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# Switchable-Polarity Solvents Prepared with a Single Liquid Component

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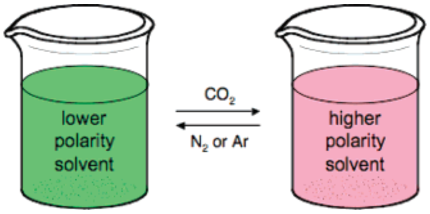
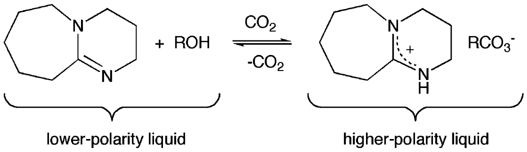


Known liquids that can reversibly switch their polarity at atmospheric pressure are all prepared as mixtures of two liquid components; we now report a series of switchable-polarity solvents that consist, in their low-polarity form, of only a single liquid component, a secondary amine. These solvents operate in a polarity range that is significantly lower than those of previously reported switchable solvents. Application to the separation and purification of a polymer and recovery of a catalyst is described.

## Introduction

Switchable solvents are liquids that can be reversibly converted from one form to another, where the two forms differ in their physical properties. Switchable-polarity solvents (SPS), for example, switch from a lower polarity form to a higher polarity form when a trigger is applied. Such solvents could have applications in processes where a solvent of a certain level of polarity is needed for one step (such as an extraction) and a solvent of a different polarity is needed for a subsequent step (such as a precipitation). So far, the few SPS that have been reported have been prepared as mixtures of two liquid components, either DBU and an alcohol (eq 1)[1,2] or DBU and a primary amine;[3] both of these systems use $CO_2$ gas as the trigger. While switchable-polarity solvents have many potential applications, their utility would be improved if the following issues could be solved: (a) the price of the amidines, (b) the fact that a mixture of two liquid components is required (complicating the handling of the liquid), and (c) the relatively high polarity of the "low-polarity" form. We have therefore been seeking new switchable solvents that use benign triggers, are cheaper than amidines, are prepared with only a single liquid component, and have a significantly less polar low-polarity form. New SPS with these advantages have now been found and are based on the reaction of $CO_2$ with secondary amines.



(1)

## Results and Discussion

Secondary and primary amines react with $CO_2$ to form carbamate salts via carbamic acids (eq 2). For such an amine/carbamate salt interconversion to form the basis of a switchable-polarity solvent, we needed to identify a liquid amine that converts into an ionic liquid carbamate salt. Carbamate ionic

$$\mathrm{NHR_2} \underset{}{\overset{CO_2}{\rightleftharpoons}} \underset{\text{carbamic acid}}{\mathrm{R_2N\overset{O}{\overset{\|}{C}}OH}} \overset{NHR_2}{\rightleftharpoons} \underset{\text{carbamate salt}}{\mathrm{[R_2NH_2][O\overset{O}{\overset{\|}{C}}NR_2]}} \qquad (2)$$

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liquids are not unknown; the carbamate salt of dimethylamine, known as dimethylammonium dimethylcarbamate or "DIMCARB", has been studied for many decades as an ionic liquid.[4−10] Unfortunately for the present purposes, DIMCARB is not a switchable polarity solvent; it cannot be converted into a low-polarity liquid because the amine from which it is derived, $NHMe_2$, is a gas. For an SPS, one needs a liquid amine that gives a liquid carbamate salt. Most liquid amines (including primary alkylamines,[3,11] allylamine,[12] piperidine,[6] pyrrolidine,[6] and benzylamine[13]) are converted into solid carbamates. Liquid anilines do not react with $CO_2$ at all. We now report four liquid dialkylamines that are converted by $CO_2$ into liquid carbamate salts, and can therefore be used as SPS. The four amines are *N*-ethyl-*N*-butylamine, *N*-ethyl-*N*-propylamine, dipropylamine, and benzylmethylamine (boiling points 111−112, unknown, 109−110, and 184−186 °C, respectively).[14−16] Lighter secondary amines such as ethylmethylamine, diethylamine, and methylpropylamine should not be used, even though they do give liquid carbamates,[6] because these amines are very volatile and highly flammable (boiling points 34 to 62 °C,[6] estimated vapor pressures 0.21 to 0.65 bar at 25 °C, and flash points below −20 °C).[17]

Notwithstanding our expectation that the reaction of $CO_2$ with neat amines would give the carbamate salt, there was the possibility that the reaction would generate only the carbamic acid or a mixture of the acid and the salt. The product of the reaction of amines dissolved in organic solvents is reported to be solvent dependent, with more polar solvents favoring carbamic acid formation and less polar solvents favoring salt formation.[18−20] To determine the nature of the product when performed neat, the reactions of the amines with $CO_2$ were monitored by spectroscopy and conductivity measurements. For example, bubbling $CO_2$ through a sample of $NHPr_2$ in an NMR tube at room temperature for 2 min gave a $^1H$ NMR spectrum containing two sets of propyl resonances (data in the Experimental Section) indicating the presence of two species and a singlet at 10.4 ppm. Note that mixtures of $NHR_2$ and $NH_2R_2^+$ give only a single set of resonances,[21] and we assume that mixtures of $R_2NCO_2H$ and $R_2NCO_2^-$ would also only give one set of signals. The two sets of observed resonances are approximately equal in intensity, which is consistent with (a) complete conversion to the carbamate salt, (b) conversion of roughly half of the amine to carbamic acid and no reaction of the other half, or (c) a mixture of carbamate salt, carbamic acid, and unreacted amine. The peak at 10.4 ppm, which is significantly higher than that of $[NH_2Pr_2]Cl$ (9.43 ppm), is believed to be a mixture of the $R_2NCO_2H$ acidic proton and the $NH_2R_2^+$ acidic protons (similar NMR behavior has been reported[22] for the case where R = Me). The IR spectrum of neat $NHPr_2$ after treatment with $CO_2$ shows dissolved $CO_2$ plus new bands at 1618 and 1537 $cm^{-1}$; the latter is consistent with the carbamate anion peak (1545 $cm^{-1}$ for $[H_2NCO_2^-]$).[23] The band at 1618 $cm^{-1}$, although a bit low, is consistent with the carbamic acid (observed[24] for solid $(PhCH_2)_2NC(O)OH$ at 1640 $cm^{-1}$). The observation of peaks at both 1618 and 1537 suggest that explanation "c" above is correct. The electrical conductivity of liquid NHEtBu changes, upon $CO_2$ treatment, from a value below the detection limit of the conductivity probe up to a constant and repeatable value of 92 $\mu$S/cm. That value is not consistent with exclusive formation of carbamic acid; the conductivity of pure acetic acid, for example, is 0.006 $\mu$S/cm.[25] Neither is the value quite as large as one would expect for the formation of a pure ionic liquid; ionic liquids of comparable viscosity (such as 1-butyl-3-methylimidazolium trifluoromethanesulfonate)[26] have conductivities an order of magnitude higher. We conclude from the spectroscopic and conductivity data that the liquid formed by the $CO_2$ treatment of these amines is a mixture of carbamate ionic liquid, carbamic acid, and amine; the acid and amine are likely hydrogen bonded to each other because they apparently prefer to be close to a 1:1 ratio. It is possible that had all of the carbamic acid protons transferred to the amine molecules, the product would have been solid at room temperature.

The mass and viscosity changes upon $CO_2$ treatment were also measured. The amount of $CO_2$ adsorbed by NHEtBu, measured gravimetrically, is 0.61 mol of $CO_2$ per mol of amine, which is consistent with 0.55 mol of $CO_2$ captured chemically (as carbamate salt and/or carbamic acid) plus 0.06 mol of dissolved $CO_2$ (2 wt %, a typical value for solvents of this polarity[27]). The viscosity of the liquid amine visibly increases during the $CO_2$ treatment. The viscosity of NHEtBu before $CO_2$ treatment was 0.57 cP at 23 °C; after treatment it rose to 60 cP. The viscosity values for $NHPr_2$, NHMeBu, and NHBnMe were 0.52, 0.48, and 1.7 cP before $CO_2$ treatment and 34, 56, and 4000 cP after treatment, respectively.

The polarities of these liquids in their low and high polarity forms were determined by using the solvatochromic probe Nile

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**TABLE 1. Solvatochromic Data for Nile Red in Selected Liquids**

| | $\lambda_{max}$ | | | |
|---|---|---|---|---|
| liquid | non-ionic liquid | ionic liquid or polar form | after $N_2$[a] | ref |
| diethyl ether | 504 | | | 29 |
| $NHEt_2$ | 511 | | | 29 |
| NHPrBu | 516 | 523 | 516 | this work |
| $[PMeDec_3]Br$ | - | 525 | | 28 |
| NHEtBu | 517 | 531 | 519 | this work |
| $NHPr_2$ | 518 | 530 | 521 | this work |
| NHMeBu | 519 | 536 | 530 | this work |
| ethyl acetate | 520 | | | 29 |
| NHMePr | 525 | 537 | 536 | this work |
| acetone | 530 | | | 29 |
| NHBnMe | 532 | 542 | 536 | this work |
| DBU/1-hexanol | 536 | 543 | | 1 |
| DMF | 541 | | | 29 |
| methanol | 550 | | | 29 |
| $[bmim]BF_4$ | | 551 | | 30 |

[a] After $N_2$ was bubbled through the ionic liquid for 2.5 h at 60 °C.

Red (NR). The more famous solvatochromic probe Reichardt's "$E_T(30)$" dye could not be used in this study because it is effectively bleached in the presence of weak acids. NR data are normally reported as $\lambda_{max}$ values (nm); higher values indicate higher polarity. As shown in Table 1, ethylbutylamine has a very low polarity, lower than that of ethyl acetate, but after reaction with $CO_2$ the polarity rises to become comparable to that of acetone. Note that the $\lambda_{max}$ for the higher polarity form is in the lower part of the range expected for ionic liquids; methyltridecylphosphonium bromide is reported to have a $\lambda_{max}$ of 525 nm.[28]

*N*-Benzylmethylamine is a significantly more polar secondary amine but otherwise behaves similarly; $CO_2$ exposure causes an increase in polarity and viscosity while treatment with $N_2$ at 60 °C reverses the change, although the final $\lambda_{max}$ is slightly higher (536 nm) than the original value for NHBnMe before exposure to $CO_2$. The benzylmethylamine SPS exhibits the same range of $\lambda_{max}$ values as the DBU/1-hexanol system.[1]

Switching the high-polarity form back into the liquid amine is achieved with heating and/or bubbling of an inert gas through the liquid phase. For example, bubbling nitrogen through the polar liquid for 2.5 h converts it back to low polarity again, as shown by the $\lambda_{max}$ value lowering back toward the original value for the starting amine. *N*-Butyl-*N*-propylamine has the same polarity after the $N_2$ treatment that it had before being exposed to $CO_2$. Two of the other secondary amines (NHEtBu and $NHPr_2$) had only slightly elevated polarity after the $CO_2$ and $N_2$ treatments. Conductivity changes also demonstrated that the reaction with $CO_2$ could be reversed: heating the high-polarity forms of the liquids to 60 °C while bubbling $N_2$ through it caused the conductivity to fall back below the detection limit of the conductivity probe.

Experiments with some other amines were less successful. Volatile secondary amines such as *N*-methylpropylamine and *N*-methylbutylamine were converted by $CO_2$ to a viscous liquid of higher polarity (as reported by NR) but attempts to lower the polarity back to the original by bubbling $N_2$ through the liquid at 60 °C were unsuccessful; the $\lambda_{max}$ lowered to a constant value, which was higher than that of the original amine. Methylaniline, in contrast, did not increase in polarity upon exposure to $CO_2$; anilines are not sufficiently basic to thermodynamically stabilize their own carbamate salts.[31] Some other amines, including *n*-hexylamine, *N*-*tert*-butylisopropylamine, and 1,3-dimethylbutylamine, gave solid carbamates upon exposure to $CO_2$.

The polar liquids derived from NHEtBu, NHBnMe, and NHMeBu do not solidify even when kept in a freezer at −80 °C for 12 h. Given that viscous ionic liquids are prone to supercooling behavior, it is expected that the actual melting point is much higher than −80 °C. Melting points close to room temperature would be consistent with the limited melting point data for the solid carbamates of related secondary amines.[6]

Various solids were tested for their solubility in NHEtBu and its polar form (50 mg of solid in 3.0 mL of amine before $CO_2$ treatment). Not surprisingly, particularly low polarity solids such as tetracosane were soluble in only NHEtBu, while solids of higher polarity were either soluble in both (e.g., benzyl benzamide) or only soluble in the polar form (e.g., tetraethylammonium *p*-toluenesulfonate and sodium *p*-toluenesulfonate). Ibuprofen, which is capable of protonating the amine, was soluble in both forms. Solids of very high polarity or hydrophilicity, such as cellulose, benzyltriethylammonium chloride, and (vinylbenzyl)trimethylammonium chloride, were soluble in neither form.

Various liquids, including toluene, mesitylene, propylene carbonate, styrene, decane, 5-*trans*-decene, hexadecane, and water, were found to be miscible with both NHEtBu and its polar form. Stilbene, in contrast, was miscible with NHEtBu and immiscible with the polar form.

Using secondary amines as switchable solvents in the presence of moisture is not as problematic as using the DBU/alcohol system in the presence of water. The latter system is converted into a bicarbonate salt that precipitates from the solution and is difficult to reconvert back into free DBU and water. The secondary amine SPS are less sensitive to small amounts of water. Four drops of water were added to 4 mL of NHEtBu. When $CO_2$ was bubbled through the amine, white solid particles were observed, but these redissolved in the amine when the solvent was switched back to its non-ionic form (by heating to 55 °C). However, in the presence of a stoichiometric amount of water, NHEtBu can be converted by $CO_2$ into a significant quantity of white salt (mp or dec at 69 °C, shows the distinctive bicarbonate out-of-plane vibration at 836 $cm^{-1}$), which was not reconverted back into a liquid when treated with $N_2$.

Application of NHEtBu for postreaction separation of a product from a homogeneous catalyst was tested. The alternating polymerization of cyclohexene oxide with $CO_2$, using $[PPN]N_3$ as cocatalyst and Cr(salen)Cl as catalyst (Scheme 1; $H_2$-salen = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine; PPN = bis(triphenylphosphorylidine)ammonium cation),[32] was performed under 35 bar of $CO_2$ without solvent. After the polymerization, the $CO_2$ was released and the solid products were dissolved in NHEtBu. It was apparent that both the Cr(salen)Cl catalyst and the polymer are soluble in the amine. $CO_2$ was bubbled through the solution to switch the solvent to

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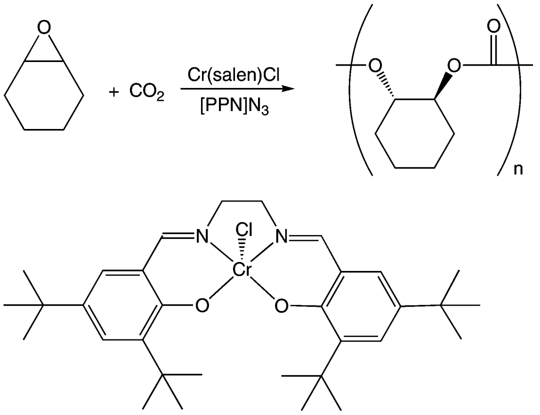
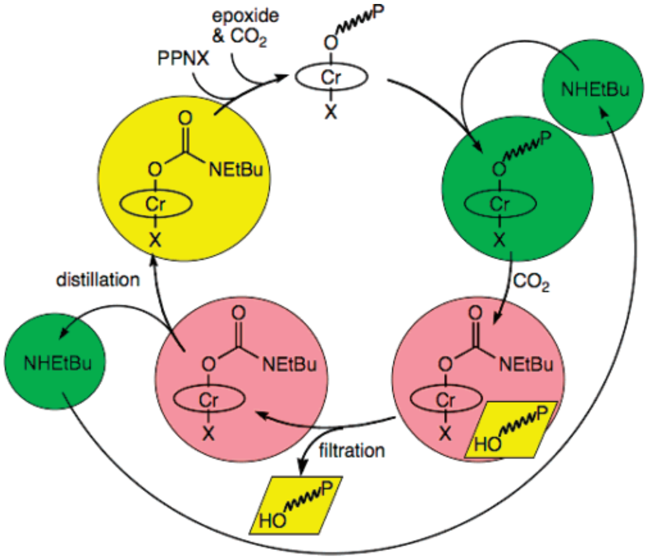
**SCHEME 1. Copolymerization of $CO_2$ and Cyclohexene Oxide**



**SCHEME 2. Recycling of Catalyst and SPS following the Copolymerization of $CO_2$ and Epoxide[a]**

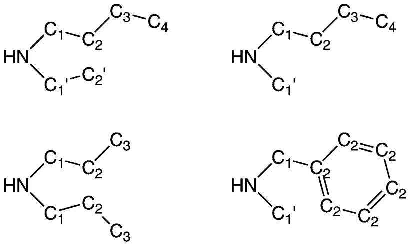


[a] Colors indicate species in low-polarity SPS (green), high-polarity SPS (pink), solid state (yellow), and without solvent (colorless). The carbamate ligand on the complex is speculative. All Cr species bear a 1- charge.

its polar form, with the result that the polymer precipitated. Filtration yielded a nearly white polymer ($M_n$ = 23 000 Daltons, PDI = 1.13) and an orange-brown solution. The color of the solution indicated that the catalyst remained primarily in the solution, but the slight color to the polymer indicated a small amount of catalyst remained in the polymer. Washing the polymer by mixing it with amine and then converting the amine to the polar liquid removes some more color from the polymer. Samples of the polymer after the first filtration and after the washing were submitted to GPC analysis to ascertain any effects of the separation process on the molecular weight of the polycarbonate. A comparison of the data obtained implies that the repetitive separation process utilizing switchable polarity solvents (SPS) does not degrade the polymer in any way.

The traditional technique for isolation of the polymer is extraction with $CH_2Cl_2$ followed by purification by repeated precipitation with acidified methanol (HCl); the acid is required to cleave the Cr catalyst from the polymer chain. With the NHEtBu SPS, the carbamic acid presumably acts in this capacity. The molecular weight value for the isolated polymer obtained by using the SPS compares nicely with polymer obtained from the traditional $CH_2Cl_2$/acid/methanol method. For example, a copolymerization reaction carried out to a high level of conversion afforded copolymer with a $M_n$ value of 40 300 Daltons (PDI = 1.06) from the traditional separation process and 39 600 Daltons (PDI = 1.06) from the SPS extraction process. The catalyst contained in the SPS eluent was recovered by distillation of the $CO_2$ and amine. The catalyst was then re-used for the solventless copolymerization of a fresh batch of epoxide and $CO_2$ (Scheme 2). Copolymer yield (17 g compared to 21 g in the first run) and $M_n$ (15 300 Daltons) decreased, while the PDI (1.10) rose slightly.

**SCHEME 3. Numbering Scheme Used for NMR Assignments**



## Conclusions

The advantages of the secondary amine switchable solvents over the DBU/ROH system include decreased sensitivity to moisture, much lower price, and the fact that the secondary amine solvents do not require the operator to monitor the molar ratio of two liquids (such as DBU and an alcohol). These SPS also operate at significantly lower polarities than those of the DBU/ROH system. However, none of the SPS are perfect; they are switchable because they are reactive. That same reactivity will prevent them from being used as solvents for any applications involving acidic or alkylating agents but the SPS offer practical benefits for other reactions. In the case of the copolymerization described above, the reactivity of the solvent allowed it to replace the HCl for the acid quench in addition to replacing the $CH_2Cl_2$ and MeOH for the extraction.

Secondary amines represent switchable solvents that use the same benign triggers as DBU/alcohol mixtures but differ in having less water sensitivity, being cheaper than amidines, being prepared from only a single liquid component, and offering a different polarity range.

## Experimental Methods

**Materials and Methods.** Amines, organic solids, dyes, carbon dioxide (supercritical fluid chromatography grade), and nitrogen (99.98%) were used as received. Spectra were obtained with a 400 MHz NMR spectrometer. Spectroscopic data for the amines before and after $CO_2$ treatment are given in the text and tables below. NMR spectra of the amines after $CO_2$ treatment were obtained by bubbling $CO_2$ through a solution of 2−3 drops of dry amine in dry $CDCl_3$ in a septum-capped NMR tube. The NMR data, using the numbering schemes shown in Scheme 3, are listed in Tables 2 and 3.

**IR Spectroscopic Data for the Amines Before and After $CO_2$ Treatment. (a) Butylmethylamine.** Before $CO_2$ treatment: 2961 s, 2921 s, 2867 m, 2787 w, 1464 w, 1380 w, 1147 w, 1124 w. After $CO_2$ treatment: 2961 s, 2928 s, 2867 s, 2464 w, 1626 m, 1552 m, 1474 s, 1377 s, 1306 s, 1255 m, 1056 w, 1032 w.

**(b) Benzylmethylamine.** Before $CO_2$ treatment: 3027 s, 2967 s, 2932 m, 2843 m, 2789 s, 1495 s, 1474 m, 1453 s, 1356 w,

**TABLE 2.** **$^1$H NMR Spectroscopic Data for Amines in $CDCl_3$ before and after Treatment with $CO_2$[a]**

| species | C1 | C2 | C3 | C4 | C1′ | C2′ |
|---|---|---|---|---|---|---|
| NHBuEt before | 2.55 t | 1.42 qn | 1.28 sx | 0.86 t | 2.59 q | 1.05 t |
| | 7.6 Hz | 7.5 Hz | 7.5 Hz | 7.4 Hz | 7.0 Hz | 7.2 Hz |
| NHBuEt after | 3.15 br | 1.44 br | 1.26 br | 0.84 t | 3.15 br | 1.02 br |
| | 2.68 br | 1.98 br | | 7.4 Hz | 2.78 br | 1.18 br |
| [$NH_2$BuEt]Cl | 2.85 t | 1.82 qn | 1.36 sx | 0.88 t | 2.97 q | 1.42 t |
| | 7.8 Hz | 7.8 Hz | 7.6 Hz | 7.4 Hz | 6.8 Hz | 7.4 Hz |
| NHBuMe before | 2.50 t | 1.40 qn | 1.27 sx | 0.85 t | 2.36 s | |
| | 7.0 Hz | 7.3 Hz | 7.2 Hz | 7.2 Hz | | |
| NHBuMe after | 2.94 br | 1.32 br | 1.04 br | 0.62 t | 2.54 br | |
| | 2.54 br | 1.20 br | | 7.4 Hz | 2.27 br | |
| NHBuMe·HCl | 2.95 t | 1.87 qn | 1.46 sx | 0.98 t | 2.70 s | |
| | 7.8 Hz | 7.8 Hz | 7.5 Hz | 7.4 Hz | | |
| $NHPr_2$ before | 2.49 t | 1.44 sx | 0.84 t | | | |
| | 7.2 Hz | 7.2 Hz | 7.4 Hz | | | |
| $NHPr_2$ after | 2.73 br | 1.70 br | 0.89 br | | | |
| | 3.17 br | 1.54 br | | | | |
| $NHPr_2$·HCl | 2.91 br | 1.96 sx | 1.03 t | | | |
| | | 7.9 Hz | 7.4 Hz | | | |
| NHMeBz before | 3.68 s | 7.1−7.3 | | | 2.39 s | |
| NHMeBz after | 4.43 s | 7.1−7.4 | | | 2.80 s | |
| | 3.78 s | | | | 2.27 s | |
| NHMeBz·HCl | 3.96 s | 7.4−7.6 | | | 2.42 s | |

[a] Abbreviations: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet or apparent quintet, sx = sextet or apparent sextet. Acid proton peak positions not listed.

**TABLE 3.** **$^{13}$C NMR Spectroscopic Data for Amines in $CDCl_3$ Before and After Treatment with $CO_2$, with All Chemical Shifts Relative to $CDCl_3$ at 77.0 ppm.**

| species | C1 | C2 | C3 | C4 | C1' | C2′ | CO |
|---|---|---|---|---|---|---|---|
| NHBuEt before | 49.4 | 32.1 | 20.4 | 13.9 | 44.0 | 15.1 | |
| NHBuEt after | 46.6 | 30.6 | 19.8 | 13.4 | 41.8 | 11.6 | 161.5 |
| | 45.7 | 28.5 | | | 40.8 | | |
| NHBuEt·HCl | 47.1 | 27.9 | 20.1 | 13.5 | 42.7 | 11.1 | |
| NHBuMe before | 51.9 | 32.1 | 20.4 | 14.0 | 36.5 | | |
| NHBuMe after | 48.1 | 29.6 | 19.5 | 13.2 | 33.4 | | 161.9 |
| | 48.5 | 27.6 | | | 32.3 | | |
| NHBuMe·HCl | 49.2 | 27.8 | 20.0 | 13.5 | 32.8 | | |
| $NHPr_2$ before | 51.9 | 23.2 | 11.7 | | | | |
| $NHPr_2$ after | 48.9 | 21.2 | 10.8 | | | | 161.2 |
| | 48.1 | 19.7 | | | | | |
| $NHPr_2$·HCl | 49.3 | 19.4 | 11.3 | | | | |
| NHMeBz before | 56.1 | 140.4 | | | 36.1 | | |
| | | 128.4 | | | | | |
| | | 128.1 | | | | | |
| | | 126.9 | | | | | |
| NHMeBz after | 51.8 | 138.8 | | | 33.5 | | 161.7 |
| | 39.8 | 132.6 | | | 31.0 | | |
| | | 125−132 | | | | | |
| NHMeBz·HCl | 52.1 | 130.3 | | | 31.2 | | |
| | | 129.8 | | | | | |
| | | 129.6 | | | | | |
| | | 129.2 | | | | | |

1104 w, 1073 w. After $CO_2$ treatment: 3029 m, 2840 m, 2787 m, 1622 m, 1555 m, 1494 s, 1447 s, 1380 s, 1261 m, 1023 m.

**(c) Dipropylamine.** Before $CO_2$ treatment: 2961 s, 2928 m, 2867 m, 2800 m, 1457 m, 1360 w, 1130 m. After $CO_2$ treatment: 2955 s, 2930 s, 2868 s, 1618 m, 1537 m, 1465 s, 1403 s, 1311 m, 1260 m, 1060 w.

**(d) Butylethylamine.** Before $CO_2$ treatment: 2956 s, 2927 s, 2871 m, 2810 m, 1462 w, 1375 w, 1128 w. After $CO_2$ treatment: 2954 s, 2927 s, 2874 m, 2356 w, 1615 m, 1548 m, 1467 s, 1410 s, 1370 m, 1296 s, 1063 w.

**Preparation of the HCl Salts.** The HCl salts of the secondary amines were prepared, for comparison of their NMR to those of the polar liquids, by adding HCl (4 M in dioxane) dropwise to the neat secondary amine (1 mL) until a precipitate formed. The material was then washed with hexane and collected on a filter. The melting points of [$NH_2$EtBu]Cl (197 °C, lit.[33] 197 °C), [$NH_2$MeBz]Cl (178−180 °C, lit.[34] 178−179 °C), [$NH_2Pr_2$]Cl (sealed tube 263−265 °C, lit.[35] 268−269 °C), and [$NH_2$BuMe]Cl (174 °C, lit.[36] 174−175 °C) match closely or exactly those reported in the literature. NMR spectroscopic data are listed in Tables 2 and 3.

**Solubility or Miscibility Evaluation.** The substrate (50 mg) and ethylbutylamine (3.0 mL) were stirred together in a septum-capped vial under $N_2$. Whether the solid had completely dissolved by that time was determined visually. $CO_2$ was bubbled through the solution for 30 min, with stirring, and the phase behavior was visually observed again. If there was a change in the phase behavior, the vial was heated to 50 °C and $N_2$ was bubbled through the solution for 2 h to see if the change was reversible. For all cases that demonstrated a change, the change was reversible, with the exception of glucose, which was insoluble before treatment with $CO_2$, soluble after $CO_2$ treatment, and remained soluble after the $N_2$ treatment.

The miscibility of liquids was tested in a similar manner except that the amount of the liquid substrate was 0.5 mL.

**Viscosity Measurements.** The Cannon−Fenske-type viscometer of appropriate range was placed in a water bath, temperature equilibrated for 20 min, and purged for 10 min with $N_2$ immediately before use. For the polar liquids, $CO_2$ was used as the purge gas instead of $N_2$.

**Conductivity Measurements.** $CO_2$ was bubbled through a 10 mL sample of ethylbutylamine in a 4 dram vial. The conductivity was measured every few minutes, using a conductivity probe, until a constant value was obtained. $N_2$ was bubbled through the solution at 55 °C until the conductivity returned to 0 $\mu$S/cm.

**Polarity Measurements.** Approximately 3 mL of the secondary amine was placed in a 1 cm glass cuvette. The solvatochromatic dye, Nile Red, was added at a concentration appropriate to give an absorbance between 0.5 and 1.0. The samples were then sealed

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with an airtight septum and bubbled with $CO_2$ from a pressurized vessel for approximately 20 min or until the heat of reaction subsided. The UV/visible spectrum was acquired again. The solvent was then switched back to the low-polarity form by bubbling nitrogen gas into the cuvette and heating in a 55−60 °C oil bath for up to 2.5 h. Spectra were acquired periodically to follow the change in $\lambda_{max}$, until it reached a constant value. The experiments were performed twice for each amine; reported $\lambda_{max}$ values are the average of the two values obtained.

**Method for Switching the liquid with NMR Spectroscopic Monitoring.** Glass vials (3.5 mL), sealed with a septum, were purged with nitrogen gas for 2 min and then $CO_2$ for approximately 1 min. Approximately 2 mL of the secondary amine was injected by syringe into the vial while under carbon dioxide. Carbon dioxide was bubbled through the liquid, with stirring, for approximately 15 min or until the heat of reaction had subsided. Switching this polar form back to the amine was achieved by bubbling $N_2$ through the liquid at 55 °C. Proton NMR was used to monitor the conversion.

**Polymer/Catalyst Separation.** Cr(salen)Cl (0.050 mg, 0.086 mmol) was stirred with $PPNN_3$ (0.050 mg, 0.086 mmol) in $CH_2Cl_2$ for 30 min in a 30 mL glass vial and dried in vacuo. The "active" catalyst was dissolved in 10 mL of cyclohexene oxide (CHO) and loaded via cannula into a 300 mL stainless steel Parr reactor at 80 °C. The vial was rinsed with 10 mL of CHO, which was also loaded into the reactor. The reaction vessel was pressurized to 35 bar of $CO_2$ and heated to 80 °C for 4 h. The $CO_2$ was vented and the reactor placed under vacuum for 10 min to remove all traces of $CO_2$. Degassed HNEtBu (20 mL) was loaded into the reactor via cannula and the reaction mixture was stirred for 1 h. The reactor was opened and the contents emptied into a 125 mL Erlenmeyer flask and washed with an additional 10 mL of degassed HNEtBu, which was added to the flask. $CO_2$ was bubbled through the reaction mixture for 30 min resulting in the precipitation of the polymer. The polymer/catalyst/SPS slurry was mechanically stirred to ensure maximum catalyst removal and filtered with a Büchner funnel resulting in an off-white polymer and an orange-brown solution. This process was repeated to further purify the polymer and increase catalyst recovery yields. The catalyst was isolated from the SPS via vacuum distillation and combined with 0.037 mg (0.065 mmol) of $PPNN_3$ in $CH_2Cl_2$, as previously described, in preparation for recycling.

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