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S_N2 Reactions in Hydrocarbon Solvents Using Ammonium Terminated Polyisobutylene Oligomers as Phase Solubilizing Agents and Catalysts

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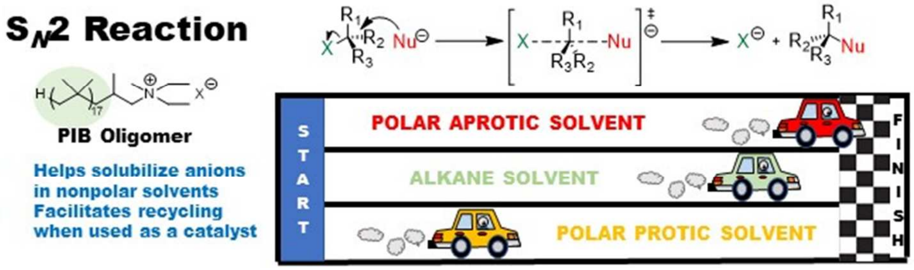


ABSTRACT: Although S_N2 reactions have been thoroughly studied in polar aprotic and protic solvents, not many studies have been done to study the rate of S_N2 reaction in nonpolar solvents like alkanes due to the insolubility of anionic nucleophiles in these solvents. In this study, we investigated the use of *N*,*N*-diethyl-*N*-methylammonium terminated polyisobutylene (PIB) oligomers as phase solubilizing agents for nucleophilic anions that could react with hydrocarbon-soluble substrates in alkanes. The results of these kinetic studies showed alkanes were comparable to MeCN as solvents in many reactions. Based on these studies, we developed a solid/liquid catalytic process using insoluble alkali metal carboxylate salts and a recyclable soluble polyisobutylene-bound catalyst that can be used to carry out S_N2 reactions both in heptane and in hydrocarbon oligomeric solvents known as poly(α-olefins) (PAOs).

INTRODUCTION

Bimolecular nucleophilic substitution reactions commonly known as S_N2 reactions are among the most common reactions in organic chemistry. They are a class of reactions that have been extensively studied. Factors that affect the rate of S_N2 reactions are the characteristics of the substrate, the nucleophile, the leaving group, and the solvent. However, while solvent effects have been extensively studied and while prior studies have demonstrated that S_N2 reactions proceed faster in polar aprotic solvents such as MeCN and in DMF than in polar protic solvents like water and MeOH,[1] there is little information about how these reactions occur in saturated hydrocarbons like alkanes. The prior studies with other solvents have shown that polar protic solvents hydrogen bond to nucleophiles, lowering their reactivity. Those studies have also shown that polar aprotic solvents that cannot form these hydrogen bonds but instead solvate the cations facilitate S_N2 chemistry. In polar aprotic solvents, solvated cations have desolvated anions, sometimes described as ‘naked’ anions, that are more reactive in S_N2 reactions. To our knowledge, rates of S_N2 reactions in alkane solvents have not been fully studied due to the insolubility of common alkali metal salts and even many tetraalkylammonium salts in alkanes like heptane. Our general interest in reactions in alkane solvents and the demonstrated ability of polyisobutyl groups to dissolve otherwise insoluble materials in alkanes led us to study this issue.

Our group has a long-standing interest in hydrocarbon soluble polymer supports and recyclable greener alternatives to typical alkane solvents like hexane and heptane.[2,3] We have in recent years shown that polyisobutylene oligomer supports make otherwise alkane insoluble species like phthalocyanines,[4] metal oxide clusters,[5] and nanoparticles[6] soluble in alkane solvents. Those successes suggested to us that we could use polyisobutylene oligomers to solubilize nucleophilic anions in alkanes and that we could in turn study homogeneous S_N2 reactions in alkane solvents. Such studies we felt would be of interest in that anionic nucleophiles in solvents like heptane would not be solvated. This poor solvation of the anion could strengthen anion nucleophilicity. However, the situation is complicated because a polar reaction and polar transition state are also not likely to be stabilized in an alkane solvent. Possible attractive electrostatic interactions of a localized or delocalized anion with the countercation are other complicating factors. Since the relative effects of these various factors are unknown, we thought it would be worthwhile to examine the kinetics of S_N2 reactions in alkanes. Such studies would satisfy our curiosity about this common chemistry in this unconventional medium and allow us to explore the notion that we could develop a new catalytic variant of this established chemistry in a medium that has hitherto not been studied.

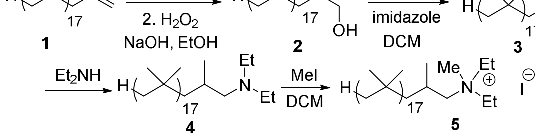
Work by our research group and others has shown that vinyl-terminated polyisobutylene (PIB) and polypropylene oligomers can be modified to form useful ligands and supports for catalysts and reagents.[2,6-8] These PIB supports are soluble in nonpolar solvents such as heptane and in slightly polar solvents like DCM and THF. However, they are not soluble in polar solvents such as acetonitrile, methanol, and DMF. They are though soluble in miscible thermomorphic solvent mixtures of some polar solvents and heptane that form on heating. When PIB supports solubilize catalysts or reagents, they allow reactions to be conducted under homogeneous conditions either in heptane or in solvent mixtures. However, when a reaction mixture is perturbed so as to be biphasic after the reaction, these supports' alkane solubility facilitates the separation of products from catalysts or spent reagents from products by a simple liquid/liquid separation after the reaction. The use of such supports also makes chemical transformations more environmentally-friendly by enabling recycling of stable catalysts and ligands or by recycling spent reagents. For example, functionalized polyisobutylene oligomers were used as supports to solubilize oxidation catalysts and reagents such as polyoxometalates (POMs) and 2-iodoxybenzoic acid (IBX),[5,9] recycling metathesis catalysts,[10] and using lipophilic silyl protecting groups to separate products from reagents and catalysts in liquid phase extraction schemes.[11]

In this work, we explored the use of *N,N*-diethyl-*N*-methylammonium terminated PIB oligomers as hydrocarbon phase-solubilizing agents for anions to study the rates of S_N2 reactions in heptane, a nonpolar solvent that cannot significantly stabilize anions or cations. As part of this study, S_N2 reactions in conventional solvents such as MeOH, MeCN, and DMF were studied as comparisons for the reactions in heptane. We then extended our work to investigate the use of *N,N*-diethyl-*N*-methylammonium terminated polyisobutylene oligomers as a catalyst in these same reactions. Finally, we explored the use of poly(α-olefins) (PAOs) as alternatives for conventional alkane solvents in S_N2 reactions in a model study.[3] The advantages in using these PAO solvents are that they are nonvolatile and relatively nontoxic. In addition, recycling of the PAOs and the PIB oligomeric catalysts is more efficient than is the case with low molecular weight solvents or potentially leachable PIB-bound species in heptane, a result noted previously.[3]

RESULTS AND DISCUSSION

Commercially available vinyl-terminated PIB_{1000} oligomers with a M_n value of 1000 Da were used to prepare *N,N*-diethyl-*N*-methylammonium terminated PIB oligomers (Scheme 1).[12]

Scheme 1. Synthesis of the *N,N*-diethyl-*N*-methylammonium iodide PIB_{1000} oligomer catalyst 5.



In this chemistry, the PIB oligomer **1** underwent a hydroboration-oxidation reaction to generate the hydroxyl-terminated PIB oligomer **2**. Then, the Appel reaction was conducted to transform **2** into an iodo-terminated PIB_{1000} oligomer **3**.[13] To make the diethylamino-terminated PIB_{1000} oligomer **4**, an excess amount of diethylamine in DMF was added to a heptane solution of **3**. Upon heating to 90 °C, the two phases become miscible and the substitution reaction took place. The heptane-soluble diethylamine terminated PIB_{1000} oligomer **4** was then methylated by CH_3I to generate the *N,N*-diethyl-*N*-methylammonium iodide terminated PIB_{1000} oligomer **5**. Other PIB_{1000}-bound diethylmethylammonium salts with benzoate, phenolate, and tetrafluoroborate (**6**, **7**, and **8**) (Figure 1) were prepared as alkane solutions from this PIB_{1000}-bound diethylmethylammonium by ion-exchange reactions. These PIB-bound ammonium salts were all soluble in heptane at concentrations of 30-35 wt% (0.3-0.35 M depending on the counteranion identity.

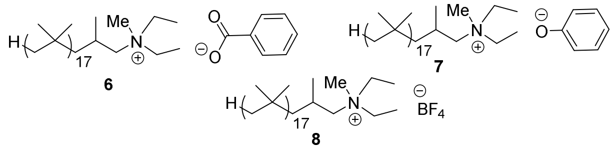
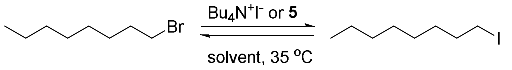


Figure 1. *N,N*-Diethyl-*N*-methylammonium terminated PIB_{1000} oligomers **6-8** with different anions.

S_N2 reactions were first investigated using commercially available tetra-*n*-butylammonium iodide (TBA-iodide) using 1-bromooctane as a substrate (eq 1). While we were able to follow the kinetics of this S_N2 reaction in methanol and acetonitrile with 0.1 M solutions of TBA-iodide, we could not use TBA-iodide in heptane because TBA-iodide was essentially insoluble in heptane. Stirring 1 g of TBA-iodide in heptane for 24 h at 35 □ followed by analysis of the filtrate showed that the TBA-iodide concentration was only ca. 2.0 x 10^{-4} M, solubility that was three orders of magnitude less than that of **5**. Other tetra-*n*-butylammonium halides were even less soluble. Thus, to study SN2 kinetics in heptane, the same substrates were studied in heptane using the heptane soluble *N,N*-diethyl-*N*-methylammonium iodide terminated PIB oligomer **5**. In our initial studies, 1-bromooctane was used as the substrate and the reactions were conducted at 35 °C. The formation of iodooctane was studied using GC analysis. The rate constant *k* was determined from the reaction data by using Solver in Excel for nonlinear curve fitting.[14,15] The results of this study are listed in Table 1. In these cases, the S_N2 reactions are second-order opposing reversible reactions that lead to an equilibrium mixture of 1-bromooctane and 1-iodooctane. The reaction rate in MeCN is comparable to that in heptane, with rate constants of 4.7 x 10^{-3} $M^{-1}s^{-1}$ and 1.3 x 10^{-3} $M^{-1}s^{-1}$ respectively. The rate is roughly an order of magnitude slower in MeOH.



(1)

Table 1. Rates of Opposing S_N2 Reactions of 1-bromooctane with tetraalkylammonium iodide and of 1-iodooctane with tetraalkylammonium bromide in various solvents.

Solvent	Nucleophile	k_1, k_{-1} (1/M·s) (x 10^3)

Heptane	PIB-NEt_2Me^+ I^- (**5**)	1,3, 1.6
MeCN	TBA-iodide	4.7, 9.0
MeOH	TBA-iodide	0.3, 2.2

The S_N2 reaction in eq. 1 is complicated because it is an equilibrium process. Iodide can replace bromide and bromide can replace iodide. Simpler non-opposing reactions were studied using benzoate or phenolate as nucleophiles in reactions with 1-bromobutane (Table 2). In these studies, tetra-*n*-butylammonium benzoate (TBA-benzoate) and tetra-*n*-butylammonium-phenol-phenolate (TBA-phenol-phenolate) (this salt is known to contain a 1:1:1 mixture of ammonium salt:phenol:phenolate)[16] were used for the kinetic studies in DMF, MeCN, and MeOH. The rates of the reactions of 1-bromobutane and benzoate anions are summarized in Table 2. In the reactions where heptane was used as the solvent, either *N,N*-diethyl-*N*-methylammonium terminated PIB_{1000} oligomer **6** or *N,N*-diethyl-*N*-methylammonium terminated PIB_{1000} oligomer **7** was used. The rate of the reaction is fastest in DMF with a k value of 902.5 x 10^{-3} $M^{-1}s^{-1}$. In the case where benzoate was the nucleophile, reactions in MeCN, heptane, and MeOH had k values of 65.1 x 10^{-3} $M^{-1}s^{-1}$, 0.6 x 10^{-3} $M^{-1}s^{-1}$, and 0.002 x 10^{-3} $M^{-1}s^{-1}$, respectively. In the case where phenolate was the nucleophile, the rate of the reaction was again fastest in DMF (Table 2) with a rate constant of 77.1 x 10^{-3} $M^{-1}s^{-1}$ and slowest in MeOH with a rate constant of 0.4 x 10^{-3} $M^{-1}s^{-1}$. The rates of this S_N2 reaction in MeCN and heptane were comparable with rate constants of 9.2 x 10^{-3} $M^{-1}s^{-1}$ and 5.9 x 10^{-3} $M^{-1}s^{-1}$ respectively.

Table 2. Kinetic studies of the reaction of 1-bromobutane with tetraalkylammonium benzoate and phenolate salts in various solvents.[a]

Solvent	Nucleophile	k_1 (1/M·s) (x 10^3)
heptane	**6**	0.6
DMF	TBA-benzoate	902.5
MeCN	TBA-benzoate	65.1
MeOH	TBA-benzoate	0.0016
Heptane	**7**	5.9
DMF	TBA-phenol-phenolate[b]	77.1
MeCN	TBA-phenol-phenolate[b]	9.2
MeOH	TBA-phenol-phenolate[b]	0.4

[a]Reactions were carried out at 55 □ and were followed by GC. [b]The TBA-phenol-phenolate is a known compound that contains equal amounts of phenol and phenolate anion (ref. 16).

The kinetic studies above show that the rates of S_N2 reactions are consistently fastest in DMF, with MeCN and heptane being slower but often comparable. Reactions in MeOH were the slowest. We also briefly explored whether adding DMF into heptane would enhance the rate of S_N2 reactions in heptane. The results showed that the reaction of 1-bromobutane with **6** in heptane saturated with DMF (ca. 2 M DMF) was ca. 10-fold faster than in the absence of DMF.

We also looked at 1-butylmesylate as a substrate using benzoate or iodide as the nucleophile. The results are shown in Table 3. Again, the substitution reaction is fastest in DMF with a rate constant of 131.6 x 10^{-3} $M^{-1}s^{-1}$. The rates of the reaction in MeCN and heptane are similar with rate constants of 27.9 x 10^{-3} $M^{-1}s^{-1}$ and 26.4 x 10^{-3} $M^{-1}s^{-1}$, respectively. The reaction in MeOH was too slow to analyze under our reaction conditions.

Table 3. Kinetic studies of the reaction of 1-butylmesylate with tetraalkylammonium benzoate anions in various solvents.

Solvent	Nucleophile	k_1 (1/M·s) (x 10^3)
Heptane	**6**	26.4
DMF	TBA-benzoate	131.6
MeCN	TBA-benzoate	27.9
MeOH	TBA-benzoate	very slow

Since the rates of reactions in heptane were reasonable and comparable to the rates of S_N2 reactions in acetonitrile, we further investigated the use of the *N,N*-diethyl-*N*-methylammonium terminated PIB oligomers as hydrocarbon phase-solubilizing catalysts in solid/liquid phase transfer catalysis in alkanes. In these reactions, insoluble solid alkali metal salts were added to an alkane reaction mixture where the *N,N*-diethyl-*N*-methyl-ammonium terminated PIB catalyst **8** was present at 0.01 M (10 mol% of **8** relative to the substrate 1-bromobutane). Under these conditions, we hypothesized that ion exchange would lead to solubilization of a carboxylate salt in a hydrocarbon like heptane. These 1 mmol scale reactions used 3 equivalents of various alkali metal carboxylate salts at 90 °C with magnetic stirring of the heterogeneous reaction mixture. We did not examine tetra-*n*-butylammonium bound anions as a phase transfer catalyst in heptane because TBA salts had solubility that was too low for useful catalysis chemistry (*vide supra*).

In the absence of the catalyst **8**, no reaction occurred over 12 h. In the presence of 10 mol% **8**, the reaction proceeded with 97% conversion of the starting bromide to ester in 24 h. Another primary bromide, (3-bromopropyl)benzene, underwent 97% conversion to an ester in 5 h. We then examined the effect of using different alkali metal salts. As shown in Figure 2, the rate is fastest with CsOAc. KOAc is nearly as reactive but NaOAc was essentially unreactive. The origin of these differences is unclear. None of these salts have any significant solubility in heptane so the difference do not reflect solubility of the alkali metal carboxylate. We speculate that it is possible that changing the nature of the cation affects the ability of the polyisobutyldiethylammonium cation to effect efficient ion exchange.

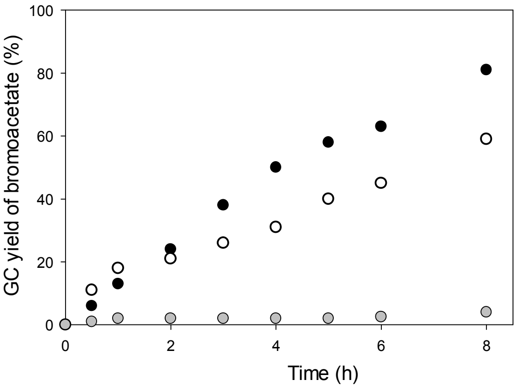


Figure 2. Effect of the metal cations on the rate of S_N2 reaction of acetates and 1-bromobutane in heptane (black filled circles, CsOAc, open circles, KOAc, and grey filled circles, NaOAc).

We also tested the scope solid/liquid catalysis with other carboxylate salts. Those results that are summarized in Table 4 show a similar trend with the potassium and cesium salts again being the most active.

Table 4. Scope of solid/liquid catalysis of carboxylate anions and bromobutane in heptane.[a]

Nucleophile	Conversion (%)[b]
Sodium acetate	1
Potassium acetate	97
Cesium acetate	100
Sodium benzoate	1
Potassium benzoate	83
Potassium *p*-nitrobenzoate	94
Potassium *p*-methoxybenzoate	35
Potassium *p*-acetamidobenzoate	41

[a] 1 mmol of 1-bromobutane, 3 mmol of the nucleophile, and 10 mol% *N*,*N*-diethyl-*N*-methylammonium terminated PIB catalyst in 10 mL heptane were allowed to react 24 h at 90 □. [b] Conversion was determined by GC using cyclooctane as an internal standard.

The success of these S_N2 reactions leading to simple esters on a 1-mmol scale, especially with Cs and K carboxylates, with a PIB bound catalyst **8** prompted us to examine catalyst recycling in these reactions. At the outset of these studies, we recognized that a biphasic extraction to remove the organic products from the heptane phase would be required if we wanted to recycle the PIB_{1000}-bound catalyst. However, such extractions that would require a polar organic solvent were expected to have potential problems in that the solvents necessary to extract an ester from heptane would likely remove some heptane too. We also recognized that the PIB_{1000} oligomers are relatively short (PIB_{1000} has 17 isobutyl repeat units) compared to the polar ammonium salt end groups and that as a result the functionalized oligomers could also leach into a polar phase during extractions in a recycling experiment. To address these issues, we explored these reactions not just in heptane but also in the greener heptane alternative hydrocarbon oligomeric PAO solvents our group recently described.[3]

The poly(α-olefin)s (PAOs) we compared to heptane in these experiments are inexpensive and commercially available.[3,17] In addition to being nontoxic and nonvolatile, our group has shown that PAOs reduce leading of PIB_{1000}-bound polar species by roughly ten-fold, a feature that should facilitate recycling of a PIB_{1000}-bound ammonium phase transfer catalyst. Equally important, compared to heptane, even modest molecular weight PAOs' leaching into a polar organic phase is minimal. Both features of PAOs were expected to be beneficial for catalyst recycling because the concentration of the PIB_{1000}-supported catalyst in the hydrocarbon solvent will be constant and because little or no alkane solvent would be lost in the recycling steps.

In the event, S_N2 reactions using 1-bromobutane, 3 eq. KOAc, and 10 mol% **8** were tested with PAO_{283} (ca. 20 carbons, 2 cSt), PAO_{432} (ca. 30 carbons, 4 cSt), and PAO_{687} (ca. 50 carbons, 10 cSt) and the solid/liquid catalysis was found to be successful. The recycling of the catalysts in these S_N2 reactions in heptane, PAO_{287}, PAO_{432}, and PAO_{687} was also investigated. In these recycling experiments, the reactions were allowed to proceed for 24 h. Then MeCN was added. After centrifugation, the two phases were separated and the cyclooctane internal standard was added into the acetonitrile phase which was then analyzed by GC. The hydrocarbon phase was recycled by adding fresh substrate and fresh KOAc. The results are demonstrated in Figure 3. As expected, the conversion for this S_N2 esterification reaction in heptane began to diminish in cycle 4 for the reaction using heptane. We believe this may be due to some leaching of the *N*,*N*-diethyl-*N*-methylammonium terminated PIB_{1000} catalyst from the heptane phase into the acetonitrile solvent used to extract the product. We also observed that in cycle 4 and 5 that the volume of the heptane phase visually lessened. In contrast, the volume of the PAO phases remained relatively constant through five cycles. This is consistent with our prior work that showed leaching of PAO solvents into

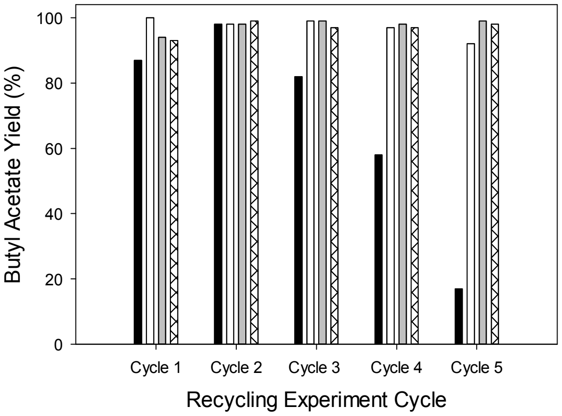


Figure 3. Recycling of a PIB-diethylmethylammonium catalyst in a phase-transfer catalyzed esterification of butyl bromide by potassium acetate in heptane (black bar), PAO_{283} (white bar, 20-carbon PAO with 2 cSt viscosity), PAO_{432} (grey bar, 30-carbon PAO with 4 cSt viscosity), or PAO_{687} (cross-hatched bar, 50-carbon PAO with 10 cSt viscosity).

polar organic solvents is substantially less than heptane. There was a slight decrease in conversion of substrate for the PAO_{287} in cycle 5 but both PAO_{342} and PAO_{687} showed no loss of reactivity through 5 cycles. Notably, the viscosity of the PAO phase which is modest with PAO_{283} and PAO_{342} but more substantial with PAO_{687} had no observed effect.

CONCLUSION

In summary, the above kinetic studies of S_N2 reactions in polar aprotic, polar protic, and nonpolar solvents show that S_N2 reactions in heptane conducted using an *N,N*-diethyl-*N*-methylammonium terminated PIB_{1000} oligomers as hydrocarbon phase solubilizing agents proceed at reasonable rates. The rates of these S_N2 reactions are still fastest in DMF. However, S_N2 reactions in heptane are much faster than similar reactions in MeOH. In addition, it was found that by adding DMF into the heptane reaction mixture can enhance the rate of these reactions. We further examined the use of *N,N*-diethyl-*N*-methyl-ammonium terminated PIB oligomer as a phase solubilizing catalyst in a solid/liquid phase transfer catalysis. In these cases, the effectiveness of the catalyst depended on the nature of the salt used. While sodium salts were generally ineffective, potassium and cesium salts were effective. In recycling studies, an S_N2 reaction that used a *N,N*-diethyl-*N*-methylammonium terminated PIB catalyst worked efficiently in heptane only for a few cycles. A loss of reactivity was observed when the catalyst was recycled presumably due to the leaching of the catalyst and/or thr heptane phase into the acetonitrile phase. Alternative PAO hydrocarbon solvents that leach less than conventional alkane solvents to the polar phase and that are more effective at phase anchoring catalysts worked well through five cycles.

EXPERIMENTAL SECTION

General Information. ^1H NMR spectra were obtained using Varian Inova 300, Mercury 300, Avance III 400, or Varian Inova 500 spectrometers at 300 MHz, 400 MHz, or 500 MHz. ^{13}C NMR spectra were obtained using Varian Inova 300, Mercury 300, Avance III 400, or Varian Inova 500 spectrometers at 75 MHz, 100 MHz, or 125 MHz. The spectra were calibrated using residual non-deuterated solvent as an internal reference (e.g. $CDCl_3$: ^1H NMR = δ 7.27 ppm; ^{13}C NMR = δ 77.2 ppm). Analyses by gas chromatography (GC) were carried out using a Shimadzu GC-2010 equipped with an FID detector and a 30-m × 0.32-mm × 0.5-μm HT5 capillary column. Polyisobutylene starting materials were provided by TPC Inc in Houston Texas.[12] Other reagents were purchased from commercial suppliers and used without further purification.

Alkene-terminated PIB (1). Alkene-terminated PIB with a molecular weight, M_n, of 1000 Da is commercially available and was obtained from Texas Polymer Corporation.[12] The starting material contains ca. 5% saturated PIB and a small amount of a trisubstituted (internal) alkene isomer. It was used without further purification.

Hydroxy terminated PIB oligomer (**2**) was prepared using a reported procedure.[5] The starting alkene-terminated PIB (**1**) (10 g, 10 mmol) was dissolved in 20 mL of hexanes. The reaction mixture was stirred under N_2 and 0.34 mL of $BH_3{\cdot}SMe_2$ (10M) was added into the reaction mixture. After stirring at room temperature for 24 h, the reaction mixture was cooled to 0 °C. Then, 8 mL of EtOH and 2.4 mL of 4N NaOH were added into the reaction mixture followed by dropwise addition of 1.6 mL of 30% H_2O_2. The reaction mixture was stirred for 2 h at room temperature and 60 mL of water was added to form a biphasic mixture. The hexane layer was washed with water (3 x 15 mL) and brine (1 x 15 mL). The hexane layer was then dried with Na_2SO_4 and the solvent was removed under reduced pressure using a rotary evaporator to afford 9.98 g of **2** (98 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.75-1.46 (m, 208H), 3.33 (dd, 1H), 3.50 (dd, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 19.7, multiple peaks between 29.1 and 38.3, 49.5, multiple peaks between 56.8-59.6, 69.7.

Iodide terminated PIB oligomer (3) was prepared using a reported procedure.[5] Hydroxy terminated PIB oligomer (**2**) (25.56 g, 25.1 mmol) was dissolved in 250 mL of DCM. The reaction mixture was charged with iodine (8.23 g, 32.6 mmol), triphenylphosphine (8.55 g, 32.6 mmol), and imidazole (2.22 g, 32.6 mmol) and stirred for 24 h. DCM was then removed under reduced pressure using a rotary evaporator and hexane was added to dissolve the crude product. The hexane layer was extracted with DMF (3 x 75mL), (2 x 75 mL), and brine (1 x 75 mL). The hexane layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified by column chromatography which yielded 25.1 g of **3** as a viscous oil yield (89 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 1.00-1.43 (m, 220H), 3.13 (dd, 1H), 3.27 (dd, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.8, 23.9, multiple peaks between 29.1 and 38.3, 52.7, multiple peaks between 56.9-59.4.

Diethylamine terminated PIB oligomer (4) was prepared using a reported procedure.[5] To a 50 mL heptane solution of iodide terminated PIB oligomer (**3**) (5.27 g, 4.7 mmol), a 50 mL of DMF solution of diethylamine (3.42 g, 46.7 mmol) was added to form a biphasic reaction mixture. Upon heating to 90 °C, the biphasic mixture became miscible. After 24 h, the reaction mixture was cooled to room temperature whereupon the reaction became biphasic again. The two layers were separated and the heptane phase was washed with DMF (2 x 25 mL), water (2 x 25 mL), and brine (1 x 25 mL). The heptane layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure using a rotary evaporator. **4** was purified by column chromatography (Brockmann aluminum oxide). This afforded an isolated yield of 4.11 g of **4** (82 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 1.00-1.50 (m, 308 H), 2.01 (dd, 1 H), 2.16 (dd, 1 H), 2.49 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 11.8, 14.0, 21.6, 22.6, multiple peaks between 30.7 and 38.0, 47.3, 51.5, multiple peaks between 57.1 and 59.5, and 62.4.

***N,N*-Diethyl-*N*-methylammonium terminated PIB oligomer with iodide anion (5)** was prepared using a reported procedure.[5] Diethylamine terminated PIB oligomer (**4**) (4.71 g, 4.2 mmol) was dissolved in 50 mL of dichloromethane. Next, iodomethane (2.96 g, 20.8 mmol) was added into the reaction solution and was stirred for 24 h. Dichloromethane was removed by reduced pressure using a rotary evaporator. *N,N*-Diethyl-*N*-methylammonium terminated PIB oligomer was purified by aluminum oxide column chromatography and to afford 4.43 g of **4** as a viscous oil (83 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 1.00-1.56 (m, 221 H), 3.22 (dd, 1 H), 3.32 (s, 3 H), 3.40 (dd, 1 H), 3.68 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 8.8, 14.3, multiple peaks between 20.9 and 38.4, 49.0, 53.4, multiple peaks between 57.3 and 59.8, 69.7.

***N,N*-Diethyl-*N*-methylammonium terminated PIB oligomer with benzoate anion (6) and phenol-phenolate anion (7)**. In general, the ion-exchange reaction was done by using an ion-exchange column made up of Amberlite IRA400 (hydroxide form) resin beads. The ion-exchange resin was first treated with a solution of sodium hydroxide to ensure that the ammonium functional groups on the resins were present as ammonium hydroxide salts. After the eluent was tested to be basic by using a pH paper, the resins were then rinsed with water until the eluent has a pH of 7 to remove any excess aqueous NaOH. A solution of benzoic acid or phenol in methanol was then added into the ion-exchange column until the eluent has the same pH as the starting solution. Again, the resins were rinsed with either methanol, acetonitrile, or heptane until the eluent has a neutral pH. Lastly, a solution of 0.6 g of **5** in heptane was passed through the column to generate either *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with benzoate anion **6** or *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with phenoxide anion **7**. The majority of the heptane solvent was removed under reduced pressure using a rotary evaporator to yield 1.2 g of **6** as a viscous oil. The conversion of **5** to **6** was measured by ^{1}H NMR spectroscopy using the integral of the aryl protons of the benzoate relative to the methyl protons of carbons adjacent to the cationic nitrogen of the ammonium salt. The conversion was quantitative (100 %). The larger than expected mass for the isolated oil and the larger than expected signal for the aliphatic protons in the ca. 0.8-2.0 δ region for **6** was ascribed to the presence of some residual heptane in the viscous oil product. While excess hexane or heptane in other syntheses of functionalized PIB oligomers can be removed on heating under reduced pressure, prior studies with PIB oligomers containing ammonium salts has indicated that heating can produce side reactions (e.g. Hofmann eliminations) so the viscous oil product was directly used. The ammonium salt **7** was similarly formed with 100% conversion of the end group. The 1.1 g of the viscous oil product **7** that was isolated in the same scale reaction was also a larger than expected mass. As discussed above, this larger mass and the larger than expected signal for the aliphatic protons in the ca. 0.8-2.0 δ region for **7** was ascribed to the presence of some residual heptane in the viscous oil product **7**. The resins used in synthesis of **6** and **7** were also reusable by retreatment of the spent resin with solutions of aqueous NaOH and benzoic acid or phenol to recycle the resins used in the ion-exchange reaction. *N,N*-Diethyl-*N*-methylammonium terminated PIB oligomer with benzoate anion **6**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86-1.92 (m, 420 H), 3.18 (dd, 1 H), 3.28 (dd, 1 H), 3.33 (s, 3 H) 3.68 (m, 4 H), 7.33 (m, 3 H), 8.11 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 8.3, multiple peaks between 23.5 and 38.3, 48.6, 53.0, multiple peaks between 57.6 and 59.7, 69.0, 127.9, 129.8, 130.7, 136.7, 171.5. *N,N*-Diethyl-*N*-methylammonium terminated PIB oligomer with phenolate anion **7**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.93-1.45 (m, 364 H), 2.88-2.92 (m, 5 H), 3.23 (m, 4 H), 6.56 (m, 1 H), 6.80 (m, 2 H), 7.07 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 8.0, 23.2, 24.7, multiple peaks between 29.0 and 38.1, 48.2, 53.0, 56.6, multiple peaks between 57.6 and 59.5, 68.5, 115.8, 117.4, 129.3, 135.6, 162.7.

***N,N*-Diethyl-*N*-methylammonium terminated PIB oligomer with boron tetrafluoride anion (8)**. *N,N*-Diethyl-*N*-methylammonium terminated PIB oligomer with iodide anion (**5**) (10 g, 8.2 mmol) was dissolved in 100 mL of heptane. Then, acetone (100 mL) and 10 equiv. of sodium tetrafluoroborate were added into the reaction mixture. The reaction was stirred for 24 h. The solvents were removed under removed pressure using a rotary evaporator. Then, hexane was added into the crude product, where the hexane solution was extracted with water (3 x 50 mL). The hexane layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure using a rotary evaporator to afford 8.73 g of **8** (94 % yield)**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.68-1.82 (m, 276 H), 2.92-3.29 (m, 5 H), 3.29-3.60 (m, 4 H).

Tetra-*n*-butylammonium benzoate (TBA-benzoate). The same procedure as mentioned in the synthesis of **6** was used with the exception that acetonitrile was used instead of heptane because of the insolubility of tetra-*n*-butylammonium salts in heptane. In this chemistry, 0.18 g (0.5 mmol) of tetra-*n*-butylammonium iodide in 10 mL of acetonitrile was converted into 0.14 g of the TBA-benzoate (78% yield). This compound was also prepared using a 1 M solution of tetra-*n*-butylammonium hydroxide in MeOH and equivalent amount of benzoic acid. The reaction was stirred for 24 h in the presence of magnesium sulfate. The reaction mixture was filtered and the solvent of removed under reduced pressure using a rotary evaporator. Then the white solids were dried under vacuum for another 24 h. **6** prepared from TBA-OH or by ion exchange was equally effective and spectroscopically identical. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.91 (m, 12 H), 1.37 (m, 8 H), 1.47 (m, 8 H), 3.40 (dd, 1 H), 3.2 (m, 8 H), 7.21 (m, 3 H) 8.00 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.4, 19.4, 23.7, 58.32, 127.1, 128.7, 129.3.

Tetra-*n*-butylammonium phenol-phenolate (TBA-phenol-phenolate). This compound can be prepared by a reported procedure.[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.92 (m, 12 H), 1.29 (m, 8 H), 1.36 (m, 8 H), 2.97 (dd, 1 H), 3.2 (m, 8 H), 6.58 (m, 2 H), 6.86 (m, 4 H), 7.06 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.6, 19.5, 23.8, 58.3, 115.8, 117.1, 129.2, 162.1

Typical procedure for kinetic studies of S_N2 reactions. For the kinetic studies, a 0.1 M solution of equivalent amounts of the substrates, the nucleophile source, and cyclooctane was prepared in MeOH, MeCN, DMF, or heptane. The reaction was either stirred at 35 °C or 55 °C. An aliquot (100 μL) of the reaction mixture was taken at different time intervals. In cases where polar solvents were used, the aliquot was diluted with 1 mL of diethyl ether and washed with 1 mL of water. The two phases with separated and the organic layer was dried with anhydrous sodium sulfate. The solution was then submitted for GC analysis. In the case of heptane, an aliquot (100 μL) of the reaction mixture was passed through a pipette silica gel column using 1 mL of hexanes. The eluent was submitted in the GC for analysis. The rate constant, *k*, was calculated by using Solver in Excel for non-linear curve fitting.

Typical procedure for solid/liquid phase catalysis and catalyst recycling. The reaction was carried out using a 0.1 M solution of 1-bromobutane and 10 mol% of **8** in heptane (10 mL). Potassium acetate (3 eq) was added into the reaction mixture and the reaction was stirred for 24 h at 90 °C. After 24 h, the solution was decanted from the solid and MeCN (2 x 10 mL) was added to remove the low molecular weight species from the heptane solution of the PIB-bound ammonium salt.

While a gravity separation worked, a better separation was achieved using centrifugation for 15 min at 25 °C with a spinning speed of 3000 rpm. The MeCN layers from two extractions were combined and a known amount of cyclooctane was added as an internal standard before analyzing the solution by GC. In recycling, fresh 1-bromobutane and potassium acetate were added to the recovered alkane solution and the reaction was repeated using the same procedure described above. Reactions using PAO_{283} (a 20-carbon PAO with 2 cSt viscosity), 4 cST PAO_{432} (a 30-carbon PAO with 4 cSt viscosity) or PAO_{683} (a 50-carbon PAO with 10 cSt viscosity) as the solvent were carried out using the same procedure used with heptane.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

> ^{1}H and ^{13}C NMR spectra of the polyisobutylene derivatives **2-8** and of the tetra-*n*-butylammonium benzoate and tetra-*n*-butylammonium phenol-phenolate are provided in the supporting information.

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Notes

The authors declare no competing financial interest.

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