Viable Utilization of Polycarbonate as a Phosgene Equivalent Illustrated by Reactions with Alkanedithiols, Mercaptoethanol, Aminoethanethiol, and Aminoethanol: A Solution for the Issue of Carbon Resource Conservation

Sohei Hata,[1] Hiroko Goto,[1] Saki Tanaka,[1] Akira Oku[2]

[1]*Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606−8585, Japan*
[2]*Material Reclamation Laboratory, Research Institute for Production Development, Morimoto-cho, Shimogamo, Sakyo-ku, Kyoto 606−0805, Japan*

ABSTRACT: Methods for the chemical recycling of polycarbonate (PC) wastes in the forms of bisphenol A (BPA) and cyclic heterocarbonates, such as 1,3-dithiolan-2-one (DTO), 1,3-dithiane-2-one (DTA), and cyclic unsymmetric heterocarbonates, were investigated to prove that PC can be utilized as a phosgene equivalent for industrial purposes. Treatment of PC pellets or waste PC compact discs with 1,2-ethanedithiol and a catalytic amount of base (e.g., 1.5 mol % NaOH) in dioxane for a short period at 40°C produced DTO and BPA, both in nearly quantitative yields. The reaction could also be carried out in DTO, which saved the use of conventional solvents. Other cyclic heterocarbonates, that is, DTA, 1,3-oxathiolan-2-one, 1,3-thiazolidine-2-one, and N-methyl-1,3-oxazolidine-2-one, were prepared in high yields under analogous conditions. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2959–2968, 2003

Key words: polycarbonates; monomers, recycling; waste; plastics.

INTRODUCTION

How to solve the problem of plastic waste at both The postmanufacturer and postconsumer stages to protect the depletion of petroleum chemical resources[1–3] is now becoming an important issue for a future sustainable society. The problems are usually biased by economical concerns. Nevertheless, they must be systematically investigated by taking various facets into accounts, for example:

1. The conceptual shift in the design of plastic materials for longevity and adaptability to material-lease systems.[4–6]
2. The development of versatile or specific recycling methods for each material.[7–11]
3. The fundamental improvement of social and industrial networks of plastic recovery systems with the least energy consumption.[4–6]
4. The assessment of total manufacturing energy on the basis of not only a single life-cycle assessment (LCA) but also on lifetime. For example, if the LCA-based energy of manufacturing material A is one-half that of material B, but the lifetime of A is less than one-half that of B, A is inferior to B whatever the lifetime of the corresponding plastic goods' might be.

To demonstrate the chemical efforts for the conservation of petroleum resources and reduction in CO_2 emissions, plastic materials must be repeatedly reproduced as many times as possible by means of the lowest energy process in the forms of plastics or monomers before their nonrenewable termination.
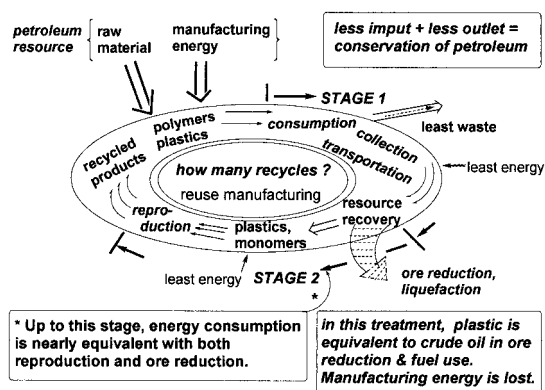
Toward this goal, though there still remain problems of energy consumption and impurity, retropolymerization to monomers seems to be the primary solution to the problem because retropolymerization can repeatedly reproduce the same and pure materials to benefit wide chemical markets.[12]

Scheme 1 presents the basic ground to the argument of the comparison of both the material and monomer recycling* methods with the energy-recovery and

*In this report, the term *monomer recycling* is used as an equivalent term as *chemical recycling,* which can be applied to the process where plastic wastes are recycled or reclaimed as monomers or industrial chemicals. The end uses of plastic wastes, such as for incineration for energy production or as a coke substitute at blast furnaces, was excluded from this definition.

Scheme 1　Conservation of organic resources.

1a: n = 1 (DTO)　2: n = 1 (OT)　3: n = 1 (TZ)　4: n = 1 (MOZ)
1b: n = 2 (DTA)

DTO : 1,3-dithiolan-2-one　　　OT : 1,3-oxathiolan-2-one
DTA : 1,3-dithiane-2-one　　　 TZ : 1,3-thiazolidine-2-one
　　　　　　　　　　　　　　　　MOZ : *N*-methyl-1,3-oxazolidine-2-one

Scheme 3　Carbonate analogs derived from PC.

coke-substitute methods. The material and monomer processes must satisfy roughly the following oil balance: (ΣE_n)
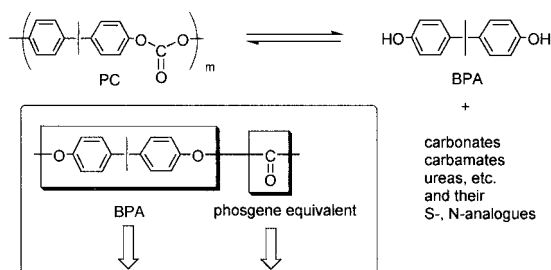
$$\sum E_n = E_1 + E_2 - E_3 - E_4 > 0 \qquad (1)$$

where E_1 is the oil required as energy for the production of plastic, E_2 is the oil required as a material resource, E_3 is the oil required as energy for the reproduction of plastic, and E_4 is the oil equivalent to the energy obtainable from thermal recovery.
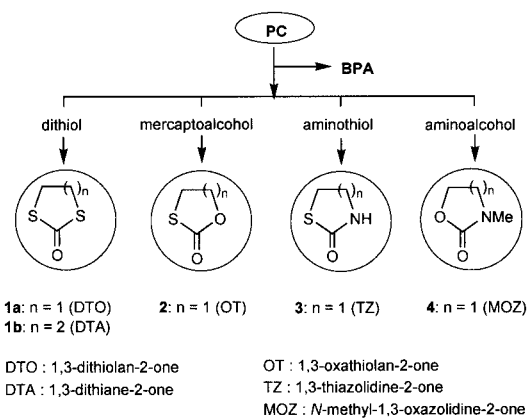
When the ΣE_n is positive, plastic wastes should not be incinerated but recycled because the oil corresponding to ΣE_n can be saved; namely, the amount of oil reproduced in addition to the plastic reproduction.

Liquefaction cannot play such a magic role because E_4 cannot exceed the sum of $E_1 + E_2$ and cannot result in an oil savings. A number of condensation plastics are known to satisfy this requirement[13,14] and so do polyolefins.[15] Additionally, not only the recovery systems in Stage I (Scheme 1) but also the recycling technologies in Stage II are being continuously innovated.

Among a variety of step-growth (condensation) polymers, the structure of bisphenol (BPA) A poly carbonate (PC) attracts our attention because it consists of two chemical units, BPA and carbon monoxide or carbonate (Scheme 2).

Scheme 2　Basic concept of recycling PC as commercial chemicals.

Although the thermal stability of PC resin is high it can be depolymerized easily under heterolysis conditions to give the monomers[16–18] BPA and carbonate derivatives. However, the use of such recycling reactions to utilize PC wastes systematically as phosgene equivalents have hitherto not been reported.[9–11] The recognition that PC can be a phosgene equivalent seems unique because PC can be handled as a solid under safety regulations.

The utilization of PC as a phosgene equivalent that we report here is summarized in Scheme 3. The characteristic features of this study were (1) waste PC could be retropolymerized readily under mild solvolytic reaction conditions with dithiols, mercaptoethanol, aminoethanethiol, and aminoethanol to afford BPA and heterocyclic carbonates (Scheme 3), and the products were practical and potential industrial chemicals or materials; (2) the objective reaction product was a chemically stable carbonate derivative that could be used as the solvent of the same retropolymerization; and (3) BPA, an important monomer of a variety of polymers, was always produced quantitatively, whereas carbonate derivatives were formed and used as industrial chemicals or monomers of other polymers.

RESULTS AND DISCUSSION

Reaction of diphenyl carbonate (DPC) with dithiols, mercaptoethanol, aminoethanethiol, and aminoethanol

Before the PC reaction, DPC was chosen as a model PC compound and the reaction conditions were investigated. The results are summarized in Table I.

The treatment of DPC with 1,2-ethanedithiol (EDT) in dioxane at 80°C for 2 h without a catalyst did not give any product, and both DPC and EDT were recovered quantitatively. However, the addition of a catalytic amount of aqueous NaOH (0.5 mol %) to the same reaction mixture followed by heating at 30–40°C

TABLE I
Treatment of DPC with Dithiols, Mercaptoethanol, AET, and 2-Aminoethanol

Run	Nucleophilic reagent	Catalyst (mol %)[a]	Temperature (°C)	Time (min)	Product (%)[b] Phenol	Cyclic carbonate		Intermediate	
1	EDT	Aqueous NaOH (0.5)	30	30	84	DTO	80		0
2	EDT	Aqueous NaOH (0.5)	40	30	86	DTO	85		0
3	EDT	Aqueous NaOH (1.0)	50	60	100	DTO	94		0
4	ME	Aqueous NaOH (0.5)	30	30	29	OT	23		0
5	ME	Aqueous NaOH (0.5)	40	30	38	OT	52		0
6	ME	Aqueous NaOH (0.5)	90	120	100	OT	91		0
7	ME	NaOH (1.0)	100	40	100	OT	94		0
8	AET	—	90	120	52	TZ	0	PMEC	93
9	AET	Aqueous NaOH (0.5)	90	80	100	TZ	100		0
10	MAE	—	90	50	56	MOZ	10	PHEC	90
11	MAE	Aqueous NaOH (0.5)	90	80	82	MOZ	60	PHEC	39
12	MAE	NaOH (1.0)	100	70	100	MOZ	99		0

Molar ratio at DPC/reagent = 1.0 in dioxane.
[a] The figures in the parentheses are the molar equivalences to one ester group of PC.
[b] Determined by ^{1}H-NMR.

for 30 min afforded 1,3-dithiolan-2-one (DTO or **1a**; 85%)[19–25] and phenol [86%; 100% conversion of DPC; Table I, runs 1 and 2; Scheme 4, eq. (3)].

For comparison, the reaction of DPC with mercaptoethanol (ME), whose molecular structure is similar to EDT, was carried out in dioxane at 90°C for 3 h without a catalyst, but no product was formed. Again, the addition of aqueous NaOH (0.5 mol %) to this reaction mixture with heating at 90°C for 2 h pro-

Scheme 4 Reaction of DPC with difunctional nucleophiles as the model reaction of PC.

moted the formation of the expected products: 1,3-oxathiolan-2-one (OT; 91%)[19,24,26] and phenol [100%; 100% conversion of DPC; run 6; Scheme 4, eq. (3)]. Although both EDT and ME afforded heterocyclic carbonates efficiently, the rate of reaction of EDT was faster that that of ME. The difference was ascribable to the difference in nucleophilicity between the thiol and alcohol.

The reaction of 2-aminoethanethiol (AET) with DPC in dioxane at 90°C for 2 h without a catalyst formed the intermediate product phenyl 2-mercaptoethylcarbamate (**5** or PMEC; 93%) and phenol (52%; 100% conversion of DPC), but the expected heterocyclic carbonate 1,3-thiazolidine-2-one (TZ)[27–30] was not formed at all. We recently reported that amines smoothly reacted with DPC and PC without a basic catalyst.[11] In conjunction with this fact and also the aforementioned reaction of EDT where the reaction required a basic catalyst to produce DTO, the formation of PMEC could be well accounted for as follows: (1) intermolecular aminolysis takes place readily without a catalyst but intermolecular thilysis requires a catalyst, and (2) intramolecular solvolytic cyclization by thiol requires a basic catalyst. On the basis of these assumptions, the reaction of DPC with AET in the presence of a catalyst (aqueous, 0.5 mol % NaOH) was carried out to produce the quantitative formation of TZ and phenol [runs 8 and 9; Scheme 4, eq. (3)].

When DPC was treated with N-methylaminoethanol (MAE) in dioxane at 90°C for 50 min without a catalyst, phenyl N-methyl-2-hydroxyethylcarbamate (**6** or PHEC; 90%), phenol (56%), and a small amount of cyclic carbamate N-methyl-1, 3-oxazolidine-2-one (MOZ;10%)[31–36] were formed. In the presence of a catalyst (aqueous 0.5 mol % NaOH), the reaction at 90°C for 80 min afforded PHEC (39%), phenol (82%),
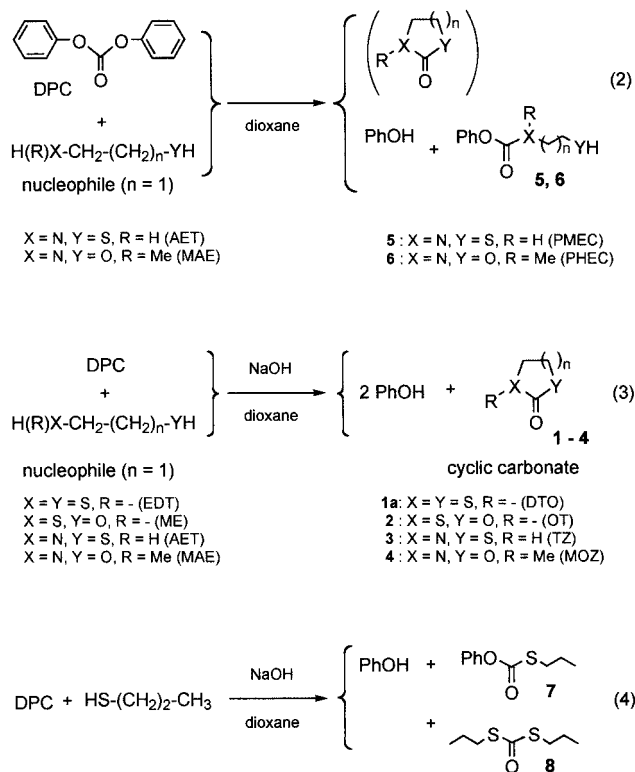
TABLE II
Treatment of PC with EDT

Run	EDT (mol equiv)[a]	Solvent[b]	Catalyst (mol %)	Temperature (°C)	Time (min)	Product (%)[c]	
						BPA	DTO
1	1	D	Aqueous NaOH (0.5)	40	30	50	65
2	1	D	Aqueous NaOH (1.0)	40	30	77	90
3	1	D	Aqueous NaOH (1.5)	40	30	90	100
4	1.5	D	Aqueous NaOH (0.5)	40	30	56	72
5	3	D	Aqueous NaOH (0.5)	40	30	66	88
6	1.5	D	Aqueous NaOH (0.5)	50	60	95	95
7	2	D	NaOH (0.5)	80	75	95	91
8	1	D	NaOH (0.5)	80	150	42	71
9	1	D	NaOH (0.5)	80	240	99	95
10	1	D	NaOH (5.0)	80	45	95	94
11	1	DTO	NaOH (5.0)	80	210	97	94

[a] Molar equivalences to one ester group of PC.
[b] D dioxane.
[c] Determined by ^{1}H-NMR for the products of runs 1–6.

and MOZ [60%; runs 10 and 11; Scheme 4, eqs. (2) and (3)]. Further, increases in the amount of catalyst (anhydrous 1.0 mol % NaOH) and the temperature (100°C) promoted the formation of MOZ (99%) and phenol (100%), thus completely preventing the formation of the intermediate **6** (run 12).

To compare the reaction of dithiols with that of monothiols, DPC was treated with 1-propanethiol (PT) in dioxane at 80°C for 2 h without a catalyst, but no product was formed. With the catalyst (aqueous NaOH, 0.5 mol%), after the reaction was warmed at 30–40°C for 30 min, small amounts of *O*-phenyl-*S*-propyl monothiocarbonate (**7**; 19–39%) and phenol (19–32%) were formed in addition to a small amount of dipropyl dithiocarbonate [**8**; Scheme 4, eq. (4)]. Thus, the dithiol EDT was more reactive than the monothiol PT.

Reaction of PC with dithiols

As described previously, the model reactions of DPC with EDT and its analogs proceeded successfully with the aid of a basic catalyst to give the expected heterocyclic carbonates. Deductively, PC was expected to react smoothly with those reagents under similar conditions.

First, PC dissolved in dioxane was treated with a molar equivalent amount of EDT without a catalyst, but no product was formed. The addition of organic base catalysts, such as triethylamine and pyridine, to the reaction was again unsuccessful. Therefore, anhydrous NaOH was adopted again as a base catalyst, and it was added (0.5 mol % vs. one ester bond of PC) to the reaction mixture. After the reaction was heated at 80°C for 4 h, the expected DTO was formed at 95% in addition to BPA (99%) without any other byproduct (Table II, run 9). Similarly, aqueous NaOH (1.5 mol%)

was also effective as a catalyst to give DTO (100%) and BPA (90%, run 3).

The effect of the catalyst amount on the reaction time was significant: as the amount of aqueous NaOH was increased from 0.5 to 1.5 mol %, the yields of DTO increased from 65 to 100% under the same conditions at 40°C for 30 min (runs 1–3), and the reaction time was shortened from 4 h at 80°C to 30 min at 40°C by the increase of the catalyst (runs 9 and 3). When the reaction was quenched by aqueous HCl before its completion to adjust the pH at 7.0, bis[4-(4-hydroxy-α,α-dimethylbenzyl)phenyl] carbonate (**13**) was isolated as an intermediate product.

In this retropolymerization, it was of interest to us to find that the product DTO could be used as the solvent. Thus, the treatment of PC with EDT in DTO in the presence of anhydrous NaOH (5.0 mol %) at 80°C for 3.5 h quantitatively produced both BPA (97%) and DTO (94%; run 11). This was an energy-saving chemical recycling system where the use of a conventional solvent could be avoided.

Similar to the reaction with EDT, 1,3-propanedithiol (PDT) reacted with PC to afford 1,3-dithiane-2-one (DTA or **1b**)[37–39] (75%) and BPA (96%) under reaction conditions at 100°C for 3 h with the aqueous NaOH catalyst (1.5 mol %). The formation of di(3-mercaptopropyl) dithiocarbonate (DMPC; or **14**) as a byproduct was inevitable in all of the run [e.g., Table III, run 6, 14%; Scheme 6, eq. (11)], thus lowering the yields of DTA.

Mechanism of the reaction with dithiols

The mechanistic sequence of the retropolymerization of PC by EDT is shown in Scheme 5. The first stage consists of a bimolecular reaction of PC with the conjugate base of EDT (**9a**) to produce the intermediate
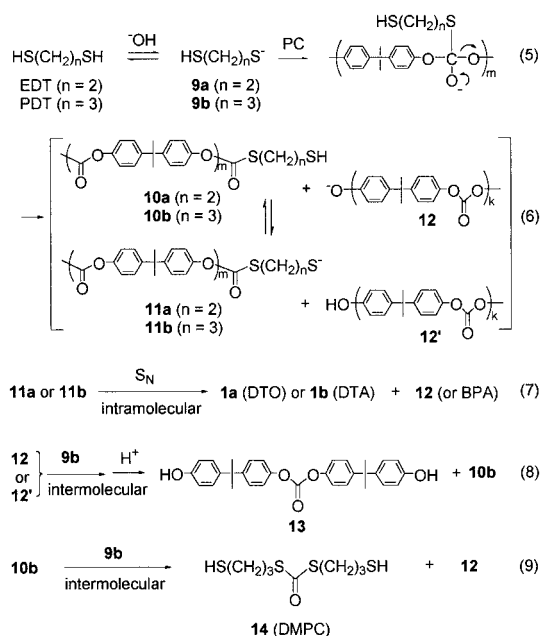
Scheme 5 Mechanism of the reaction of PC with EDT.

products **10a**, **11a**, and **12**, and they compose an equilibrium state as shown by eq. (6). Thereafter, three different reaction routes starting from each intermediate take place: (1) the intramolecular cyclization route to produce **1a** via the nucleophilic attack by the thiolate group of **11a** to the thiol ester group [eq. (7)]; (2) the intermolecular route to form **13**, particularly when $n = 3$, by the attack of the thiolate **9b** to the carbonate **12** [eq. (8)]; and (3) the intermolecular route to form **14** by the nucleophilic attack of **9b** to the thiol ester group of **10b** [eq. (9)]. The intramolecular route [eq. (7)] is clearly favored over the intermolecular routes [eqs. (8) and (9)], although the reacting carbonyl groups are different. In the reactions with PDT, the formation of cyclic dithiocarbonate (**1b**) was always accompanied by the formation of byproduct **14**, [13–20%; Table III; Scheme 5, eq. (9)]. This may be because the intramolecular route was less favorable for the formation of the six-membered DTA than the five-membered DTO, although the nucleophilicities of both dithiols were nearly equal. Hence, the intramolecular route from **11b** ($n = 3$) to **1b** had to compete with the intermolecular routes [e.g., eq. (9)].

The kinetic profile of the reaction with dithiols must have been quite similar to that recently reported by our group for the reaction of PC with N,N'-dimethyl-α, ω-diaminoalkanes.[11] Therefore, the kinetic study was abbreviated in this study.

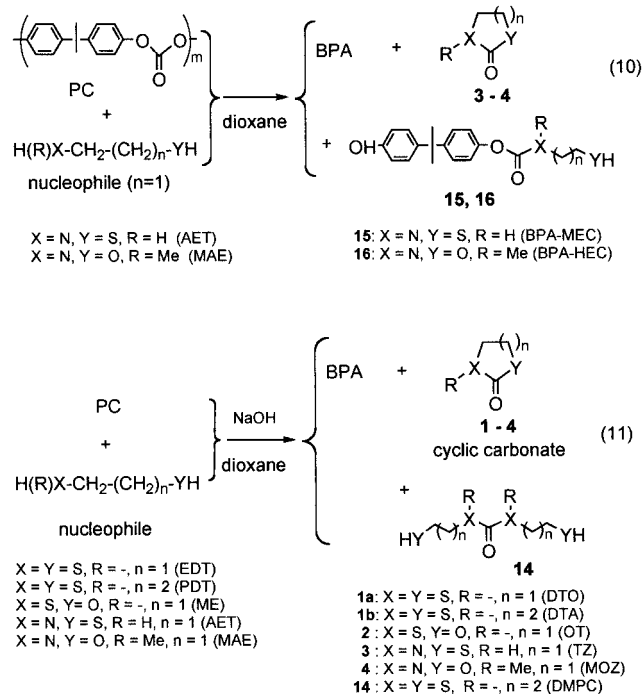## Reaction of PC with other difunctional nucleophiles

In addition to dithiols and their homologs, other difunctional nucleophile analogues, for example, ME,

AET, and MAE, were also investigated, and the results are summarized in Table IV. The reaction of PC with a stoichiometric amount of ME in dioxane at 90°C for 3 h did not form any product, but a catalytic amount (0.5 mol%) of aqueous NaOH accelerated the reaction, as expected, to produce OT (70%) and BPA [(90%; Scheme 6, eq. (11)]

As the reaction time was prolonged, the yield of OT decreased. We suspected that OT may have underwent a secondary decomposition reaction, and indeed, the decomposition was proven independently by the treatment of OT with aqueous NaOH in an NMR glass tube. To improve the yield of OT, anhydrous NaOH (1 mol %) was used instead of the aqueous catalyst, and after treatment at 100°C for 3 h, the product yields were improved, 87% for OT and 92% for BPA (run 8).

The reaction of PC with a stoichiometric amount of AET in dioxane at 100°C for 1.5 h without a catalyst afforded 4-(4-hydroxy-α, α-dimethylbenzyl) phenyl 2-mercaptoethylcarbamate (BPA-MEC or **15**; 54%), the precursor of TZ, together with BPA (46%) and TZ (47%). The results are summarized in Table V [Scheme 6, eq. (10)]. The formation of **15** indicate that the amino group of AET reacted much faster than the thiol group. Also indicated was that the intramolecular cyclization of **15** to TZ did not necessarily require a catalyst. Nevertheless, the use of anhydrous NaOH (1 mol %) as a catalyst of the reaction at 100°C for 1 h increased the yields to a quantitative level [100% each for TZ and BPA; run 4; Scheme 6, eq. (11)].

Similar to the reaction with AET, the treatment of PC with a stoichiometric amount of MAE in dioxane at

Scheme 6 Reaction of PC with difunctional nucelophiles.

TABLE III
Treatment of PC with PDT

Run	PDT (mol equiv)[a]	Catalyst (mol %)	Temperature (°C)	Time (min)	Product (%)[b]		
					BPA	DTA	DMPC
1	1	Aqueous NaOH (0.5)	80	60	51	46	17
2	1	Aqueous NaOH (0.5)	80	120	60	55	20
3	3	Aqueous NaOH (0.5)	80	120	96	40	58
4	1	Aqueous NaOH (1.5)	80	120	73	65	18
5	1	Aqueous NaOH (0.5)	100	180	94	73	13
6	1	Aqueous NaOH (1.5)	100	180	96	75	14

[a] Solvent = dioxane; molar equivalences to one ester group of PC.
[b] Determined by ^{1}H-NMR.

100°C for 1.5 h without a catalyst afforded the intermediate product 4-(4-hydroxy-α, α-dimethylbenzyl)-phenyl N-methyl(2-hydroxyethyl)carbamate (BPA-HEC or **16**) at 89% together with BPA (11%) and MOZ (9%; run 5). The isolation of the intermediate product **16**, which was slowly converted into MOZ as the reaction was prolonged, indicate that the amino group of MAE reacted much faster than the hydroxyl group in the first-step reaction.

Again, the hydroxyl group of **16**, though less nucleophilic than the mercapto group, did not necessarily require a basic catalyst for the cyclization to MOZ. Nevertheless, the use of anhydrous NaOH (1 mol %) as a catalyst increased the yields to a high level, 88% for MOZ and 97% for BPA [run 8; Scheme 6, eq. (11)].

CONCLUSIONS

The reclamation reactions of PC (Schemes 2 and 3), in which the carbonyl moiety of PC was reassembled into the form of DTO, DTA, OT, TZ, and MOZ, and where the aromatic moiety was quantitatively recovered in the form of BPA, were realized in this study. All of the reactions can be carried out with low-energy procedures, on average below 100°C for 0.5–3 h under atmospheric pressure and with conventional apparatus and an easy operation. Also, some products (i.e., DTO, DTA, and TZ) could be used as the solvent of the corresponding retropolymerization reaction. Such reactions where the product is used as the solvent instead of conventional solvents can be regarded as energy-saving and material-saving systems. These features are apparently beneficial by lowering the environmental risk factors required for many inventories of the LCA of plastic waste reclamation.

We also stress that besides the reclamation of BPA, which is an important industrial chemical, PC was proven useful as a phosgene equivalent, as illustrated by the efficient production of heterocyclic carbonates. In conclusion, PC plastic wastes can be and must be recycled repeatedly as chemicals under industrial safety controls to contribute more or less to a sustainable society.

EXPERIMENTAL

General

Pure PC pellets (3 mm in length × 2.5 mm in diameter; molecular weight = 22,000) were mainly used as model plastics. Commercially available chemical-grade DPC, PT, ME, AET, EDT, PDT, and MAE were

TABLE IV
Treatment of PC with ME

Run	ME (mol equiv)[a]	Catalyst (mol %)	Temperature (°C)	Time (min)	Product (%)[b]	
					BPA	OT
1	1	Aqueous NaOH (0.5)	90	60	90	70
2	1	Aqueous NaOH (0.5)	100	30	62	60
3	1	Aqueous NaOH (1.5)	100	30	59	62
4	3	Aqueous NaOH (0.5)	100	30	100	64
5	1	Aqueous NaOH (0.5)	100	60	94	50
6	1	Aqueous NaOH (0.5)	100	120	98	30
7	1	NaOH (1.0)	100	60	88	74
8	1	NaOH (1.0)	100	180	92	87
9	1	KOH (1.0)	100	60	100	47
10	1	KOH (2.0)	100	90	100	40

[a] Solvent = dioxane; molar equivalences to one ester group of PC.
[b] Determined by ^{1}H-NMR.

TABLE V
Treatment of PC with AET and MAE

Run	Nucleophilic reagent	Catalyst (mol %)[a]	Temperature (°C)	Time (min)	Product (%)[b] BPA	Cyclic carbonate		Intermediate[c]	
1	AET	—	100	90	46	TZ	47	BPA-MEC	54
2	AET	Aqueous NaOH (0.5)	100	60	92	TZ	53		0
3	AET	Aqueous NaOH (0.5)	90	120	97	TZ	63		0
4	AET	NaOH (1.0)	100	60	100	TZ	100		0
5	MAE	—	100	90	11	MOZ	9	BPA-HEC	89
6	MAE	Aqueous NaOH (0.5)	100	120	25	MOZ	41	BPA-HEC	59
7	MAE	NaOH (1.0)	100	70	98	MOZ	81		0
8	MAE	NaOH (3.0)	100	60	97	MOZ	88		0

Molar ratio of PC/reagents = 1.0 in dioxane.
[a] The figures in the parenthesis are molar equivalences to one ester group of PC.
[b] Determined by ^{1}H-NMR.

used without further purification. Chemical shifts in the ^{1}H-NMR spectra (300 MHz) and ^{13}C-NMR spectra (75.6 MHz) in CDCl$_3$ are expressed here in parts per million (δ) unless otherwise stated. Flash-column chromatography was performed on silica gel (Wako-gel C-300) with a mixed eluent of ethyl acetate (AcOEt) in hexane.

Reaction of DPC with EDT in dioxane in the presence of a catalyst

DPC (0.641 g or 3 mmol/carbonate unit = 6 mmol/ester unit) was dissolved in 8 mL of dioxane, to which was added EDT (0.283 g or 3 mmol). After the temperature was adjusted at 40°C, the reaction mixture was stirred for 30 min in the presence of NaOH (0.5 mol % equiv) dissolved in water. After the reaction was over and the mixture was cooled, aqueous HCl (1.0 mol/dm^3) was added to the reaction mixture until the mixture became slightly acidic. The solution was concentrated *in vacuo*, and the residue was subjected to flash-column chromatography on silica gel (eluting solvent = 20–50% AcOEt in hexane). Two major products, DTO (85%) and phenol (86%) were obtained. The results are summarized in Table I. The spectral data of DTO were the same as those reported.[22–24]

Reaction of DPC with ME in the presence of a catalyst

The reaction procedures and conditions were analogous to those described previously, except ME was used as the nucleophile in the place of EDT. The isolated products were OT (94%) and phenol (100%). The results are summarized in Table I. The spectral data of OT were the same as those reported.[24]

Reaction of DPC with AET in the absence or presence of a catalyst

To a solution of DPC (0.641 g or 3 mmol/carbonate unit = 6 mmol/ester unit) dissolved in 8 mL of diox-

ane was added AET (0.231 g or 3 mmol), and the mixture was heated at 90°C for 2 h. The workup procedure was analogous to that described for EDT, and the product mixture was subjected to flash-column chromatography on silica gel (eluting solvent = 40–100% EtOAc in hexane). The isolated products were phenol (52%) and 5 (93%), but TZ was not formed.

When the reaction was carried out at 90°C for 80 min in the presence of aqueous NaOH (0.5 mol % equiv), TZ and PhOH were formed quantitatively. The results are summarized in Table I (runs 8 and 9) 5:

Melting point (mp) = 44–45°C;

^{1}H-NMR (δ): 1.38–1.43 (t, J = 8.5 Hz, 1H, —CH$_2$CH$_2$SH), 2.67–2.74 (m, 2H, —CH$_2$CH$_2$SH) 3.40–3.46 (m, 2H, —CH$_2$CH$_2$SH), 5.54 (s, 1H, N—H), and 7.12–7.39 (m, 5H);

^{13}C-NMR (δ); 24.73, 44.07, 121.55, 125.39, 129.31, 150.90, and 154.59;

IR (KBr, cm^{-1}): 3330 (m, N—H), 2580 (s, —SH), and 1710 (m, C=O);

HRMS (CI calcd for C$_9$H$_{12}$O$_2$NS (MH$^+$): 198.0590. Found: 198.0543;

ANAL. Calcd for C$_9$H$_{11}$O$_2$NS: C, 54.80%; H, 5.62%; N, 7.10%. Found: C, 55.12%; H, 5.14%; N, 7.24%

The spectral data of TZ were the same to those reported.[30]

Reaction of DPC with MAE in the absence or presence of a catalyst

DPC (0.641 g or 3 mmol/carbonate unit = 6 mmol/ester unit) was dissolved in 8 mL of dioxane, to which was added MAE (0.319 g or 3 mmol), and the total reaction mixture was heated at 90°C for 50 min. The workup procedure was analogous to that described for EDT. After the flash-column chromatographic separation, The products were isolated: MOZ (10%), phenol (56%), and 6 (90%).

When DPC was treated with MAE at 100°C for 70 min in the presence of anhydrous NaOH (1.0 mol %

equiv), the product yields were much improved to a quantitative level (100%). The results are also summarized in Table I (runs 10–12) and Scheme 4. **6:**

^{1}H-NMR (1:1 mixture of conformers,[40] δ): 2.16 (s, 2H, —CH$_2$CH$_2$*OH* for two isomers), 3.06 (s, 3H, N—CH$_3$ isomeric), 3.16 (s, 3H, N—*CH$_3$* isomeric), 3.50–3.58 (m, 4H, N—CH$_2$— for two isomers), 3.81–3.85 (m, 4H, —*CH$_2$*—OH for two isomers), and 7.11–7.38 (m, 10H);

^{13}C-NMR (mixture of conformers;[40] δ): 35.69, 35.81, 51.33, 51.74, 60.31, 121.72, 125.30, 129.23, 151.35, 155.02, and 155.69;

IR (liquid film, cm^{-1}): 3420 (br, OH), 2950 (m), 1720 (m), and 1450 (m);

HRMS (FAB) calcd for C$_{10}$H$_{14}$O$_3$N (MH$^+$): 196.0974. Found:196.0964.

The spectral data of MOZ were the same as those reported.[31,32]

Reaction of DPC with PT in the presence of a catalyst

The reaction conditions were similar to those described for EDT, except that PT was used as the nucleophile in place of EDT. The products were **7** (27%), phenol (27%), and a small amount of the byproduct **8.**

7:

^{1}H-NMR (CDCl$_3$); (δ): 1.04 (t, J = 7.4 Hz, 3H, —CH$_2$CH$_2$*CH$_3$*), 1.68–3.80 (m, 2H, —CH$_2$*CH$_2$*CH$_3$), 2.93 (t, J = 7.2 Hz, 2H, —*CH$_2$*CH$_2$CH$_3$), and 7.15–7.41 (m, 5H);

^{13}C-NMR (δ) 13.08, 22.88, 33.12, 121.19, 125.93, 129.33, 151.13, and 170.2;

IR (liquid film); cm^{-1}): 1730 (m), 1500 (s), and 1100 (m).

HRMS (EI) calcd for C$_{10}$H$_{12}$O$_2$S (M$^+$): 196.0555. Found: 196.0552:

ANAL Calcd for C$_{10}$H$_{12}$O$_2$S: C, 61.20%; H, 6.16%. Found: C, 60.98%; H, 5.96%

8:

^{1}H-NMR (δ): 0.95–1.03 (m, 6H, —CH$_2$CH$_2$*CH$_3$*), 1.59–1.75 (m, 4H, —CH$_2$*CH$_2$*CH$_3$), 2.67 (t, J = 7.2 Hz, 2H, —*CH$_2$*CH$_2$CH$_3$ isomeric), and 2.97 (t, J = 7.2 Hz, 2H, —*CH$_2$*CH$_2$CH$_3$ isomeric);

IR (liquid film, cm^{-1}): 1650 (m) and 1110 (m).

$^{-1}$ HRMS (EI) calcd for C$_7$H$_{14}$OS$_2$ (M$^+$):178.0487. Found: 178.0458.

Reaction of PC with EDT in dioxane in the presence of a catalyst: general procedure

Pellets of PC (0.763 g or 3 mmol/carbonate unit = 6 mmol/ester unit) were dissolved in 8 mL of dioxane, to which was added EDT (0.283 g or 3 mmol). The mixture was warmed at 80°C for 4 h in the presence of anhydrous NaOH (0.5 mol % equiv) or at 40°C for 30 min in the presence of aqueous NaOH (1.5 mol % equiv).

After the reaction was complete and the reaction mixture cooled, aqueous HCl (1.0 mol/dm^3) was added to make the solution weakly acidic. Then, the mixture was poured to methanol (50 ml) to remove polymeric substances, and the filtrate was concentrated. The residue was again dissolved in ethyl acetate (30 mL), and the solution was washed with 50 mL of water. The aqueous phase was extracted three times by ethyl acetate (30 mL each), and the combined organic solution was dried over anhydrous Na$_2$SO$_4$. After the solvent was removed the residue was subjected to flash chromatography (silica gel, 10–100% EtOAc in hexane). Two products DTO (95%) and BPA (99%) were obtained without byproducts. When the reaction time was short, **13**,[41] that is a, 1:2 adduct of a carbonate group and BPA, was isolated. The results are summarized in Table II. **13:**

^{1}H-NMR(δ^{-1});1.64 s, 12H, C(CH$_3$)$_2$], 4.67 (s, 2H, —OH), and 6.71–7.25 (m, 16H);

IR (KBr,); cm^{-1} 3530 (w), 3460 (w), 1770 (m), 1510 (m), 1260 (m), 1190 (m), and 1160 (m).

HRMS (EI) calcd for C$_{31}$H$_{30}$O$_5$ (M$^+$); 482.2094. Found: 482.2098.

For the spectral data of DTO, see the authentic refs. 22–24.

Reaction of PC with EDT in the presence of a catalyst and with DTO as the solvent

The reaction conditions were the same as described for the reaction of PC with EDT except that DTO was used as the solvent in place of dioxane. The method to determine the yield of product DTO, which was the same chemical as the solvent, was different from that in dioxane. An increase in the amount of DTO was determined by two methods, namely, (1) product isolation by column chromatography and (2) gas chromatographic determination with an internal standard. The results are summarized in Table II (run 11).

Reaction of PC with PDT in dioxane in the presence of a catalyst

PC pellets (0.763 g or 3 mmol/carbonate unit = 6 mmol/ester unit) were dissolved in 8 mL of dioxane, to which was added PDT (0.324 g or 3 mmol) and aqueous NaOH (1.5 mol % equiv). The mixture was heated at 100°C for 3 h, and the workup procedure was analogous to that described for PC with EDT. The products were DTA (75%), BPA (96%), and **14** (14%).

^{1}H-NMR (δ); 1.38 (t, J = 8.1 Hz, 2H, —CH$_2$*SH*), 1.86–1.96 (quintet, J = 7.0 Hz, 4H, —*CH$_2$*CH$_2$—), 2.53–2.61 (quartet, J = 7.3 Hz, 4H, —*CH$_2$*SH), and 3.09 (t, J = 7.0 Hz, 4H, —S*CH$_2$*CH$_2$—;

^{13}C-NMR (δ); 23.19, 28.95, 33.65, and 189.13;

IR (liquid film,); cm^{-1} 2740 (S), 2560 (S), 1640 (m), and 1440 (m).

HRMS (EI) calcd for $C_7H_{14}OS_4$ (M^+):241.9929. Found: 241.9932:

ANAL. Calcd for $C_7H_{14}OS_4$: C, 34.68%; H, 5.82%. Found: C, 34.75%; H, 5.66.

The results are summarized in Table III. For the spectral data of DTA, see authentic refs. 37 and 39.

Reaction of PC with ME in dioxane in the presence of a catalyst

Pellets of PC (0.763 g or 3 mmol/carbonate unit = 6 mmol/ester unit) were dissolved in 8 mL of dioxane, to which was added ME (0.234 g or 3 mmol) and anhydrous NaOH (1.0 mol% equiv). The total reaction mixture was heated at 100°C for 3 h. The workup procedure was analogous to that described for DPC with MAE. The products were BPA (92%) and OT (87%). The results are summarized in Table IV. For the spectral data of OT, see authentic ref. 24.

Reaction of PC with AET in dioxane in the absence or presence of a catalyst

PC pellets (0.763 g or 3 mmol/carbonate unit = 6 mmol/ester unit) were dissolved in 8 mL of dioxane, to which was added AET (0.231 g or 3 mmol). The total mixture was heated at 100°C for 1.5 h. The workup procedure was analogous to that described for DPC with MAE. The products were TZ (47%), BPA (46%), and **15**, (54%). When anhydrous NaOH (1.0 mol% equiv) was added as a catalyst, the reaction was carried out at 100°C for 1 h. The results are summarized in Table V. **15**.

mp = 107–108°C;

^{1}H-NMR(δ);1.41 (t, J = 8.5 Hz, 3H, —CH$_2$$SH$), 1.62 [s, 6H, C(CH$_3$)$_2$], 2.69–2.76 (q, J = 8.2 Hz, 2H, —CH$_2$$CH_2$SH), 3.41–3.48 (q, J = 6.3 Hz, 2H, —CH_2CH$_2$SH), 5.30 (s, 1H, —NH), 5.47 (s, 1H, ArOH), and 6.67–7.26 (m, 8H);

^{13}C-NMR (δ): 24.75, 31.00, 42.01, 44.07, 114.76, 120.82, 127.68, 127.88, 142.43, 148.19, 148.53, 153.60, and 154.92;

IR (KBr cm^{-1}): 3380 (br, OH), 1710 (w), 1515 (s), 1450 (w), and 835 (s).

HRMS (EI) calcd for $C_{18}H_{22}NO_3S$ (M^+): 332.1320. Found 332.1332;

ANAL. Calcd for $C_{18}H_{21}NO_3S$: C, 65.23%; H, 6.39%; N, 4.23%. Found: C, 65.01%; H, 6.41%; N, 4.28%.

For the spectral data of TZ, see authentic ref. 30.

Reaction of PC with MAE in dioxane in the absence or presence of a catalyst

After PC pellets (0.76 g or 3 mmol/carbonate unit = 6 mmol/ester unit) were dissolved in 8 mL of dioxane, MAE (0.319 g or 3 mmol) was added, and the mixture was warmed at 100°C for 1.5 h. After the workup and chromatographic separation (silica gel, 40–100% EtOAc in hexane), three products were isolated: MOZ (9%), BPA (11%), and **16** (89%). In some runs, 0.5–3.0 mol% equiv of NaOH was used as the catalyst. The results are summarized in Table V. **16;**

mp-145.5–146.5°C;

^{1}H-NMR (d$_6$-DMSO, 1:1 mixture of conformers;^{40} δ) 1.57 [s, 12H, C(CH$_3$)$_2$], 2.93 (s, 3H, N—CH$_3$ isomeric), 3.05 (s, 3H, N—CH$_3$ isomeric), 3.30–3.33 (m, 2H, N—CH$_2$—isomeric), 3.42–3.45 (m, 2H, N—CH$_2$— isomeric), 3.54–3.59 (m, 4H, N—CH$_2$CH$_2$— isomeric for two isomers), 4.78 (s, 1H, N—CH$_2$CH$_2$$OH$ isomeric), 4.84 (s, 1H, N—CH$_2$CH$_2$$OH$ isomeric), 6.64–7.19 (m, 16H), and 9.20 (s, 2H, phenolic OH);

^{13}C-NMR (mixture of conformers 40° δ) 30.89, 35.56, 41.58, 51.36, 58.66, 59.06, 114.89, 121.29, 127.33, 127.53, 140.56, 147.72, 149.17, 154.30, and 155.28;

IR (KBr, cm^{-1}); 3325 (br, OH), 3200 (br, OH), 1680 (m), 1510 (s), 1450 (m), and 835 (s)/cm;

HRMS (FAB) calcd for $C_{19}H_{24}O_4N$ (MH$^+$); 330, 1705, Found; 330. 1707;

ANAL, Calcd for $C_{19}H_{23}NO_4$: C, 69.28%; H, 7.04%; N, 4.25% Found; C, 68.95%; H, 7.02%; N, 4.27.

For the spectral data of MOZ, see authentic refs. 31 and 32.

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