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Polymer 43 (2002) 2109–2116

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Polymer Communication

Chemical conversion of poly(carbonate) to 1,3-dimethyl-2-imidazolidinone (DMI) and bisphenol A: a practical approach to the chemical recycling of plastic wastes

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Received 13 November 2001; received in revised form 11 December 2001; accepted 11 December 2001

Abstract

A method for the chemical recycling of poly(carbonate) (PC) plastic wastes in the forms of bisphenol A (BPA) and 1,3-dimethyl-2-imidazolidinone (DMI) was investigated. Treatment with *N*,*N*′-dimethyl-1,2-diaminoethane (DMDAE) of PC pellets or PC wastes, derived from compact discs, in dioxane with/without a catalytic amount of base (e.g. Na_2CO_3 0.5 mol%) for a short period at 100 °C produced DMI and BPA, both in nearly quantitative yields. The aminolysis reaction can be carried out also in DMI, thus saving the use of conventional solvents. A sequential profile of this reaction was verified by examining two model reactions of diphenyl carbonate with *N*-methylbutylamine and DMDAE, respectively, both proceeded through low-activation energy processes. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(carbonate); Chemical recycling; Dimethyl-2-imidazolidinone

1. Introduction

How to solve the problem of plastic wastes at both post-manufacturer and post-consumer stages is now an important issue for the global conservation of carbon resources and the protection of petroleum chemical resources from their depletion [1–3]. The problem should systematically be investigated from different facets, e.g. (1) conceptual revolution in the material design of plastic merchandise directed toward longevity, recycling, and the concept of material lease [4–6], (2) development of versatile and efficient recycling technologies [7–10], and (3) adjustment of social, economical, and industrial networks to low-energy systems of plastic recovering [4–6]. To actuate our efforts toward carbon resource conservation in chemical ways, plastic products must be used repeatedly as plastics or chemical materials before reaching non-renewable termination, e.g. thermal energy recovery or coke-substitute at blast furnaces. Toward this goal, the authors have been proposing that plastics must be recycled to monomers by means of retro-polymerization, and that this method should be the primary solution of the issue, because retro-polymerization can reproduce virgin plastics to benefit the original chemical market. Based on this concept, we studied *chemical recycling*[1] of plastic wastes of poly(ethylene terephthalate) (PET) [7,8] and bisphenol A poly(carbonate) (PC) [9,10] by conventional methods, which can be performed with simple industrial equipments and low-energy operation processes.

Scheme 1 presents a ground basis for the argument of comparing material- and monomer-recycling methods with energy recovery and coke-substitute methods. First of all, we must notice that plastics are composed of two potential features of petroleum, i.e. material resource and manufacturing energy resource. Therefore, these two potentials are still conserved even after the commercial consumption of plastics at the post-consumers stage. Because manufacturing energy, that is, inherited in plastic wastes, cannot be recovered by any mean of incineration or coke-substitute, plastic wastes are not equivalent to crude oils and must be regarded as more highly valued materials than the oil. Additionally, we must note that both material/monomer recycling and coke-substitute/liquefaction methods consume nearly comparable amounts of energy

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[1] In this report, the term ‘chemical recycling’ is equivalent to ‘monomer recycling’ with which plastic wastes can be recycled as plastic monomers or industrial chemicals. The end-use of plastic, such as energy production or coke-substitute at blast furnaces, is strictly excluded from this definition.

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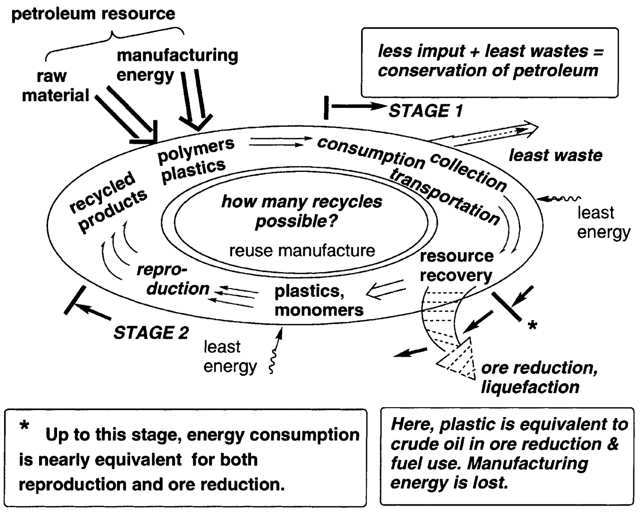
PII: S0032-3861(01)00800-X

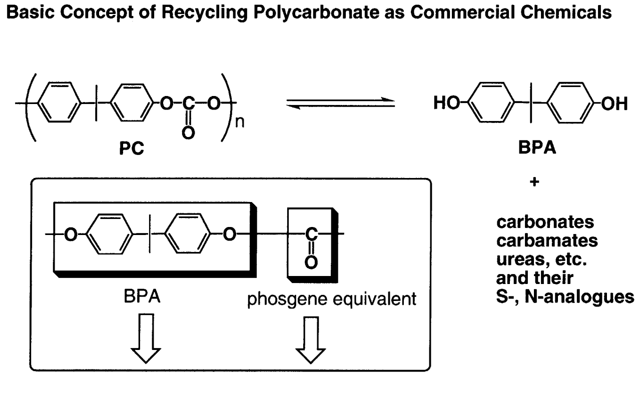


Scheme 1.

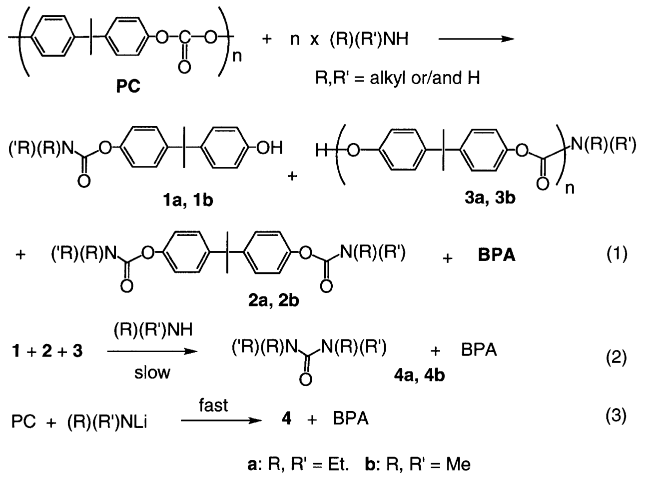
(in Stage I, Scheme 1), because both consist of similar processes of collection, transportation, sorting and rinsing. On this basis, therefore, the choice between these two critical pathways depends on the balance of the following equation. First, the monomer/material process must satisfy the following energy balance (Eq. (1))

$$[\text{oil for energy of manufacturing}] + [\text{oil as material source}] - [\text{oil for energy of plastic reproduction}] > 0. \qquad (1)$$

When the balance is positive, the plastic wastes should not be incinerated but recycled, thus the oil corresponding to the balance can be saved, i.e. reproduced. Liquefaction method cannot play such a magic, because the incineration energy recovery from plastic can never exceed the sum of [oil for energy of manufacturing] + [oil as material source] and never be led to saving the oil. Many polycondensation polymers are known to satisfy this requirement (Eq. (1)) [14,15] and so does even polyolefins [16]. To be additionally stressed is that not only recovery systems in Stage I (Scheme 1), but also recycling technologies in Stage II shall be innovated continuously and rapidly.



Scheme 2.



Scheme 3.

Among a variety of poly(condensation) polymers, the structure of PC attracts our interest, because it consists of two chemical units, i.e. bisphenol A (BPA) and carbon monoxide or carbonate (Scheme 2). Both are important industrial chemicals and, in this mean, PC can be regarded as an industrial reagent that can supply not only BPA but also phosgene or its equivalents. In this regard, we already reported easy retro-polymerization reaction of PC plastic wastes to reproduce a pair of monomers, BPA and dimethyl carbonate (DMC) [9], and also chemical transformation of PC to BPA-bis(hydroxyethyl) ether [10]. In this report [11–13],[2] we describe a unique chemical recycling of waste PC as a phosgene equivalent of manufacturing 2,5-dimethyl-2,5-diazacyclopentanone (1,3-dimethyl-2-imidazolidinone, DMI), which are used as a versatile polar solvent in laboratory and industry.

2. Results and discussion

2.1. Aminolysis of PC with alkylamines

Esters and carbonates are known to be highly reactive under solvolytic aminolysis conditions [17–20].[3] In comparison of this knowledge with our preliminary study on the alcoholysis of PC, in that easy and quantitative reproduction of BPA and dialkyl carbonates was achieved [9], we first expected that the aminolysis of PC with dialkylamines will be roughly as fast as, or even faster than the methanolysis. However, with diethylamine, the reactions of PC at 90 °C for 5 h did not take place. Analogous treatment in the presence of a Lewis acid for 6 h in a mixed solvent of toluene and dioxane proceeded slowly to give BPA (16–24%), carbamates of BPA, **1a** (18–31%) and **2a**

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[2] The preliminary parts of this series of aminolysis have been reported.

[3] To the best of our knowledge, our concept of using PC plastic wastes as chemical reagents in both laboratory and factory settings, regarding them as a 'CO' synthon or phosgene equivalent, is original.

Table 1
Treatment of PC with monoamines and lithium amide

Run	Amine[a] (equiv)	Catalyst (equiv)	Temperature (°C)	Time (min)	Product yield (%)[b]				
					BPA	**1a**,**b**	**2a**,**b**	**3**	**4a**,**b**
1	DMA (2)	–	55	70	16	37	17	–	0
2[c]	DMA (3)	NaOH (0.05)	100	60	20	33	16	–	0
3[c]	DMA (3)	NaOH (0.05)	110	180	18	39	17	–	0
4	DEA (2)	–	90	300	0	0	0	0	0
5	DEA (4)	ZnCl$_2$ (1.0)	90	360	21	28	15	15	0
6	DEA (4)	Zn(CH$_3$COO)$_2$ (1.0)	90	360	24	31	9	18	0
7	DEA (4)	AlCl$_3$ (1.0)	90	360	24	23	31	6	5
8	DEA (4)	Al(OC$_2$H$_5$)$_3$ (1.0)	90	360	16	18	22	12	0
9	LDEA (2)	–	0	30	87	–	–	–	76

[a] DMA, dimethylamine in tolene/dioxane; DME, diethylamine in dioxane; LDEA, lithium diethylamide in THF; and Equiv, molar equivalence.
[b] **a** = derivative of dimethylamine; **b** = derivative of diethylamine.
[c] In autoclave.

(9–31%), but tetraethylurea (**4a**) was not formed [21].[4] Only by the addition of Lewis acids, such as AlCl$_3$, **4a** was formed in a low yield (5%). All the reactions with diethylamine were accompanied by the formation of oligomer **3** (6–18%) (Scheme 3, Eq. (1)). The reaction of PC with dimethylamine exhibited similar results, but proceeded relatively faster than with diethylamine. For example, a non-catalyzed reaction at 55 °C for 70 min gave **1b** (37%), **2b** (17%), and BPA (16%), but no **4b**. In any reaction with either amine, the formation of tetra-alkylurea (Eq. (2)) was slow indicating that the aminolysis of intermediate carbamates **1** and **2** is much slower than the first step aminolysis of the carbonate groups, and therefore, in most cases, **1** and **2** were easily isolated and identified. This observation is rational, because the nucleophilicity of secondary amines toward carbamate groups, in general, is known to be smaller than that toward carbonate groups [22]. Therefore, for the transformation of primary products **1** and **2** to the corresponding ureas, more drastic reaction conditions or the use of alkali amide seems to be required. Indeed, when PC was treated with lithium diethylamide at 0 °C for 30 min in THF, tetraethylurea was formed in 76% (Eq. (3)). The results of the aminolysis of PC with both monoamines and a metal amide are shown in Table 1 together with varying reaction conditions. With this preliminary study, we concluded that the aminolysis of waste PC with alkylamines under conventional conditions is not appropriate for preparing acyclic ureas.

2.2. Aminolysis of PC with diamines

In contrast to the reluctant aminolysis with monoamines, however, diamines reacted smoothly with PC to give cyclic urea derivatives in nearly quantitative yields. This remarkable difference can be ascribed to the mechanistic difference in the second step aminolysis. With monoamines, the second step aminolysis must overcome mechanistic disadvantage, which is characteristic of intermolecular bimolecular reactions. Whereas with diamines, the second-step is intramolecular being gifted with kinetic advantage for cyclization. In fact, the reaction with diamines, such as N,N'-dimethyl-1,2-diaminoethane (DMDAE) or N,N'-dimethyl-1,3-diaminopropane (DMDAP) proceeded fast in both the first and second steps (Scheme 4) and, in consequence, the intermediate aminocarbamate was not isolated.

The targeted compounds to obtain in the aminolysis of PC with DMDAE were BPA and DMI, the latter being a versatile solvent for industrial and laboratory purpose.[5] The commercial market of DMI is expanding, because of its characteristic physical and chemical properties, such as high-boiling (bp 225.5 °C/760 mmHg), large dielectric constant ($e = 37.60$/MHz/25 °C),[6] aprotic dipolar nature, and tolerance at high temperatures under strongly acidic or even basic conditions. It is industrially manufactured from urea and DMDAE (Scheme 5) [25–27]. In comparison to the industrial reaction sequence and other preparative methods [28], our aminolysis reaction uses PC as a phosgene-equivalent reagent. Additionally, in our reaction, DMI itself can be used as the solvent (Table 2, runs 8–11) though dioxane was used in preliminary reactions and kinetic study. Thus, when DMI was used, DMDAE was the only one commercially purchased chemical for the reaction.

The reaction of PC with DMDAE was simple (see Section 4). Basically, the reaction does not require a catalyst but, sometimes, sodium or potassium carbonate or hydroxide accelerates the reaction. Normally, reactions were carried out at 100 °C for 30 min in dioxane or DMI to afford BPA (87%), DMI (82%), and a small amount of bis(carbamate) (BCA, **6**) (2–5%). Results are summarized in Table 2.

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[4] Ammonolysis of PC was reported, see Ref. [21].

[5] For dipole moments of DMI, see Ref. [23].

[6] For dielectric constants of DMI, see Ref. [24].

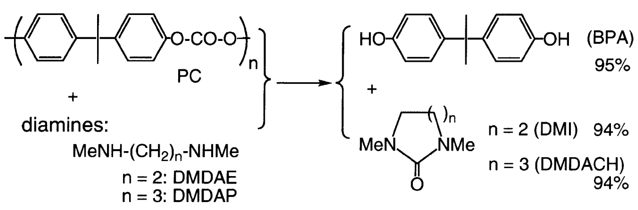
Table 2
Treatment of PC with DMDAE without or with catalyst (reaction time = 30 min, molar ratio PC:DMDAE = 1:1 in dioxane)

Run	Catalyst (equiv)	Solvent[a]	Temperature (°C)	Product yield (%)	
				DMI	BPA
1	–	D	60	53	52
2	–	D	80	76	76
3	–	D	100	88	87
4[b]	Na_2CO_3 aq (0.05)	D	100	94	95
5[b]	Na_2CO_3 aq (0.005)	D	100	88	94
6[b]	K_2CO_3 aq (0.05)	D	100	93	90
7[b]	K_2CO_3 aq (0.005)	D	100	91	91
8	–	DMI	100	82	84
9	–	DMI	100	93	91
10	Na_2CO_3 aq (0.05)	DMI	100	91	91
11	K_2CO_3 aq (0.05)	DMI	100	92	92

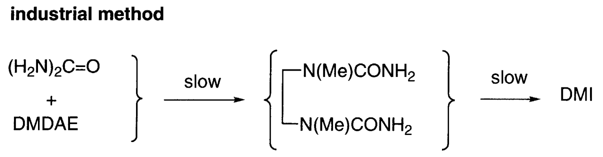
[a] Solvent: D, dioxane; DMI, 1,3-dimethyl-2-imidazolidinone.

[b] Biscarbamate **6a** (BCA, see Scheme 6) was formed (<5%).

Not only DMDAE, but also DMDAP reacted with PC as well to afford six-membered cyclic urea 2,6-dimethyl-2,6-diazacyclohexanone (DMDACH), though the reaction was slightly slower than that of DMDAE. Results of the reaction of PC with DMDAP are summarized in Table 3 and Scheme 4.



Scheme 4.



Scheme 5.

Table 3
Treatment of PC with DMDAP without catalyst (reaction temperature = 100 °C; molar ratio PC:DMDAE = 1:1; solvent = dioxane)

Run	Time (min)	Yield (%)[a]	
		DMP	BPA
1	30	67	64
2	60	80	88
3	90	94	91

[a] Determined by ^1H NMR. In all runs, biscarbamate **6b** was formed in less than 4%.

2.3. *Mechanism of the reaction with diamines*

Most rational reaction sequences for the retro-polymerization of PC by using DMDAE is shown in Scheme 6. The first reaction stage consists of a bimolecular aminolysis of PC with DMDAE to produce intermediate monoaminocarbamate (MAC, **5**). Thereafter, two different reactions of **5** take place. (1) Intramolecular route to produce DMI via the nucleophilic attack by the amino group of **5** to the carbamate group of the same molecule. (2) Intermolecular route to form BCA (**6**) via the nucleophilic attack by the amino group of **5** to the carbonate group of other PC molecules or oligomeric intermediates.[7] The competing reaction between (1) and (2) clearly favors for (1) over the other, because the former is intramolecular, whereas the latter intermolecular albeit the reacting carbonyl groups are different.

2.4. *Kinetic study on the models of aminolysis with diamines*

First step of the aminolysis of PC with DMDAE can be easily estimated to proceed quite fast on the basis of reasons already mentioned in Sections 2.1 and 2.2 (vide supra). Nevertheless, a question remains concerning the kinetic profile of second step aminolysis, because this ring-closing step is the aminolysis of carbamate, not carbonate, and because it is known that carbamates are less reactive to amines than carbonates or carboxylic esters. To clarify the reason for the favored cyclization of MAC over the formation of BCA, model reactions are designed by choosing diphenyl carbonate (DPC) [29,30] instead of PC and butyl(methyl)amine (BMA) instead of a diamine in the first step aminolysis. With this model reaction, we expected to avoid the complexity of polymer reaction.

As the model of second aminolysis, namely cyclization, the reaction of DPC with DMDAE was chosen on the

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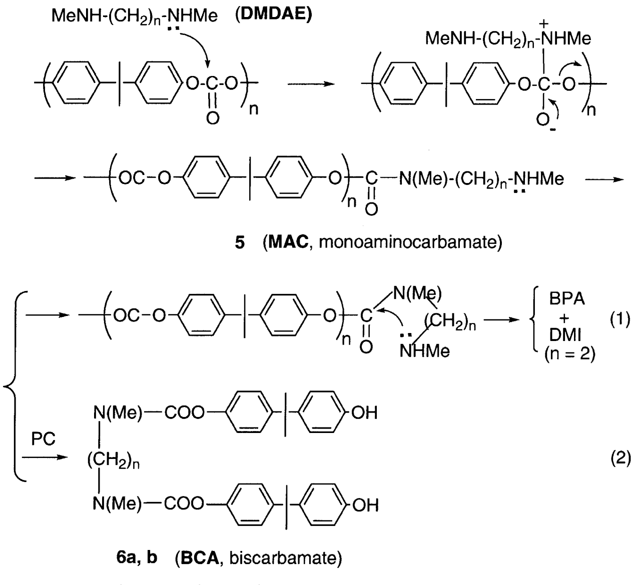
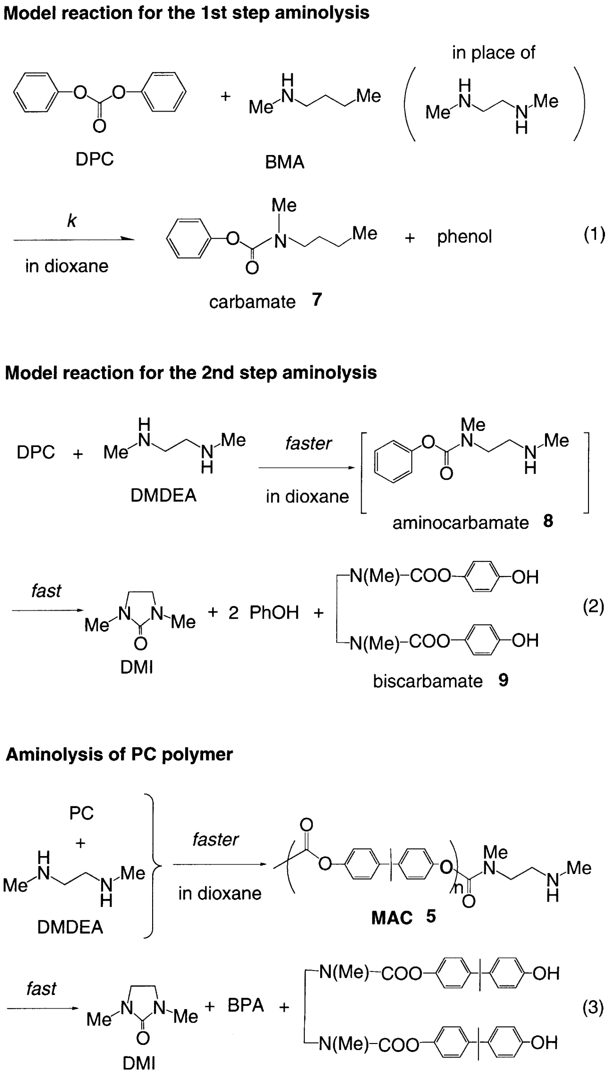
[7] These are oligomers of PC bearing either one or two of DMDAE or a phenolic group.



Scheme 6.

assumption that the second step must be rate-determining, if the overall reaction rate turns out to be slower than that of the first step model reaction. These model reactions are shown by Eqs. (1) and (2) in Scheme 7.

Model reactions were carried out in dioxane solutions at temperatures 30, 40, and 50 °C for specified periods and quantitative analyses on the formation of products were performed by the vpc analysis. Rates of reactions for both steps (Eqs. (1) and (2)) are shown in Figs. 1 and 2. The model reaction (Eq. (1)) took place rapidly at 30 °C to be completed in 60 min. Indeed, the activation energy E_{a_1} obtained from the plotting in Fig. 1 was only 7.57 kJ mol^{-1} in good accord with similar reactions reported [31].[8] The second model reaction (Eq. (2)) was also fast although the activation energy E_{a_2} was found to be 27 kJ mol^{-1}, somewhat larger than that of the first reaction, suggesting that the intramolecular cyclization of **5** takes place smoothly, but slightly slower than the first step reaction (Eq. (1)). It is a matter of course that the best kinetic study is the one carried out on polymer reactions (Eq. (3)), which was difficult for us. Consequently, the disadvantage of the aminolysis of carbamate intermediates, that was encountered in the reaction of PC with monoamine, seems to be overcome by the intramolecular pathway with diamines.



Scheme 7.

3. Conclusion

The initially designed reaction (Schemes 2 and 4) in that the carbonyl moiety of PC is reassembled in the form of DMI is realized in the present study. To be noted also is that one of the products, i.e. DMI, can be used as the solvent of this recycling reaction. This is an advantage for practical industrial procedure in saving not only manufacturing

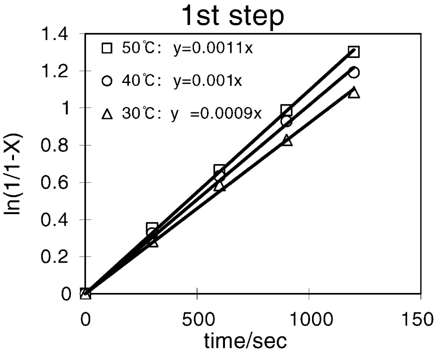


Fig. 1. Rates of reaction of DPC with butyl(methyl) amine in dioxane $E_{a_1} = 7.43$ kJ mol^{-1}, $E_{a_2} = 7.57$ kJ mol^{-1}.

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[8] The activation energy of the reaction of PET with hexamethylenediamine was reported to be as low as 4.69 kJ mol^{-1}.

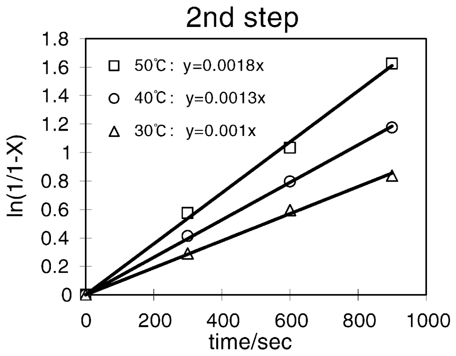

Fig. 2. Rates of reaction of DPC with *N*,*N*′-dimethylethylenediamine in dioxane. $E_{a_1} = 27.5\ \mathrm{kJ\ mol^{-1}}$, $E_{a_2} = 27.0\ \mathrm{kJ\ mol^{-1}}$.

energy, but also conventional solvent. The reaction procedure is simple requiring only low temperatures, conventional apparatuses, and easy operation to separate products. These features are essential to realize the concept of conserving organic resources in any mean of the life cycle assessment (LCA) on plastic wastes.

4. Experimental

4.1. General

Pure PC pellets (3 mm length × 2.5 mm diameter, MW = 22,000) were used as model plastics. Commercially available chemical-grade monoamines (dimethylamine, diethylamine, *N*-methylbutylamine), dried and distilled DMDAE and DMDAP, DMI, and BPA were used without further purification. Chemical shifts of ^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75.6 MHz) in $CDCl_3$ were expressed in ppm (δ) unless otherwise stated. Flash column chromatography was performed using silica gel (Wakogel C-300) and a mixed eluent of AcOEt in hexane.

4.2. Aminolysis of PC with diethylamine in the absence or presence of catalysts

Pellets of PC (2.00 g, 7.88 mmol/carbonate unit) were dissolved in 40 ml of tetrahydrofuran (THF), to which was added diethylamine (2.30 g, 31.5 mmol) and the total mixture was stirred at 90 °C for 5 h under a nitrogen atmosphere. After cooling, the reaction mixture was analyzed on a tlc plate to find that the reaction did not take place under this condition. Analogous treatment of PC with diethylamine in the presence of NaOH (5 mol%) was also unsuccessful. However, the treatment in the presence of Lewis acid, such as $ZnCl_2$, $Zn(AcO)_2$, or $AlCl_3$ (1 mol equiv) at 90 °C for 6 h afforded product spots on tlc. Thus, for example, the reaction mixture with $AlCl_3$ was poured to MeOH (50 ml) to remove polymeric substances, and the filtrate was condensed and dissolved in ether, and subjected to flash chromatography (eluting solvent 10–40% EtOAc in hexane) to isolate four products. BPA (24%), mono(*N*,*N*-diethyl)carbamate (**1a**) of BPA (23%), bis(*N*,*N*-diethyl)carbamate (**2a**) of BPA (31%), and tetraethylurea (**4a**, 5%) [32]. The substance, which did not elute from the column, was separately extracted from the column to characterize as oligomers of PC (**3**). 2-(4′-Hydroxyphenyl)-2-[4″-(*N*,*N*-diethylcarbamoyloxyphenyl)]-propane (**1a**): mp 116–117 °C; ^{1}H NMR 1.21 (m, 6H, methyl of ethyl), 1.62 (s, 6H, $=C(CH_3)_2$), 3.40 (m, 4H, methylene of ethyl), 5.28 (s, 1H, phenolic OH), 6.67 (d, $J = 8.7$ Hz, 2H), 6.99 (d, $J = 8.7$ Hz, 2H), 7.05 (d, $J = 8.7$ Hz, 2H), 7.18 (d, $J = 8.7$ Hz, 2H); IR (KBr) 3350 (s), 1690 (s) $\mathrm{cm^{-1}}$; HRMS (EI) calcd for $C_{20}H_{25}O_3N$ (M^+) 327.1828, found 327.1812. 2,2-Bis[4′-(*N*,*N*-diethylcarbamoyloxyphenyl)]propane (**2a**): mp 103–104 °C; ^{1}H NMR 1.21 (m, 12H, methyl of ethyl), 1.64 (s, 6H, $=C(CH_3)_2$), 3.40 (m, 8H, methylene of ethyl), 7.00 (d, $J = 8.7$ Hz, 4H), 7.22 (d, $J = 8.7$ Hz, 4H); IR (KBr) 1720 (s) $\mathrm{cm^{-1}}$; HRMS (EI) calcd for $C_{25}H_{34}O_4N_2$ (M^+) 426.2510, found 426.2518. Tetraethylurea (**4a**): mp −23 °C, bp 209 °C/760 Torr; ^{1}H NMR 1.10 (t, $J = 7.2$ Hz, 12H), 3.16 (q, $J = 7.2$ Hz, 8H); IR (liquid film) 1650 $\mathrm{cm^{-1}}$; HRMS (EI) calcd for $C_9H_{20}ON_2$ (M^+) 172.1571, found 172.1572.

4.3. Aminolysis of PC with dimethylamine

Similar treatment of PC 2.00 g, 7.88 mmol) with dimethylamine (0.71 g, 15.8 mmol) in toluene (40 ml)/dioxane (2 ml) at 55 °C for 1.1 h in the absence of catalyst gave three products. They were BPA (16%), monocarbamate of BPA (**1b**, 37%), and biscarbamate of BPA (**2b**, 17%), but no tetramethylurea. 2-(4′-Hydroxyphenyl)-2-[4″-(*N*,*N*-dimethylcarbamoyloxyphenyl)]propane (**1b**): mp 159–160 °C; ^{1}H NMR 1.64 (s, 6H), 3.02 (s, 3H), 3.10 (s, 3H), 5.30 (s, 1H), 6.70 (d, $J = 8.5$ Hz, 2H), 7.01 (d, $J = 8.5$ Hz, 2H), 7.08 (d, $J = 8.5$ Hz, 2H). 7.21 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR 31.0, 36.4, 36.7, 41.9, 114.7, 121.0, 127.6, 127.8, 142.2, 148.0, 149.0, 153.7, 155.3; IR (KBr) 3410 (s), 1700 (s) $\mathrm{cm^{-1}}$; HRMS (EI) calcd for $C_{18}H_{21}O_3N$ (M^+) 299.1516, found 299.1524; Anal. calcd for $C_{18}H_{21}O_3N$: C, 72.22; H, 7.07; N, 4.68. Found: C, 71.99; H, 7.09; N, 4.60. 2,2-Bis[4′-(*N*,*N*-dimethylcarbamoyloxyphenyl)]propane (**2b**): mp 165–166 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 1.66 (s, 6H), 3.02 (s, 3H), 3.10 (s, 3H), 7.02 (d, $J = 8.6$ Hz, 4H), 7.22 (d, $J = 8.6$ Hz, 4H); ^{13}C NMR (126 MHz) 31.0, 36.0, 36.6, 42.3, 121.0, 127.6, 147.2, 149.3, 154.9; IR (KBr) 1730 (s) $\mathrm{cm^{-1}}$. HRMS (EI) calcd for $C_{21}H_{26}O_4N_2$ (M^+) 370.1886, found 370.1891; Anal. calcd for $C_{21}H_{26}O_4N_2$: C, 68.09; H, 7.07; N, 7.56. Found: C, 68.18; H, 7.14; N, 7.40.

4.4. Reaction of PC with lithium diethylamide

Pellets of PC (2.00 g, 7.88 mmol/carbonate unit) were dissolved in 40 ml of THF, to which was additionally mixed lithium diethylamide (1.15 g, 15.8 mmol) and the total mixture was stirred at 0 °C under a nitrogen atmosphere for a specified time (30 min). After cooling, the reaction mixture was poured to MeOH (50 ml) to remove polymeric substances. The filtrate was condensed and dissolved again in ether, and the solution was subjected to flash chromatography on silica gel (eluting solvent 10–40% EtOAc in hexane). Two products, tetraethylurea (**4**, 76%) and BPA (87%) were obtained. Results are also summarized in Table 1.

4.5. General procedure of the reaction of PC with N,N′-dimethyl-1,2-diaminoethane in dioxane without catalysts

Pellets of PC (0.76 g, 3 mmol/carbonate unit = 6 mmol/ester unit) were dissolved in 8 ml of dioxane, to which was added DMDAE (0.296 g, 3 mmol) in a dropwise manner by using a syringe, and the total mixture was warmed at 100 °C under a nitrogen atmosphere for 30 min. After cooling, the reaction mixture was poured to MeOH (50 ml) to remove polymeric substances. The filtrate was condensed and dissolved again in ether, and the solution was subjected to flash chromatography on silica gel (eluting solvent 10–100% EtOAc in hexane). Two major products, DMI (87.7%) and BPA (87.2%) were obtained and characterized. A minor by-product was also formed (3%), which was identified as bis(BPA-carbamate) **6a** of DMDAE. Results are summarized in Table 2. 1,3-Bis-{4-[2-(4-hydroxyphenyl)-2-propyl]phenoxy-*N*-methylcarbamoyl}ethane (**6a**): mp 224.5–225.5 °C; ^{1}H NMR (500 MHz, d$_6$-DMSO) δ 1.58 (s, 12H, =C(CH$_3$)$_2$), 2.93–3.63 (m, 10H, N–CH$_3$ and –CH$_2$– with isomeric conformational structures), 6.67–7.19 (m, 16H), 9.23 (s, 2H, phenolic OH); IR (KBr) 3390 (br, OH), 1700 (w), 1520 (s), 840 (s) cm^{-1}; Anal. calcd for $C_{36}H_{40}O_6N_2$ C, 72.45; H, 6.77; N, 4.70. Found C, 72.37; H, 6.74; N, 4.28.

4.6. Aminolysis of PC with DMDAE in dioxane with alkali-catalyst

Analogous aminolysis reactions with DMDAE in dioxane in the presence of a basic catalyst, e.g. Na_2CO_3, K_2CO_3 (0.5, 5.0 mol%) were also examined and compared with the authentic reactions as described in Section 4.5. Results are also summarized in Table 2.

4.7. Aminolysis of PC with DMDAE in DMI

The reaction conditions are the same as described for Section 4.5 except that DMI was used as the solvent in place of dioxane. The method to determine the product yields of DMI, which is the same to the solvent, however, was different from that of the reaction in dioxane. Increase in the amount of DMI was determined by two methods, i.e. product isolation by column chromatography and gas-chromatographic determination using an internal standard. Results are also summarized in Table 2.

4.8. Aminolysis of PC with N,N′-dimethyl-1,3-diaminopropane

Pellets of PC (0.76 g, 3 mmol/carbonate unit = 6 mmol/ester unit) were dissolved in 8 ml of dioxane, to which was added DMDAP (0.31 g, 3 mmol) in a dropwise manner by a syringe, and the total mixture was warmed at 100 °C for 90 min. The workup procedure that followed was analogous to that described in Section 4.5. Products were BPA (91%), DMDACH (94%), and bis-carbamate **6b** formed between BPA and DMDAP (4%). 1,3-Bis-{4-[2-(4-hydroxyphenyl)-2-propyl]phenoxy-*N*-methylcarbamoyl}propane (**6b**): mp 88–89 °C; ^{1}H NMR 1.59 (s, 12H, =C(CH$_3$)$_2$), 1.97 (m, 2H, –CH$_2$–), 3.00 (s, 3H, N–CH$_3$, isomeric), 3.08 (s, 3H, N–CH$_3$, isomeric), 3.42 (m, 4H, N–CH$_2$–), 6.64–7.18 (m, 16H); IR (KBr) 3390 (br, OH), 1700 (w), 1520 (s), 840 (s) cm^{-1}. Results are summarized in Table 3.

4.9. Reaction of diphenyl carbonate with butyl(methyl)amine: a model reaction of the first step aminolysis of PC with diamine

DPC (2.57 g, 12 mmol) was dissolved in dioxane (8 ml), to which was added butyl(methyl)amine (BMA) (0.105 g, 1.2 mmol) at one time under a nitrogen atmosphere, and the total mixture was immediately warmed at a specified temperature (30, 40, or 50 °C) for a specified time (5, 10, 15, or 20 min). An aliquot of the reaction mixture was directly analyzed on gas-chromatography using pentadecane $C_{15}H_{32}$ as the internal standard, to determine the formation of products, i.e. phenyl *N*-butyl-*N*-methylcarbamate (**7**, 75%), phenol (75%), and unreacted DPC. The column temperature should be kept below 200 °C, because at high temperatures DPC tends to decompose. Results are summarized in Fig. 1. Phenyl *N*-butyl-*N*-methylcarbamate (**7**): ^{1}H NMR (mixture of conformers) 0.97 (m, 3H, –CH$_2$*CH$_3$*), 1.38 (m, 2H, –*CH$_2$*CH$_3$), 1.61 (m, 2H, –*CH$_2$*CH$_2$CH$_3$), 3.03 (s, 3H, N–CH$_3$), 3.39 (m, 2H, N–CH$_2$–), 7.11–7.38 (m, 5H); ^{13}C NMR (mixture of conformers) [33] 13.84, 19.84, 19.49, 30.14, 34.38, 34.70, 48.93, 49.06, 121.74, 125.06, 129.16, 151.59, 154.77. IR (liq. film) 2950 (w), 1720 (w) cm^{-1}; Anal. calcd for $C_{12}H_{17}O_2N$: C, 69.52; H, 8.28; N, 6.76. Found: C, 69.34; H, 8.04; N, 6.69.

4.10. Reaction of DPC with DMDAE: a model reaction of the second step aminolysis of PC with diamine cyclization

DPC (0.064 g, 0.3 mmol) was dissolved in dioxane (8 ml), to which was added DMDAE (0.026 g, 3 mmol) at one time under a nitrogen atmosphere, and the reaction flask was immediately immersed in a warmed bath controlled at 30, 40, or 50 °C. After a specified period (5, 10 or 15 min), an aliquot of the mixture was directly analyzed on the gas-chromatograph to determine the formation of DMI and phenol using dodecane $C_{12}H_{26}$ as the internal standard. Results are summarized in Fig. 2. In this reaction, the intermediate MAC was not detected, but byproduct biscarbamate **9** was formed in a trace amount. The authentic compound of **9** was separately prepared and its spectroscopic data agreed with those of product **9**. 1,2-Bis[*N*-methylphenoxycarbamoyl]ethane (**9**): mp 95.0–96.0 °C; ^{1}H NMR (mixture of conformers) 3.08–3.18 (m, 6H, N–CH_3, isomeric), 3.60–3.71 (m, 4H, N–CH_2–, isomeric), 7.06–7.39 (m, 10H); ^{13}C NMR (mixture of conformers) [33] 35.00, 35.19, 35.45, 46.60, 46.71, 47.08, 121.72, 121.76, 121.94, 125.27, 125.36, 125.47, 129.25, 129.30, 129.36, 129.38, 151.29, 151.40, 151.44, 154.63, 154.81, 154.95, 155.18; IR (KBr) 1700 (w), 1400 (s), 1200 (w) cm^{-1}; Anal. calcd for $C_{18}H_{20}O_4N_2$: C, 65.83; H, 6.15; N, 8.53. Found: C, 65.87; H, 6.15; N, 8.49.

4.11. Kinetic analysis of model reactions

Pseudo first order reaction rates of the aminolysis between DPC and butyl(methyl)amine (BMA) were measured at 50–30 °C, without catalysts, to estimate the rates and activation parameters of the first-step polymer reaction between PC and DMDAE. For this study, conventional methods were adopted [34]. In the study, DPC was used in 10-times excess molar amount versus BMA or one tenth versus DMDAE[9] to obtain pseudo first order rates. The pseudo first order rate constants were obtained from the inclination of the logarithmic plotting of the yield of carbamate versus the time. The second order rate constants were also obtained by dividing the first order rate constants by an average concentration of DPC. Activation energies were obtained by the Arrhenius plotting. The data for the second-step cyclization reaction were estimated by measuring those of the model reaction between DPC and DMDAE based on the assumption that the second step is slower than the first step in this model reaction. Kinetic data thus obtained are summarized in Figs. 1 and 2.

Acknowledgements

The study was partially supported by Grant-in-Aid for Scientific Research on Priority Area, No. 12015228.

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[9] In the first model reaction, an excess amount of DPC was used to suppress the formation of urea byproduct, whereas in the second reaction, DMDAE was used in excess to suppress biscarbamate byproduct.