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Chemical recycling of polycarbonate wastes into bisphenol A by using green solvent composition

Summary — Polycarbonate contained in waste compact discs (CDs) and digital versatile (video) discs (DVDs) have been chemically recycled into bisphenol A (BPA) — using a ternary solvent system: glycerin, sorbitol, water under conventional heating method. The obtained results show that the mixture of glycerin, sorbitol, water in the ratio 6:3:1 undergoes recycling with high yield within 45 minutes. The recovered BPA was identified by spectroscopic methods and the results were compared with the data corresponding to standard sample.

Keywords: chemical recycling, polycarbonate, bisphenol A, CD & DVD waste.

CHEMICZNY RECYKLING POLIWĘGLANOWYCH ODPADÓW DO BISFENOLU A PRZY UŻYCIU KOMPOZYCJI „ZIELONYCH" ROZPUSZCZALNIKÓW

Streszczenie — Odpady używanych poliwęglanowych płyt CD i DVD poddano chemicznemu recyklingowi do bisfenolu A (BPA), za pomocą trójskładnikowego systemu rozpuszczalników (gliceryna/sorbitol/woda), w warunkach konwencjonalnego ogrzewania. Wyniki dowodzą, że układ, w którym stosunek gliceryna:sorbitol:woda wynosi 6:3:1 umożliwia przebieg reakcji z dużą wydajnością w ciągu 45 min. Odzyskany BPA badano metodami spektroskopowymi a uzyskane dane porównano z danymi odpowiadającymi próbce pierwotnego bisfenolu A.

Słowa kluczowe: chemiczny recykling, poliwęglany, bisfenol A, odpady CD i DVD.

INTRODUCTION

Chemical recycling of waste polymers has gained much attention as a common root in obtaining valuable products from waste plastics. The decomposition of polycarbonate into its monomer, bisphenol A (BPA) which is the main raw material for PC manufacturing have been reported in many works.

The chemical conversion of PC to bis(hydroxyethyl) ether of bisphenol A (BHE-BPA), what can be used as a diol for condensed polymers preparation was studied by Oku *et al.* [1]. PC was recycled using conventional heating method in the presence of ethylene glycol (EG) and catalytic amounts of NaOH.

The effect of metal chlorides on thermal degradation of waste polycarbonate has been examined by Chin *et al.* [2] and the obtained results showed the performances of $ZnCl_2$ and $SnCl_2$ in formation of liquid products. In another report, Pinero's research group investigated chemical recycling of PC in a semi-continuous lab-plant, using methanol and methanol-water mixtures as destroying reagents [3]. In the work of Pah *et al.* [4] the depolymerization of PC in toluene under subcritical and supercritical conditions was presented. In the meantime, some other paper concerning recycling of PC alone or blended with other polymers have been published and all of them have their own merits and drawbacks [5—13]. Liu and his coworkers reported the performances of ionic liquid in methanolysis of PC. 95 % BPA recovery and carbonate formation yields were achived in the presence of 1-*n*-butyl-3-methylimidazolium chloride ([Bmim][Cl]) under the conditions: the ratio of $m(PC):m(CH_3OH):m([Bmim][Cl]) = 2:3:2$, reaction time: 2.5 h, reaction temperature: 105 °C [14]. The same research group also studied alkali-catalyzed methanolysis and hydrolysis of PC in solvent in which PC can substantially dissolve such as *N*-methyl-2-pyrrolidone, 1,4-dioxane, tetrahydrofuran and BPA recovered in 94 % yield [15]. In our earlier research on PC chemical recycling [16] and in this report we present a green, eco-friendly and convenient method in recovering of BPA from CD wastes.

EXPERIMENTAL

Materials

PC pellets were obtained from waste CDs and DVDs and washed with hot water and dried before being

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charged into the reactor. BPA, glycerin, sorbitol and sodium hydroxide were purchased from Merck and used as received without further purification. Twice-distilled water was used to perform the reactions.

General procedure

Two-necked flask was filled with PC wastes (1.00 g), glycerin, sorbitol and water (solvent total weight 1.00 g) and NaOH (1 and 2 % based on all reactants) as the catalyst. The mixture was refluxed. Dissolution of the PC waste was considered as the reaction end-point. The collected data are shown in Table 1. Separation and purification of bisphenol A was done by crystallization in water, further filtration and drying. The finally obtained product was characterized structurally using spectroscopic method and the spectra were compared with those of standard sample. In all experiments the PC waste:solvent ratios were constant and set as 1:1.

Table 1. Glycerol/sorbitol/water compositions role on BPA recovery yields[*)]

Entry	BPA recovery yield, %	Reaction time min	Glycerin/sorbitol/ /water
1	100	45	0.6/0.1/0.3
2	97	55	0.4/0.1/0.5
3	95	360	0.2/0.1/0.7
4	93	510	0.1/0.1/0.8
5	90	600	0.0/0.1/0.9

[*)] In all reactions, PC wastes were set as 1.0 g, NaOH 1.0 % and reaction temperature 180 °C.

Methods of testing

FT-IR spectra were obtained using a BRUKER Tensor 27 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were collected by a BRUKER CRX 300 instrument using deuterated $CDCl_3$ as a solvent and TMS as an internal standard.

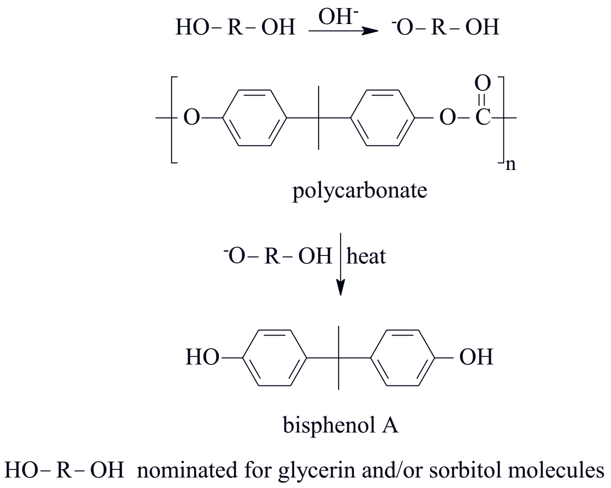
RESULTS AND DISCUSSION

Study on catalyst concentration

According to our earlier work on recovering of BPA under microwave irradiation condition [16], where high recovery yield were achieved by using 2.0 % of NaOH as the catalyst as well as for comparing data from MW and conventional heating methods, the base catalyst concentration was set as 2.0 % in all reactions.

Reaction scheme

Hydroglycolysis of PC wastes is shown in the Scheme A where the first step in the reaction is related to a acid-base reaction and conversion of glycerin and/or sorbitol molecules to the corresponded alkoxide ions which act as a nucleophile and are responsible for breaking down of carbonate functional groups. It is mentionable that by using water as a solvent, hydroxide ions act as the nucleophile which are weaker in nucleophilicity in comparison with alkoxide ions and cause prolonged reaction times for adequate PBA recovery (see Table 1).



Scheme A. BPA recovery from PC wastes

Solvent composition studies

Results from experiments showed the performances of alkoxide ions in shortening of reaction times. These results imply the ability of deprotonation of selected solvents namely, glycerin, sorbitol and water and formation of corresponded nucleophiles. In order to find a green solvent composition containing high water content, the effects of various ratios of water and glycerin were studied in BPA recovering yields and data are collected in Table 1. As one can see, the highest recovery of BPA was achived under the conditions described in entry 1. Increasing water content causes increase in the required time of reaction and decrease of BPA recovery yields. The usage of water alone calls the procedure totally green but it increases reaction time which is not economically interesting. Therefore reaction needs the application of glycerin as a co-solvent. To study the role of catalyst concentration, some experiments were carried out using an additional 1 % NaOH in comparison with nominated experiments shown in Table 1. By using 2 % sodium hydroxide and setting the glycerin/sorbitol/water ternary system as 0.6/0.2/0.2 ratios, 90 and 95 % recovery yields here reached 10 and 35 min, respectively. However the results show the performance of base catalyst concentration in decreasing of reaction time, but the main drawback will come in catalyst recovering and reusing.

Spectroscopy studies of recovered BPA

Recovered BPA was characterized and studied by spectroscopic methods in order to elucidate its chemical

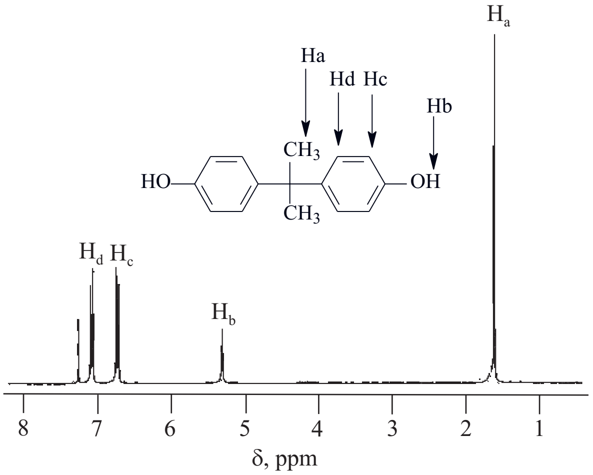


Fig. 1. ^{1}H NMR spectrum of recovered BPA

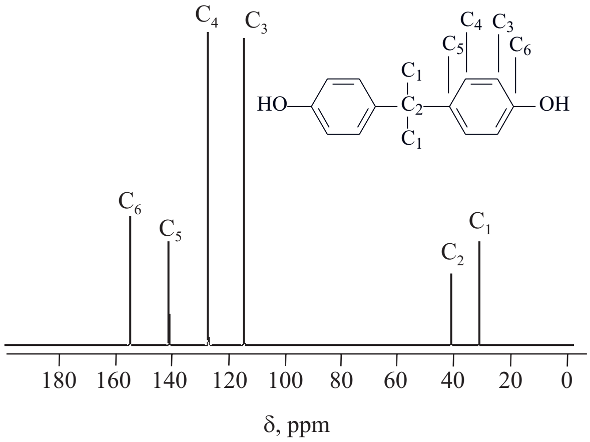


Fig. 2. ^{13}C NMR spectrum of recovered BPA

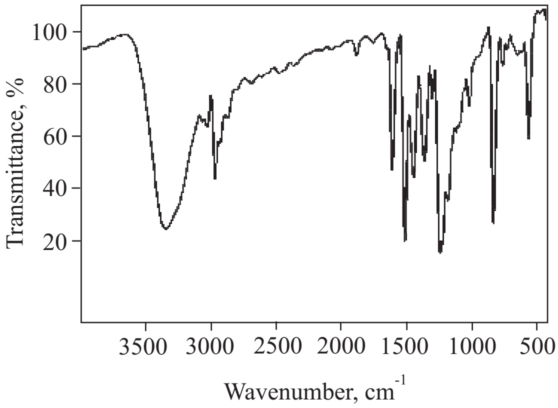


Fig. 3. FT-IR spectrum of recovered BPA

structure and compare the obtained spectra with those of standard sample. 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 5.4 ppm is relative to hydroxyl groups and the peaks at 6.5—7.0 ppm corresponds to aromatic hydrogen's, respectively. All ^{1}H NMR data were similar to data collected for standard BPA sample what indicates successful recovering under designed experimental conditions.

The spectrum obtained from ^{13}C NMR studies is shown in Fig. 2. The peaks at 115 (C_3), 127 (C_4), 141 (C_5) and 155 (C_6) ppm are related to aromatic ring carbons. In addition, the signals at 31 and 41 ppm are attributed to methyl groups (C_1) and C_2 carbons, respectively. FT-IR spectrum fully corresponds with NMR data (Fig. 3). The structure of recovered BPA can be confirmed by FT-IR spectrum which is similar to standard sample spectrum.

CONCLUSIONS

Glycerin/sorbitol/water ternary system was performed as a green solvent composition in high yield BPA recovering from CD and DVD wastes. The presented methodology overcomes the disadvantages and drawbacks existed in traditional methods such as unfeasible reuse of solvents, tedious workup procedure and environmental problems.

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Received 7 V 2012.