Direct extraction of carbonyl from waste polycarbonate with amines under environmentally friendly conditions: scope of waste polycarbonate as a carbonylating agent in organic synthesis†

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An efficient green method for converting waste polycarbonate into urea derivatives by reacting with primary amines has been developed. Simple treatment of polycarbonate plastic with primary amines in a closed vial at 80 °C without using any catalyst and toxic solvents made this process environmentally friendly. Digestion of the waste polycarbonate obtained from CDs and DVDs with amines affords functionalized urea and 4,4′-(propane-2,2-diyl)diphenol (BPA, bisphenol-A). The procedure is optimized to get maximum conversion of polymer to urea and its derivatives as a major product. The purification procedure to isolate the urea derivatives in the presence of bisphenol-A has been tuned to avoid chromatographic procedures. This environmentally friendly method provides (i) an alternative for recycling BPA from polycarbonate, (ii) a method of obtaining useful product like urea derivatives, (iii) scope for new carbonylating agents in organic synthesis, (iv) an amine functionalized polycarbonate surface.

Introduction

Since the early 1900s, synthetic polymers have been introduced as man-made materials that have been used for many purposes in our daily life. In addition to the first examples of polymer like bakelite, polyethylene, polystyrene etc., polycarbonate (PC) has received a great success in the plastic industry. Due to its high-performance properties like transparency, temperature resistance and toughness the utility of this polymer has spread to medical, construction, electronic and multimedia industries. This way a huge amount of synthetic polycarbonate has been introduced to our ecosystem. The major challenge is the management of the waste polycarbonate. Therefore, polymer recycling methods are of high importance in the present time where environment protection is at priority. One way is the mechanical recycling or blending of PC that provides material which is not suitable for high-performance applications.1 Another way is the thermal degradation or pyrolysis that is limited by its low selectivity and large amount of side products.2 Still another way is the chemical recycling that deals with the depolymerization or digestion of PC to obtain BPA as monomer that can be reused for the synthesis of fresh polycarbonate.3

Recently there are some chemical methods appeared in the literature that are suitable to recover BPA from waste PC. Most of them are using alcoholysis and aminolysis as main chemical processes for retro-polymerization of PC to BPA. In case of alcoholysis methanol has proven to be the suitable solvent in presence or absence of catalytic amount of alkali.4–6 The reaction delivers BPA and dimethylcarbonate (DMC) as main products. Though DMC is a useful by-product but it is a volatile organic compound (VOC), which is difficult to handle under high temperature conditions. On the other hand aminolysis of PC produced urea derivatives as by-product that is not a volatile organic compound but this method is known to be performed in toxic organic solvents like DCM, toluene and dioxane.6,7 In order to avoid toxic organic solvents in this process, supercritical water8 and ethanol9 was used for depolymerization of PC. However, these processes are requiring special reactors that have to be operated at high temperature and pressures.

In this research article we are presenting an innovative chemical transformation for waste polycarbonate. The proposed process has two advantageous features: one is the recovery of BPA, and the other is the utilization of carbonyl of polycarbonate as carbonylating agent under green conditions. Traditionally, carbonylation is a metal catalyzed process that involves the use of toxic carbon monoxide (CO), e.g., for the formation of amide bonds and ureas.10 Other chemical reagents that are used for carbonylation are phosgene,11 triphosgene,12 dimethyl carbonate13 and carbon dioxide.14 Recently commercial devices for carbonylation through ex situ generation of CO
has also been introduced. Recently, Yalfani et al. has developed a green protocol for the carbonylation by using base catalyzed in situ generation of CO from methyl formate as reagent of choice. These reagents have very well served the purpose of carbonylation in organic synthesis but they are suffering from their extreme toxicity, complex reaction conditions and use of other co-reagents.

In this study, we are introducing an environmentally and user friendly protocol for harvesting carbonyl from waste polycarbonate that is suitable to be used under normal laboratory conditions. The procedure is optimized to achieving a minimum use of toxic solvents, high temperature and pressure conditions and high efficiency in terms of processing time. In addition to recover BPA as raw material for PC synthesis, the main attention has been given to trap carbonyl monomer in the form of urea derivatives. These useful by-products can serve as starting material for the synthesis of new drug-like precursors.

Result and discussion

Looking at the chemical composition of the polycarbonate (PC), it consists of two monomers one is 4,4’-(propane-2,2-diyl) diphenol (BPA) and other is carbonyl group (Scheme 1). Most often the green methods for chemical recycling of the PC are emphasizing on the recovery of BPA, but the carbonyl group is either wasted or converted to simple chemicals like dimethyl carbonate (DMC). Few other, non-green chemical recycling methods of PC are showing utilization of the carbonyl unit by reacting with mono and bi-dentate amine, alcohols and thiols. Our aim in this study is to develop a green method that can be used for harvesting carbonyl from polycarbonate for making useful derivatives, and to keep this method as green as possible by obeying the 12 principles of green chemistry.

Therefore, during optimization experiments we have limited our self to safe solvents that don’t possess high toxicity e.g. ethanol, i-propanol and water. Initially, we have chosen simple benzylamine as reactant and reaction temperatures of 40 °C, 60 °C, 80 °C and 100 °C. Because all the reactions were performed in closed vial we limited the reaction screening to 100 °C only. Technically, minimum 2.0 equivalents of 4a are required to react with the carbonate functional group in order to make N,N’-dibenzyurea 3a. In order to screen the best solvent and temperature conditions for this reaction, we have used little excess of benzylamine (2.5 equivalents) so that the reaction occurrence can be monitored simply by disappearance of PC solid (Table 1). For 100 mg of polycarbonate 1.0 mmol of benzylamine was used, which is about 2.5 equivalent as compared to preserved carbonyl or BPA in the polymer matrix.

At 40 and 60 °C in all the reactions no conversion can be seen over 72 hours (Table 1, entry 1, 2, 5, 6, 9, 10). However at 80 °C both EtOH and i-PrOH have shown disappearance of the polymer by reaction with benzylamine over 12 hour heating. After cooling at 0 °C 58% and 55% N,N’-dibenzyurea (3a) has been isolated from EtOH and i-PrOH respectively (Table 1, entry 3 and 11). In case of treatment of PC with benzylamine at 100 °C in EtOH and i-PrOH the polymer gets completely dissolved only after 4 hours and upon cooling furnished 3a in 44 and 42% isolated yields (Table 1, entry 4 and 12). In order to recover BPA, from such reaction mixtures where polymer gets completely consumed, the dried filtrate was dissolved in 1 : 1 mixture of EtOH and H2O and slow evaporation furnished BPA 2 (yields are given in Table 1). The water based reactions have shown no disappearance of polymer at 40 and 60 °C. At 80 and 100 °C a melting effect on the polymer has been seen. Moreover upon cooling the reaction mixture furnished a solid product which appears to be complex mixture of polymers that is why water was not considered as optimal reaction solvent under these conditions (Table 1, entry 7 and 8). From the optimization experiment it is clear that both ethanol and 2-propanol can be used as reaction medium at 80 °C and 100 °C. Among these two alcoholic solvents we opted for ethanol as reaction solvent for further investigations. The temperature 80 °C has been considered as optimal instead of 100 °C due to safety issues of using ethanol in close vial at 100 °C. After screening the reaction conditions in terms of temperature and solvent, we reduced the

![Scheme 1 Polycarbonate as source of BPA and carbonyl equivalent.](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>% Yield(^b) (2)</th>
<th>% Yield(^a) (3a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EtOH</td>
<td>40</td>
<td>—</td>
<td>5%</td>
</tr>
<tr>
<td>2</td>
<td>EtOH</td>
<td>60</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>EtOH</td>
<td>80</td>
<td>62</td>
<td>58</td>
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<tr>
<td>4</td>
<td>EtOH</td>
<td>100</td>
<td>60</td>
<td>44</td>
</tr>
<tr>
<td>5</td>
<td>H2O</td>
<td>40</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>H2O</td>
<td>60</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>H2O</td>
<td>80</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>H2O</td>
<td>100</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>i-PrOH</td>
<td>40</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>i-PrOH</td>
<td>60</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>i-PrOH</td>
<td>80</td>
<td>63</td>
<td>55</td>
</tr>
<tr>
<td>12</td>
<td>i-PrOH</td>
<td>100</td>
<td>60</td>
<td>42</td>
</tr>
</tbody>
</table>

\(^a\) Combined isolated yield. \(^b\) Slow evaporation of residual mixture from 1 : 1 mixture of EtOH : H2O. \(^c\) Undigested polymer recovered. \(^d\) Complex polymer melt is obtained.
amine concentration to find the required amount. It has been noticed that minimum 2 equivalent of benzylamine are necessary to consume whole polymer under above stated conditions. Which is logical, as the synthesis of urea derivative requires reaction of one carbonyl equivalent with 2 amine molecules. When lower concentrations of benzylamine were reacted with polycarbonate the reaction solution turns turbid and partially broken polymer was also recovered from these reactions.

After optimizing the reaction conditions we explored the scope of this reaction by using differently substituted benzylamines (4, Table 2). In case of the reaction of polycarbonate with p-methoxy (4b) and m-methoxy benzylamines (4c) the required products 3b and 3c were isolated in 62% and 60% isolated yields. To keep this method green we avoid chromatography with toxic solvents, therefore, the reported yields are from the sum of directly precipitated products from crude ethanol reaction mixture at 0 °C. It’s important to mention that in the cases where substituted dibenzylurea is having similar solubility in ethanol like BPA, the pure product isolation by precipitation method became difficult.

In order to see the influence of electron withdrawing groups on this reaction we have chosen fluoride and trifluoromethyl groups on benzylamine. Reaction of p-fluoro benzylamine with PC furnished required product 3d in 52% isolated yield. The second component bisphenol-A (BPA) has been precipitated by slow evaporation from ca. 1 : 1 ethanol–water mixture of crude filtrate.

In case of ortho substituted trifluoromethyl benzylamine prolong heating at 80 °C did not helped in digesting the PC for yielding 3e under optimized reaction conditions. Unreacted but damaged PC pieces were recovered from this reaction. The bulk and electron withdrawing property of the o-trifluoromethyl group hinders the nucleophile addition of the primary amine on the carbonate functional group of polymer. In order to understand this particular reaction, we investigated the effect of trifluoromethyl group on meta and para positions of the benzene ring. It has been noticed that in case of m-trifluoromethyl benzylamine and p-trifluorobenzylamine the required products 3f (28%) and 3g (48%) were formed under these conditions. This concluded that it’s not the high electron-withdrawing capacity of trifluoromethyl group that hinders the reaction but the steric hindrance of bulky group at ortho position. The other component BPA was recovered from crude filtrate as described before. For investing further the effect of bulk near the amine functional group, we explored the use of diphenylmethyamine 4h and triphenylamine 4i under optimized set of conditions. In both the cases the polymer gets completely digested and left clear reaction mixture behind. Upon cooling the crude ethanolic reaction mixture, where 4h was used as reactant, the required product 3h has been obtained in 81% yield. However, in second case where triphenylamine 4i was reacted with PC, though the polymer get completely digested, no pure N,N’-diphenylurea (DTU) can be isolated using green solvents. Lastly, we used p- amino benzylamine 4j as reactants for this transformation because it provides aromatic amine on the benzene ring which could be used as functional group for further chemical transformations. This reaction went smoothly and furnished desired product 3j in 72% yield.

In an independent experiment we have checked the utility of this reaction when a mixed polymer waste is considered. We have deliberately mixed the pieces of 100 mg each of polystyrene, polypropylene, polyethylene and polycarbonate in the same vessel and treated with 200 µL of benzylamine in 3 ml ethanol at 80 °C. As expected only PC pieces disappeared from the reaction, while the other polymers remain unreacted and can be filtered away. Upon cooling the mixture N,N’-dibenzylurea 3a is precipitated (NMR) and BPA remains in the filtrate. We consider this reaction as a valuable method to selectively treat and separate waste PC from mixed plastic waste, which can be a very valuable method where type of polymer is not defined.

For extending the scope of this reaction we have chosen few alkyl amines in order to see if the reactivity varies by the way (Table 3). The reaction of the commercially available 40% solution of methyl amine (4k) in methanol with PC went very smoothly. The polymer chip disappeared completely within 5 minutes of heating at 80 °C. We have performed the reaction in excess amount of methyl amine, which can be easily removed from reaction by simple evaporation. However, both BPA and N,N’-dimethylurea (3k) are very well soluble in ethanol, which was a suitable green solvent in the optimized cases discussed before. Therefore, we opt water as another friendly solvent for precipitating BPA (low solubility in water) instead of N,N’-methylurea (relatively high solubility in water). In this case urea derivative has been purified by first removing BPA from water solution by filtration and then concentrating filtrate water. However, after multiple crystallization steps a trace amount of BPA was always present in the purified sample of 3k. Though the sample of N,N’-methylurea (~50% yield) thus obtained is sufficiently pure for being further use as reactant in organic synthesis (for NMR purity see ES1). Similarly, direct reaction of excess of 30% solution of ammonia (4l) in water with PC pieces, under these conditions furnished clear solution at 80 °C. Upon cooling the reaction mixture at room temperature BPA gets first precipitated and isolated by filtration. After extracting three crops of BPA from filtrate solution pure urea (4l) has been left in the filtrate, which is isolated in 68% yield. In case of long chain alkyl amines like decylamine (4m) the reaction was performed in ethanol and the product 3m get separated immediately upon cooling at room temperature. However the product is highly insoluble in most organic solvents. The reaction of cyclohexylamine (4n) under similar conditions furnishes N,N’-bis (cyclohexyl)urea 3n in 81% isolated yield. For providing further diversity to this method we have chosen propargylamine (4o) as nucleophile in ethanol. The terminal alkyne in this case can act as a very good functional group to react further chemical moieties through click chemistry. This reaction has furnished desired product 3o in 72% yield. Overall, we have noticed that the reactions of alkylamines with PC are relatively faster than that of benzylamines (2). With an exception of aqueous NH₃ (Table 3, entry 2) with PC, where the reaction time was relatively longer. The probable reaction for this could be the hydrophobicity of the PC which repels the water from the surface and could delay the digestion process.
After checking the feasibility of the reaction for benzyl (Table 2) and alkyl (Table 3) amines, we tested the same reaction conditions for its performance when aryl amines are used. We have examined various derivatives of aniline with electron withdrawing and releasing substitutions. Unfortunately, none of them seems to be reacting with the PC even when treated for long period of time. Even raising the temperature until 100 °C does not pushed the reaction and undigested PC was recovered.
as it is. The probable reason for this reaction failure is low nucleophilicity of the aryl amines, which can be increased using some catalyst or base. To keep present method green and catalyst free this does not come under the scope of present study.

For the mechanism of this reaction there are two possibilities how urea can be formed by harvesting carbonyl from PC. One possible way is the base (amine) catalyzed reaction of ethanol with PC forming diethylcarbonate (DEC, B) as intermediate. Thus formed DEC can react with amines (C) present in solution and form urea derivatives D (Scheme 2). Other possible route of this reaction is the direct addition of amine as nucleophile on the carbonate group of the polymer to form urethane linkage (B') as first step. In the second step another molecule of amine (C) react with urethane functional group and release urea derivative D from polymer into solution. After carefully examining the reaction we have found no evidence of the formation of DEC. It has also been reported in the literature that in case of digestion of PC with supercritical ethanol DEC is formed only when reaction is performed at 290 °C by using a high-pressure batch autoclave reactor. Therefore, looking at the reaction conditions of presented method that uses 80 °C, and no signs of DEC in analysis rules out the possibility of first route.

For proving the second reaction route as a probable sequence, we have done an independent experiment where PC (A) is reacted with bidentate 1,5-pentyldiamine (E) just below the concentration where polymer get started cracking. In order to see if 1,5-pentyldiamine is incorporated to the PC surface a washed sample is treated with dansyl chloride (G) in ethanol at room temperature to covalently bind dye molecule to free terminal amines (F). As expected the dye gets very well integrate to the polymer surface (Scheme 3, image H). However, when monodentate pentyamine (I) reacted with polymer surface and

Table 3  Derivatives of N,N'- dialkyurea 3 synthesized from reaction of alkylamine 4 with PC 1 in EtOH after 12 h at 80 °C

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkylamine (4)</th>
<th>Urea derivatives (3)</th>
<th>Isolated yield</th>
</tr>
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<tbody>
<tr>
<td>k</td>
<td>MeNH₂</td>
<td></td>
<td>~50</td>
</tr>
<tr>
<td>l</td>
<td>NH₃</td>
<td></td>
<td>68</td>
</tr>
<tr>
<td>m</td>
<td>CH₃(CH₂)₉NH₂</td>
<td></td>
<td>78</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>81</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72</td>
</tr>
</tbody>
</table>

Scheme 2  Proposed reaction mechanism.

Scheme 3  Polycarbonate surface functionalization.
Similarly treated with dansyl chloride (G) have not shown incorporation of dye as indicated by LSM imaging (Scheme 3, image K). These experiments hint towards the validity of the second proposal of the reaction mechanism (Scheme 2). Additionally, this experiment provides another method that can be used to functionalize the surface of the PC with primary amine groups. This indicates that in addition to be a green method for urea derivatives, BPA recovery from waste PC and harvesting carbonyl from PC this method is useful also for functionalizing PC surface with various amines. Therefore, by controlling the concentration of stock solution all of the amines used in this study (Table 2 and 3) are capable for being grafted on the polymer surface without causing any serious damage to the surface (SEM images of samples reacted with propargyl amine under different concentrations are given in ESIf). It makes this method further useful for surface modification of polycarbonate with applications in biomaterials and biotechnology.

**Conclusion**

In summary, we have described an unprecedented green and user friendly method for the treatment of polycarbonate plastic for recovering useful monomer BPA. Apart from the polymer recycling, in the reported method a proof of the concept to extract carbonyl group from polycarbonate has been successfully demonstrated. To the best of our knowledge, it is the first green method where carbonate group of polycarbonate has been extracted to make useful urea derivatives under environmentally friendly conditions. Further, this methodology provides a scope to remove PC from the mixed plastic waste, which could be helpful for the waste management of unspecific plastic material. Using this chemical approach, polycarbonate can be explored as source of carbonyl equivalent that can be used under green set of conditions to make chemically and biologically interesting molecules.

**Experimental**

**Materials and regents**

Commercially available CD and DVDs are used as PC source (as waste polycarbonate). For obtaining PC from CDs and DVDs they were treated 30 minutes in ultra-sonication followed by mechanical removal of unwanted layers. Most of the benzylamine, aliphatic amines and solvents were purchased from Sigma Aldrich and were used without further purification. All the reactions were performed in closed glass vials under shaking conditions.

**General procedure for reaction of amine with polycarbonate**

In a typical procedure 100 mg of PC, 2.0 equivalent of amine were suspended in 2 ml ethanol in a closed glass vial. The reaction temperature was raised to 80 °C and shaking was continues until all polymer disappeared from the reaction mixture. The reaction time depends upon the type of amine used. However most of the reactions discussed in this publication are completed in maximum of 12 hours.

**Separation of N,N'-disubstituted ureas and bisphenol-A**

After complete digestion of the polymer under above described conditions, the reaction has been transferred at 0 °C and stored until the crystallization occurs. The precipitates are washed with 2 ml cold ethanol to obtain pure crystals of N,N'-disubstituted ureas. Thus obtained filtrate has been treated same way to obtain further crop of the urea derivatives.

After complete extraction of urea derivatives (usually in three crops) the rest of ethanoic mixture is diluted with equal amount of distilled water. A slow evaporation of the mixture at room furnished amorphous bisphenol-A as pure product which has been checked with NMR and elemental analysis.

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**References**


