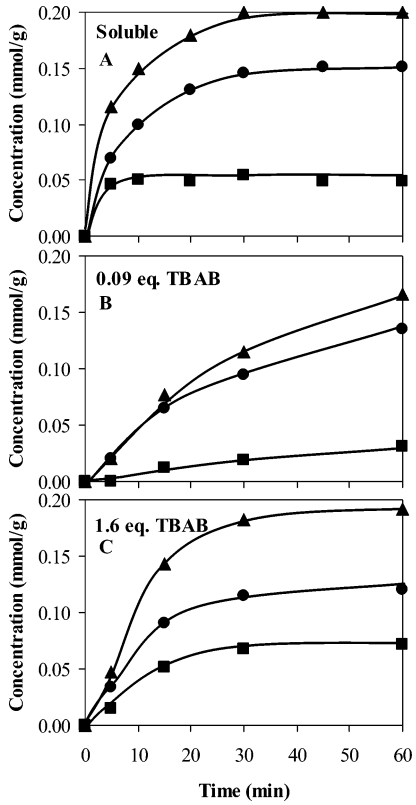


Figure 4. Dynamics of the solvent-free esterification of BIIR (140 °C; 60 rpm; ▲, total allylic ester; ■, exo-ester; ●, endo-ester): (A) 3.5 equiv of TBA*t*BuAc; (B) 3.5 equiv of K*t*BuAc + 0.09 equiv of TBAB; (C) 3.5 equiv of K*t*BuAc +1.6 equiv of TBAB.

described above. This behavior is evident in Figure 4a. We cannot, however, eliminate the possibility that the solubility of TBA*t*BuAc in BIIR is incomplete and that a reduced nucleophile concentration is partially responsible for a shift in the balance of exo allylic bromide substitution and isomerization rates.

From the standpoint of overall efficiency, a more attractive approach to BIIR esterification would employ PTC principles, wherein TBAB is used in catalytic amounts under solvent-free conditions to activate alkali carboxylate salts, thereby yielding KBr as a benign substitution byproduct. In addition to improving

Table 1. Solvent-Free PTC Reactions of BIIR[a]

				allylic ester (%)			
M^+	R	Q	time (min)	total[b]	exo:endo	conjugated diene (%)	allylic bromide (%)
K	**3**	TBAB	50	95	17:83	5	0
K	**3**	Aliquat 336	50	98	23:77	2	0
K	**3**	PEG 750	55	24	33:67	6	70
K	**3**	IIR-DMOABr[c]	60	96	27:73	4	0
K	**3**	IIR-PPh_3Br[d]	60	27	29:71	12	61
K	**3**	DMOA	45	45	19:81	5	50
K	**4**	TBAB	60	91	15:85	2	7
Na	**5**	TBAB[e]	50	96	0:100	2	2

[a] BIIR + MOOCR (1.1 equiv) + Q (0.08 equiv); 140 °C; 60 rpm. [b] Includes ca. 10% stearate derivative. [c] Dimethyloctylammonium bromide ionomer (0.16 equiv). [d] Triphenylphosphonium bromide ionomer (0.13 equiv). [e] 0.16 mol equiv.

reaction economy, this strategy could also mitigate ammonium carboxylate salt decomposition, since at any time the concentration of TBA*t*BuAc would be limited to the catalytic amounts of TBAB charged to the system.

A definitive example of such a solvent-free PTC modification is illustrated in Figure 4b. Using 0.09 equiv of TBAB relative to allylic bromide and an excess of K*t*BuAc, the desired allylic ester was produced in 85% yield. Since K*t*BuAc is insoluble in BIIR and completely unreactive in isolation,[3] a small amount of TBAB can only support this extent of allylic bromide conversion through a PTC mechanism in which an ammonium cation engages in not only ion exchange between bromide and carboxylate anions but also phase transfer between BIIR and salt phases. This example demonstrates the viability of a solvent-free PTC polymer modification in which high yields are achieved without incurring complications derived from side-reactions, without generating undesirable byproducts, and without need for product isolation or purification.

Figure 4c plots the progress of a phase transfer mediated reaction, in which 1.6 equiv of TBAB was used to activate an excess of K*t*BuAc salt. As expected, a heightened availability of nucleophile raised the reaction rate to approach that observed for the TBA*t*BuAc example (Figure 4a), and it increased the proportion of exomethylene allylic ester (**3a**). A detailed analysis of the relationship between reaction dynamics and TBAB concentration is complicated by the instability of BIIR and ammonium carboxylate salts, the uncharacterized phase equilibria for the reaction components, and mass transfer effects in phase-partitioned systems.[18] Nevertheless, parallels exist between solution-phase TBA*t*BuAc reactions and solvent-free reactions employing K*t*BuAc and TBAB, in that rates and product distributions respond to nucleophile concentration in a similar manner.

Mass Transfer. The dynamics of a multiphase reaction can be influenced as much by interfacial mass transfer as by intrinsic reaction kinetics.[1,19] Under PTC reaction conditions, there is an insufficient amount of active nucleophile at any one time to fully convert BIIR into its ester derivative. Therefore, the transport of TBAB and TBA*t*-BuAc between elastomer and salt phases is necessary if the substitution reaction is to reach full conversion. Figure 5 shows the effect of mixing speed on the dynamics of a solid-state PTC reaction. The rate observed when premixed masterbatches were reacted under compression-molding conditions (0 rpm) was much less than that recorded at the mixing speed used throughout this work (60 rpm). The dramatic influence of mass transfer on the process dynamics suggests that nucleophile concentrations may not be maintained at their equilibrium levels throughout the reaction. This may contribute to unexpected variations of reaction rate and selectivity in cases where mass transfer is an influential component of the overall process.

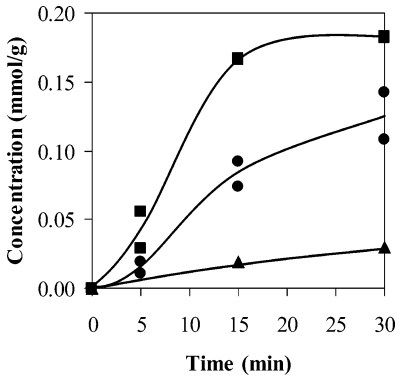


Figure 5. Solvent-free synthesis of *tert*-butyl acetate derivatives in the solid-state (140 °C; 40 g of BIIR; 1.1 equiv of K*t*BuAc; 0.08 equiv of TBAB; ■, 60 rpm; ●, 20 rpm; ▲, 0 rpm).

Other PTC Systems. Trioctylmethylammonium chloride, known as Aliquat 336, exhibits outstanding phase transfer properties in conventional organic−aqueous systems.[1] In the present application, the reaction rates supported by TBAB and Aliquat 336 were indistinguishable, with both catalysts yielding >90% allylic bromide conversion to ester within 50 min (Table 1). The activation of alkali metal salts by crown ethers and polyethers is also well established,[20] and a low-molecular-weight poly(ethylene glycol) (PEG 750) generated an appreciable amount of allylic ester when applied to solvent-free PTC modifications of BIIR.

A more interesting PTC example employed an ammonium bromide ionomer of butyl rubber, IIR-NR_3Br, which is prepared by the alkylation of *N*,*N*-dimethyloctylamine (DMOA) with BIIR.[21] Table 1 reports the activity generated by IIR-NR_3Br containing 0.20 mmol/g of quaternary ammonium bromide functionality. The use of 15 wt % of this ionomer in conjunction with K*t*-BuAc at 140 °C resulted in the full conversion of the allylic bromide within BIIR to ester within 1 h. The corresponding phosphonium bromide ionomer (IIR-PPh_3Br) was less efficient than its quaternary ammonium analogue.

Appreciable PTC activity was also observed when catalytic amounts of DMOA were charged to a BIIR/K*t*-BuAc mixture. Figure 6 reveals a brief induction period for this process, during which time HBr elimination was the only discernible reaction outcome. However, beyond this early stage, the desired ester was formed at a significant rate. We note that since N-alkylation of tertiary amines by BIIR can be reversible,[4] two possible mechanisms exist for the PTC activity exhibited by IIR-NR_3Br and DMOA. It is conceivable that the ammonium bromide ionomer, whether charged to the system deliberately or prepared in situ, serves as a polymeric phase transfer catalyst. However, it is also possible that BIIR dehydrobromination generates a

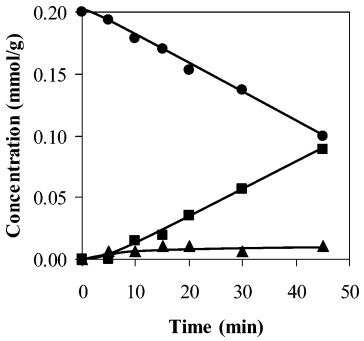


Figure 6. Solvent-free synthesis of *tert*-butyl acetate derivatives in the solid-state (140 °C; 1.1 equiv of *t*-BuAcK; 0.08 equiv of DMOA; ●, allylic bromide; ■, ester derivative; ▲, elimination products).

Table 2. Solvent-Free Esterification Reactions of BIIR[a]

R[b]	time (min)	% allylic ester[b] aromatic	% allylic ester[b] stearate	conjugated diene (%)	allylic bromide (%)
6	50	38	22	11	29
7	45	21	39	12	27
8	45	20		10	70

[a] BIIR + KOOCR (1.1 equiv) + TBAB (0.08 equiv); 140 °C; 60 rpm. [b] No exomethylene derivatives (**6**−**8a**) were observed.

hydrobromide salt of free amine (R_3NHBr), which is also reported to support PTC processes.[22]

Other Carboxylate Nucleophiles. The sodium and potassium salts of long-chain alkanoates reacted with BIIR with rates and selectivities that were comparable to *t*BuAc. Under solvent-free PTC conditions, stearate and linoleate ester derivatives analogous to **4** and **5** were obtained in high yield, with endomethylene isomers dominating the product distributions (Table 1). The production of a stearate ester from its calcium salt is more complicated. Neither TBAB nor Aliquat 336 activated calcium stearate at 140 °C after 40 min, which suggests that ion exchange between Ca^{2+} and Bu_4N^+ does not occur to the extent required to functionalize BIIR. However, the application of these phase transfer catalysts in combination with KOH produced the stearate ester in good yield, presumably through reaction of potassium stearate that is generated in situ.

Substitutions involving aromatic carboxylates were less efficient than similar reactions of their aliphatic counterparts (Table 2). Potassium salts derived from benzoic acid, (*N*,*N*-dimethylamino)benzoic acid, and anthracene-9-carboxylic acid were activated by TBAB to produce ester derivatives analogous to **6**, **7**, and **8**, but their yields were relatively poor, and products contained significant amounts of conjugated diene (**2**) and stearate esters. As noted above, calcium stearate is only activated by the use of TBAB in conjunction with alkali metal hydroxide. Since aliphatic carboxylates are better nucleophiles than their aromatic analogues under PTC conditions,[3] it is likely that small amounts of potassium and TBA stearate salts compete effectively with the aromatic carboxylate salts that are deliberately charged to the system.

Conclusions

PTC principles can be extended to solvent-free conditions, thereby avoiding the need to isolate and/or purify polymer derivatives. Catalytic amounts of tetraalkylammonium halides activate alkali metal carboxylates sufficiently to avoid potential complications such as BIIR dehydrobromination, ammonium carboxylate salt instability, and interfacial mass transfer limitations. As a result, new aliphatic and aromatic ester derivatives of BIIR can be prepared in moderate to high yields using conventional polymer processing equipment.

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