MIR MOHAMMAD ALAVI NIKJE
Imam Khomeini International University
Faculty of Science
Department of Chemistry
Qazvin, Iran, P.O. Box 2888
e-mail: alavim2006@yahoo.com

Glycolysis of polycarbonate wastes with microwave irradiation

Summary — Polycarbonate contained in waste compact discs have been glycolized with ethylene glycol using microwave irradiation in the presence of sodium hydroxide as catalyst in order to obtain bisphenol A (BPA) as the sole product. The influence of various parameters such as the concentration of the alkali metal catalyst and microwave irradiation power on product yield was studied in detail. The recovered BPA was analyzed with spectroscopic methods (^{1}H NMR, ^{13}C NMR, FT-IR) and the obtained results compared with standards.

Keywords: polycarbonate, depolymerization, bisphenol A, microwave irradiation, recycling.

GLIKOLIZA ODPADÓW POLIWĘGLANOWYCH POD WPŁYWEM PROMIENIOWANIA MIKROFALOWEGO

Streszczenie — Poliwęglanowe (PC) odpady, pochodzące z płyt kompaktowych, poddawano glikolizie przy użyciu wodorotlenku sodu jako katalizatora oraz glikolu etylenowego (EG) w charakterze czynnika glikolizującego, pod wpływem działania promieniowania mikrofalowego (MW). Głównym produktem prowadzonego procesu był bisfenol A (BPA). Oceniano zależność wydajności reakcji glikolizy od zastosowanych, zmiennych warunków: zawartości katalizatora w układzie, czasu reakcji oraz mocy promieniowania (tabele 1—3). Otrzymany bisfenol A badano metodami spektroskopowymi (^{1}H NMR, ^{13}C NMR, FT-IR, rys. 1—3).

Słowa kluczowe: poliwęglany, depolimeryzacja, bisfenol A, promieniowanie mikrofalowe, recykling.

The rise in the industrial use of polycarbonates (PC) has necessitated demands for appropriate treatment or recycling of their waste products. Two main methods have been adopted for PC recycling namely: physical and chemical, whereby the chemical method involves the conversion of the waste products into versatile monomers and other useful chemicals.

The main goal in the chemical recycling of polycarbonates is the extraction of bisphenol A (BPA) and its oligomers from the electronic wastes. Various recycling methods has been reported and they all have their merits and drawbacks.

Oku and co-workers described the chemical conversion of PC to the bis(hydroxyethyl) ether of BPA (BHE-BPA), which can be used as a diol for the preparation of condensed polymers. PC was degraded using conventional heating in the presence of ethylene glycol (EG) and catalytic amounts of NaOH and the further addition of ethylene carbonate (EC) to the reaction mixture had to the synthesis of BHE-BPA [1].

Shwu-jer Chiu *et.al.* investigated the effect of metal chlorides on the thermal degradation of waste PC and found $ZnCl_2$ and $SnCl_2$ to be suitable catalysts for this process [2]. Pinero and co-workers discussed the chemical recycling of PC in a semi-continuous lab-plant, using methanol and methanol-water mixtures as decomposition reagents [3]. The depolymerization of PC in toluene under subcritical and supercritical conditions has also been reported in [4]. Liu *et.al.* methanolized PC wastes under conventional heating conditions in order to recover BPA as the sole product and a 94 % recovery yield was achieved after 8 h [5]. PC wastes have been pyrolized under critical conditions and BPA recovered with a maximum yield of 91 % at 300 °C. When the reaction temperature was raised to 500 °C, BPA degradation products namely, phenol and 4-isopropenyl phenol were obtained [6, 7].

The kinetics of PC degradation has been studied by Kim and co-workers and they suggested two mechanistic path-ways for the glycolysis reaction [8]. Chemical recycling of PC was studied at high temperature (steam at 573 K) and pressure conditions and BPA recovered within 5 min [9]. Environmentally benign methanolysis of PC has been performed using ionic liquids as the reaction media and recycled BPA and dimethyl carbonate obtained as the reaction products [10]. Moreover, other publications have covered PC recycling either separately, or blended with other polymers [11—19]. In this article, we have explored the application of microwave irradiation as a powerful and "green" energy source in the chemical recycling of PC wastes for the first time. The method is quick and simple and BPA is recovered from PC wastes at short reaction times.

EXPERIMENTAL

Materials

PC samples were obtained in the form of waste compact discs and processed without preliminary treatment.

EG and NaOH were used as the recycling agent and catalyst respectively.

Recycling process: general procedure

The recycling processes were performed in a Milestone Mico SYNTH "NP" Ethos 1600 programmable microwave instrument under ambient pressure.

Table 1. Microwave program in PC glycolysis

Entry	Fixed temperature, °C	Step	Reaction time, min	*MW*, temperature program, °C	Maximum power, W
1	160	1	3	ramp to 160	up to 500
		2	5	hold at 160	up to 400
2	180	1	3	ramp to 180	up to 600
		2	5	hold at 180	up to 600
3	200	1	3	ramp to 200	up to 1000
		2	5	hold at 200	up to 800

PC chips (1.27 g), EG (6.4 g, 100 mmol) and NaOH as catalyst were placed in a two-necked 250 ml flask and the reaction mixture irradiated at 180 °C at various catalyst concentrations and different reaction times (Table 1). The addition of cold water led to precipitation of recycled BPA. The obtained BPA was filtered, recrystalized in water, filtered once more and then dried. The product was identified using spectroscopic methods and the spectra compared with those of a standard sample.

Methods of testing

— FT-IR spectra were obtained using a BRUKER Tensor 27 spectrometer.

— ^{1}H NMR and ^{13}C NMR spectra were collected using a BRUKER CRX 300 instrument in deuterated $CDCl_3$ as a solvent and TMS as an internal standard.

RESULT AND DISCUSSIONS

Catalyst concentration

In order to investigate the influence of the concentration of the alkali metal on the depolymerization of PC, a series of experiments was performed using different amounts of catalyst from 0.5 to 2.0 wt. % of NaOH and irradiated. Data collected in Table 2. The results in the table indicate, that an increasing concentration of the catalyst leads to an increase in yield of recovered BPA in all the applied microwave — assisted processes, and reached a maximum (92 %) for 2 wt. % with the entry 2 procedures. The application of concentrations higher than 2.0 wt. % caused the neutralization of the unreacted catalyst. Thus, 2.0 wt. % of NaOH was regarded as the optimum catalyst concentration. Moreover, of the three microwave programs applied higher yields were generally achieved by using the entry 2 procedure. Low MW power leads to low recovery yields, while an increase was observed in using entry 3 MW program, but the BPA recovery yields decreased dramatically at high catalyst concentrations in comparison with entry 2.

Table 2. Effects of NaOH concentration in BPA recovery yield at various MW irradiations

Entry	NaOH %	BPA yield %	Entry	NaOH %	BPA yield %	Entry	NaOH %	BPA yield %
1	0.5	10	2	0.5	37	3	0.5	42
	1.0	35		1.0	87		1.0	82
	1.5	42		1.5	89		1.5	80
	2.0	55		2.0	92		2.0	87

Reaction times

As mentioned earlier, in order to establish the optimum reaction time, various microwave irradiation programs were examined and entry 2 was found to be the most effective (see Tables 1 and 2). To investigate the reaction details, experiments were performed at various reaction times for the optimized entry (entry 2) and the results collected in Table 3. The results medicate, that the

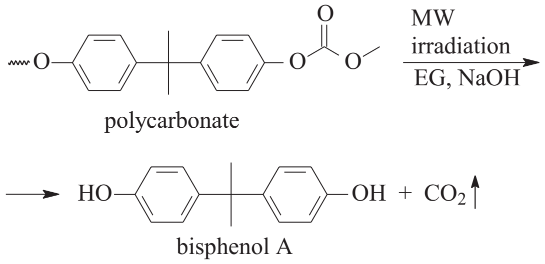
Table 3. Effect of reaction times on BPA recovery yields

Entry	Reaction time, s	BPA recovery yield, %
1	100	15
2	200	40
3	300	76
4	400	84
5	500	93
6	600	93

BPA recovery yield is considerably affected by the reaction time and increases with an increase in the reaction duration and reached to an optimum yield at 500 s. Longer MW irradiation did not lead to significant BPA recovery yields in comparison with entry 5 (Table 3).

Reaction scheme and spectra analysis

Equation (1) illustrates the reaction mechanism for PC depolymerisation under alkali conditions where BPA is recovered.



(1)

The structure of the recovered BPA was determined using spectroscopic methods and the results compared with standards. The ^{1}H NMR spectrum of recovered BPA is presented in Fig. 1. The peak at 1.53 ppm corresponds with methyl hydrogen and the peak at 4.5 ppm is relative to hydroxyl groups and the peaks at 6.5—7.0 ppm corresponds to aromatic hydrogen.

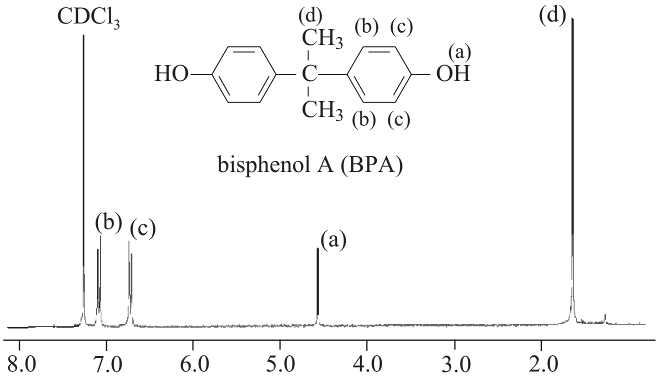
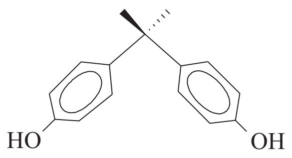


Fig. 1. ^{1}H NMR spectrum of recovered BPA

Furthermore, phenol hydroxyl group appeared at 4.5 ppm due to steric hindrance from the neighboring ring as presented in the chemical structure (I).

The additional peaks at 115, 127, 141 and 154.7 ppm observed in the ^{13}C NMR spectrum are generated by aromatic rings. The signals at 31 and 41 ppm represent methyl groups and C4 respectively (Fig. 2). FT-IR spectrum correspond fully with NMR data (Fig. 3).



(I)

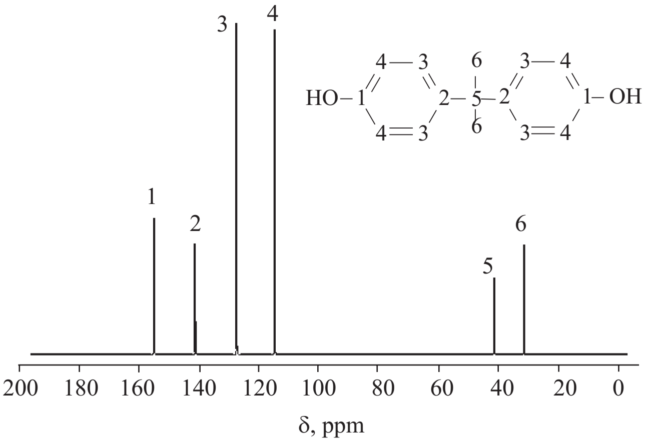


Fig. 2. ^{13}C NMR spectrum of recovered BPA

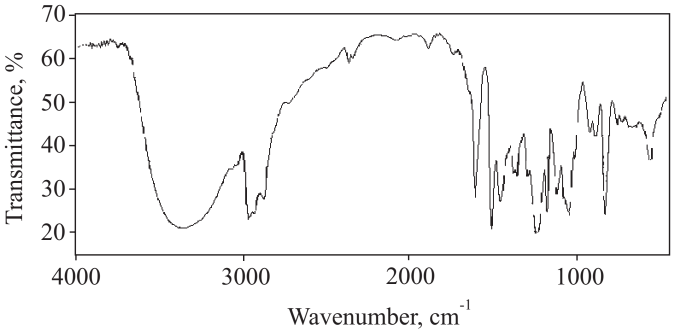


Fig. 3. FT-IR spectrum of recovered BPA

CONCLUSIONS

The recycling of PC has been performed using microwave irradiation at atmospheric pressure and BPA recovered as the sole product. Recovery yields increased with increasing reaction times as well as catalyst concentration to optimum values at specific MW irradiation procedures. The results confirm, that microwave energy can be used as an energy source in PC chemical recycling as an adequate, simple and convenient method with considerable performance at short reaction times.

REFERENCES

1. Oku A., Tanaka S., Hata S.: *Polymer* 2000, **41**, 6749.
2. Chiu S. J., Chen S. H., Tsai C. T.: *Waste Manag.* 2006, **26**, 252.
3. Pinero R., Garcia J., Cocero M. J.: *Green Chem.* 2005, **7**, 380.
4. Pan Z. Y., Bao Z., Chen Y. X.: *Chinese Chem. Lett.* 2006, **17**, 545.
5. Liu Fu-S., Li Z., Yu Shi-T., Cui X., Xie C. X., Ge X. P.: *J. Polym. Environ.* 2009, **17**, 208.
6. Grause G., Tsukada N., Hall J. W., Kameda T., Paul T. W., Yoshioka T.: *Polym. J.* Advanced online publication 31 March 2010.

7. Grause G., Sugawara K., Mizoguchi T., Yoshioka T.: *Polym. Degrad. Stab.* 2009, **94**, 1119.
8. Kim D., Kim B. K., Cho Y., Han M., Kim B. S.: *Ind. Eng. Chem. Res.* 2009, **48** (2), 685.
9. Watanabe K. M., Matsuo Y., Matsushita T., Inomata H., Miyake T., Hironaka K.: *Polym. Degrad. Stab.* 2009, **94**, 2157.
10. Liu F., Li Z., Yu S., Cui X., Ge X.: *J. Hazard Mater.* 2010, **174**, 872.
11. Lin C. H., Lin H. Y., Liao W. Z., Dai S. A.: *Green Chem.* 2007, **9**, 38.
12. Jang B. N., Wilkie C. A.: *Thermochim. Acta.* 2005, **426**, 73.
13. Kim J., Gracz H. S., Roberts G. W., Kiserow D. J.: *Polymer* 2008, **49**, 394.
14. Jang B. N., Wilkie C. A.: *Polym. Degrad. Stab.* 2004, **86**, 419.
15. Bozi J., Czegeny Z., Meszaros E., Blazso M.: *J. Anal. Appl. Pyrol.* 2007, **79**, 337.
16. Margon V., Agarwal U. S., Bailly C., Wit G. de., Van Kasteren J. M. N., Lemstra P. J.: *J. Supercrit. Fluids.* 2006, **38**, 44.
17. Uyar T., Tonelli A. E., Hacaloglu J.: *Polym. Degrad. Stab.* 2006, **91**, 2960.
18. Fraisse F., Verney V., Commereuc S., Obadal M.: *Polym. Degrad. Stab.* 2005, **90**, 250.
19. Jung J. H., Ree M., Kim H.: *Catal. Today* 2006, **115**, 283.

Received 28 IV 2010.

Politechnika Wrocławska, Wydział Chemiczny, Zakład Inżynierii i Technologii Polimerów
zaprasza do udziału w

XX KONFERENCJI NAUKOWEJ

MODYFIKACJA POLIMERÓW

Wrocław, 12—14 września 2011 r.

Patronat Honorowy:
— J. M. Rektor Politechniki Wrocławskiej, prof. dr hab. inż. Tadeusz WIĘCKOWSKI
— Dziekan Wydziału Chemicznego PWr, prof. dr hab. inż. Andrzej MATYNIA
— Zarząd Oddziału Wrocławskiego SITPChem
Przewodniczący Komitetu Naukowego: prof. dr hab. inż. Ryszard STELLER
Wiceprzewodniczący Komitetu Naukowego:
prof. dr hab. inż. Stanisław KUCHARSKI, prof. dr hab. inż. Jacek PIGŁOWSKI
Przewodnicząca Komitetu Organizacyjnego: dr inż. Wanda Meissner
Sekretarz: dr inż. Grażyna Kędziora
Tematyka Konferencji:
— Modyfikacja chemiczna i reaktywne przetwarzanie polimerów
— Modyfikacja fizyczna i kompozyty/nanokompozyty polimerowe
— Fotooptyczne oraz ciepło- i elektroprzewodzące układy polimerowe
— Recykling i tworzywa polimerowe z surowców odnawialnych/wtórnych
— Nowe zastosowania oraz metody badań właściwości polimerów
Program naukowy konferencji będzie obejmować: referaty plenarne i sekcyjne, sesję plakatową i sesję dyskusyjną.
Zgłoszenia prosimy przesyłać na adres Sekretarza: e-mail: grazyna.kedziora@pwr.wroc.pl, tel.: 71 320 26 60, tel./fax: 71 320 27 39 lub Przewodniczącego Komitetu Naukowego: e-mail: ryszard.steller@pwr.wroc.pl, tel.: 71 320 33 21
Prace zaakceptowane przez Komitet Naukowy zostaną wydane po pozytywnej recenzji w formie pracy zbiorowej pt. „Modyfikacja Polimerów".
Termin nadsyłania materiałów — 17 czerwca 2011 r.
Opłata konferencyjna: do 17 czerwca 2011 r.
— 1350 zł (doktoranci 1100 zł), pok. 1-osob.
— 1150 zł (doktoranci 900 zł), pok. 2-osob.
— opłata po terminie — odpowiednio, 1450 zł i 1250 zł
Opłata konferencyjna obejmuje: zakwaterowanie, wyżywienie, materiały konferencyjne i imprezy towarzyszące.
Adres do korespondencji i informacje:
dr inż. Grażyna Kędziora lub prof. Ryszard Steller
Politechnika Wrocławska, Zakład Inżynierii i Technologii Polimerów, Wydział Chemiczny, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław
Miejsce konferencji: Hotel DIAMENT, ul. Muchoborska 10, 54-424 Wrocław, tel.: 71 7 350 350, (www.hotelediament.pl)