

The Effect of Temperature, Concentration of Catalyst and Reactants on Yield of BPA Synthesized from Industrial Starting Materials

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ABSTRACT

Bisphenol A (BPA) is the product of condensation reaction of phenol with acetone in the presence of an acid catalyst. BPA is a major raw material for the manufacture of relatively new high-temperature polycarbonate resins and epoxy resins. These two applications consume over 90% of the BPA output. So, we decided to investigate its different preparation methods to find the optimum industrial production conditions which satisfy the economy, and operational conditions of Iran Industry. With this aim, we synthesized BPA from industrial grade starting materials, with high degree of purity(92%) and high yield (90%). In this article we discuss the effect of different parameters such as temperature, concentration of catalyst, reactants, and the presence of a promoter on yield of BPA and report the optimum conditions to obtain the 90% yield of BPA with high degree of purity..

Key Words: bisphenol A, synthesis, temperature, concentration, catalyst effect

INTRODUCTION

Bisphenol A (4,4'-isopropylidene diphenol) is a white solid in which the molecules consist of two phenol groups joined through the centre carbon atom of a propane molecule. It has molecular weight of 228 and a solidification point about 157 °C [1].

Bisphenol A is the most important bisphenols which is used industrially. Epoxy resins based on bisphenol A have achieved greatest significance in recent years. Research in this field is continuing in the

areas of production technology and the use of new raw materials such as phenols, amines, carboxylic acids, polyhydric alcohols and others to produce various epoxy networks to be used as matrices for composite materials [2-5].

Bisphenol A polycarbonate is an engineering thermoplastic which is well known for its outstanding combination of toughness, optical clarity, dimensional stability and heat resistance. A vast amount of work is done on commercial production of many types of bisphenol A polycarbonate for different applications

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[6–10].

Further research is being done on the synthesis, characterization, analysis and study of different behaviour and properties of BPA derivatives and compounds [11–16].

Bisphenol A was produced in our laboratory by the reaction of acetone with excess phenol using concentrated hydrochloric acid as a condensation agent. After purifying and drying, the solidification point of the white solid product was found about 156–157 °C. The purity of bisphenol A obtained was also examined by infra-red (IR), nuclear magnetic resonance (NMR) spectroscopy and differential scanning calorimetry (DSC). The results indicate that the product is in high state of purity (Figures 1–3).

EXPERIMENTAL

Materials and Equipment

The following materials were used in the synthesis of bisphenol A:

Industrial grade phenol, acetone, and hydrochloric acid were purchased from Iran's markets. The other materials which are being used in small proportions were obtained from Merck Chemical Co.

IR Spectra of the product were recorded with the Philips PU 9712 infra-red spectrometer. ¹H NMR Spectra were recorded on a JEOL-PMX 60 M Hz spectrometer. Differential scanning calorimetry reading and their corresponding values of thermal studies were carried out on Polymer Laboratory STA 625.

Preparation Method

A mixture of phenol, acetone, catalyst (HCl) and sulphur containing promoter were transferred in a three necked-flask equipped with teflon-coated magnetic stirrer and thermometer and it was kept in a thermostat bath at desired temperature. After a definite period of time, the reaction mixture was transferred to cold water to quench the reaction at any time. Then, the product was washed, dried and weighed. This experiment was repeated with different concentrations of reactants, catalyst, and promoter at various temperatures. The purity of each sample was

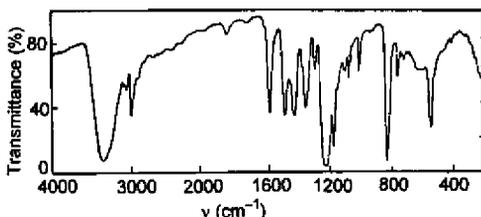


Figure 1. IR Spectrum of synthesized BPA.

examined by its solidification point measurement, DSC, IR, and ¹H-NMR spectroscopy.

RESULTS AND DISCUSSION

Bisphenol A was prepared by condensation reaction of acetone and phenol in presence of an acid catalyst and promoter. Anionic mechanism is suggested for this reaction by researchers [17].

The details of synthesis and purification of bisphenol A were discussed in previous report [1]. In this work, the influence of temperature, concentration of reactants, catalyst and promoter on bisphenol A yield are discussed.

The effect of temperature on percent conversion of bisphenol A was studied as follows: A series of experiments were carried out at various temperatures, while the concentration of reactants (phenol and acetone), catalyst and promoter (if any) were kept

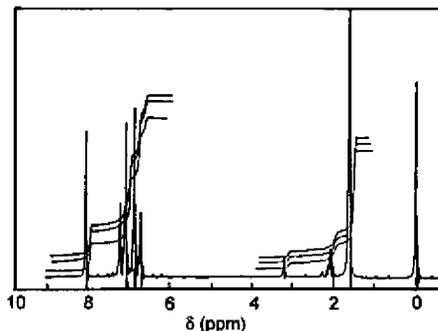


Figure 2. ¹H NMR Spectrum of synthesized BPA.

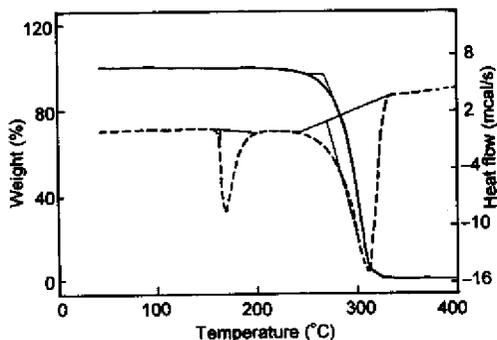


Figure 3. DSC-TG Thermograph of synthesized BPA.

constant. After definite period of time (every 2 h for four consecutive times of reaction mixtures), the reaction mixture was quenched in cold water. The BPA precipitate was filtered, water washed in several stages at specific thermal conditions, dried and weighed until finally the percent conversion of BPA was obtained.

The results of the first series of experiments carried out in the presence of promoter, is shown in Figure 4. As it is represented in temperature-conversion curves at 2, 4, 6, and 8 h of reaction mixtures, the BPA yield shows positive temperature dependence in the range of 40–60 °C, and above 60 °C, and the conversion product is white at 60 °C, which is an indication of its high quality, and turns yellow above this

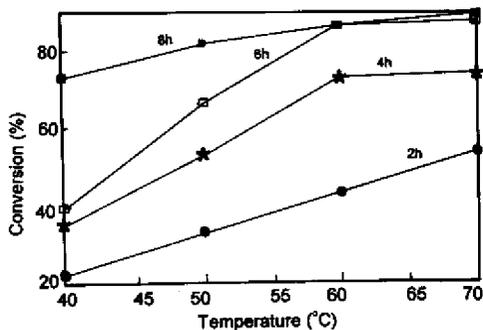


Figure 4. The effect of temperature on conversion of BPA with promoter.

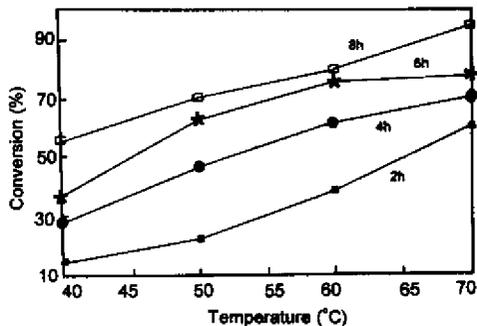


Figure 5. The effect of temperature on conversion of BPA without promoter.

temperature which needs further treatment. In the absence of promoter (Figure 5), the BPA yield increases with temperature within the range of 40–70 °C, but the colour of the product turns yellowish with increasing the temperature.

The variation of percent conversion with reaction time in the presence of promoter and in its absence is presented in Figures 6 and 7, respectively. As these time-conversion curves show, at a temperature of 60 °C, with promoter, the BPA yield reached about 87% in 8 h reaction time, while at 40 °C and after 8 h, the BPA yield was only 72%. In the absence of promoters BPA yield is even lower.

The effect of temperature on conversion is also

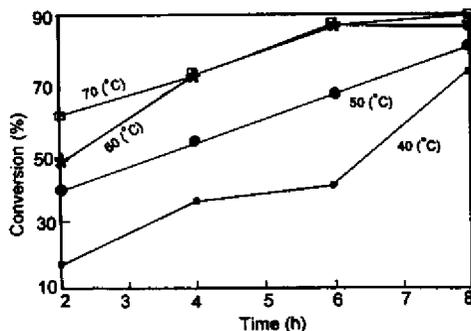


Figure 6. Variation of conversion of BPA with reaction time with promoter.

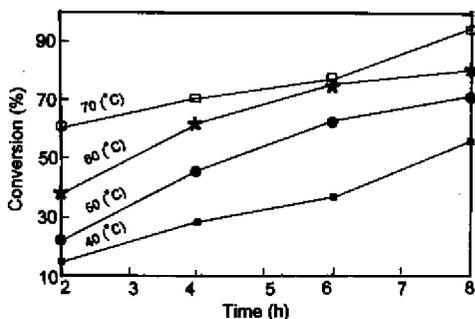


Figure 7. Variation of conversion of BPA with reaction time without promoter.

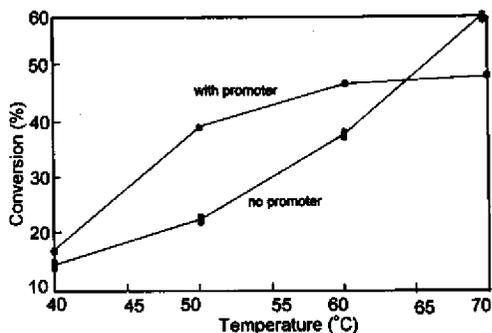


Figure 8. The effect of temperature on conversion of BPA (for 2 h reaction).

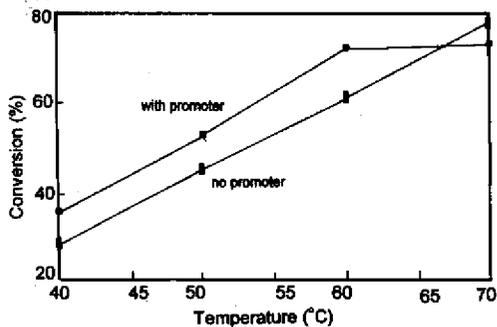


Figure 9. The effect of temperature on conversion of BPA (for 4 h reaction).

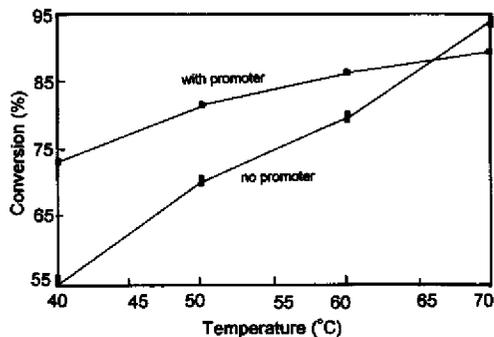


Figure 10. The effect of temperature on conversion of BPA (for 6 h reaction).

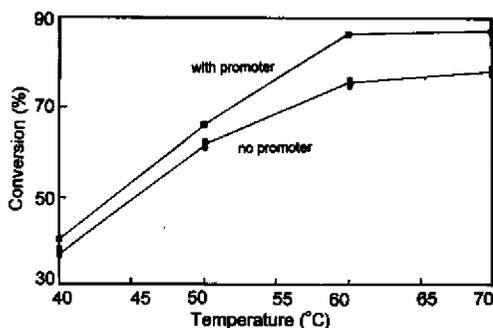


Figure 11. The effect of temperature on conversion of BPA (for 8 h reaction).

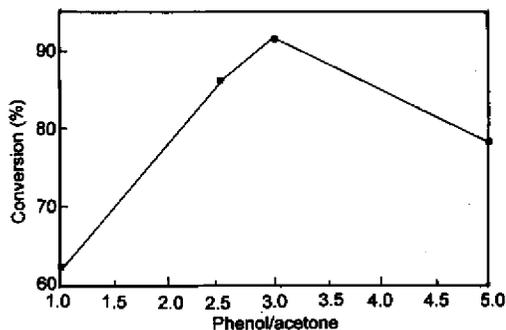


Figure 12. The effect of phenol:acetone ratio on conversion.

presented in Figures 8–11 for reaction time of 2, 4, 6 and 8 h. As it is indicated, the BPA yield is low in the absence of promoter but it increases in the presence of promoter in the range of 40–60 °C.

At 70 °C, it seems that the BPA yield in the absence of promoter is higher, but, because of the presence of traces of the by-products the quality of BPA is not so good and it is yellowish in colour. Other researchers also found the following BPA isomers and co-dimers with freezing point range of 133–191 °C as by-products [17, 18]: –2-(2-hydroxyphenyl)-2-(4-hydroxyphenyl) propane or *o,p'*-bisphenol A, freezing point = 111 °C; –2,4-bis(α,α -dimethyl-4-hydroxybenzyl) phenol or bisphenol X, freezing point = 191 °C; –4,4'-hydroxyphenyl-2,2,4-trimethylchroman or co-dimer of Dianin's compound, freezing point = 158 °C; –2,4'-hydroxyphenyl-2,4,4-trimethylchroman or isomeric co-dimer, freezing point = 133 °C.

The trace impurities which cause discoloration in the product, should be eliminated by further purification. This means that additional purification stages and so more cost investment are needed. We obtained a very white colour BPA by recrystallization of the yellowish product in appropriate solvents, but this process is cost effective.

The concentration of reactants, phenol:acetone ratio have a significant effect on BPA yield, and a 90% yield was obtained by reaction of 3 moles of phenol with 1 mole of acetone (Figure 12). When the phenol:acetone ratio was reduced, the yield

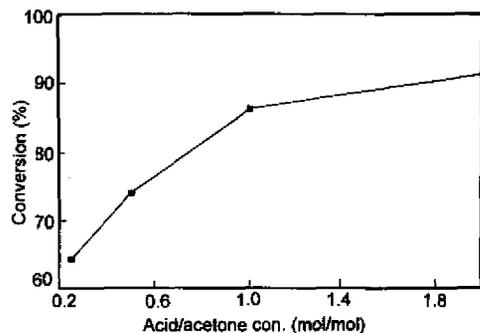


Fig. 13. The effect of acid concentration on BPA conversion.

dropped significantly and the colour of the product changed from white to dirty yellow. It should be mentioned that the excess phenol can be recycled after recovery. The concentration of acid catalyst for highest yield is also found to be at acid ratio of 1 for each mole of acetone (Figure 13).

CONCLUSION

As discussed before, to evaluate the effect of temperature, concentrations of the catalyst, reactants, and promoter on conversion, a series of experiments were carried out at different conditions. As the results show, the yield and quality of the BPA depend greatly on temperature and other variables. Therefore, the optimum conditions to obtain a high yield of BPA with good quality is a reaction time of 6 h, at 60 °C and 3:1 molar ratio of phenol to acetone in the presence of promoter. The quality of the sample at these conditions is standard. The next stage of this work is to scale up this process of BPA production to be able to design the pilot plant.

REFERENCES

1. Rahimi A. and Farhangzadeh S., *Iran. J. Polym. Sci. Tech.*, **8**, 28, 97–103, 1995.
2. *Ulman's Encyclopedia of Industrial Chemistry*, **A19**, 348–352, 1991.
3. Penczek P. and Wiertel M., *Inter. Polym. Sci. Tech.*, **20**, 8, T/91, 1993.
4. Galloudec F., Costa-Torro F., Laupretre F. and Jasse B., *J. Appl. Polym. Sci.*, **47**, 823–832, 1993.
5. Iranov D. G., Rejnik M. G. Chekhovskoi B. Ya., Sorokin V. P. and Shil'galis Yu., *Inter. Polym. Sci. Tech.*, **18**, 2, PT/60, 1991.
6. Dabiri H. E., Rahimi A. and Farhangzadeh S., *Iran. J. Polym. Sci. Tech.*, **7**, 3, 191–203, 1994.
7. Marks M. S. and Sekinger J. K., *Polymer*, **36**, 1, 209–215, 1995.
8. Andreeva L., Kolerov A. S., Vakhtinskaga T. N., Soloveva I. I. and Yudakova T. N. *Inter. Polym. Sci. Tech.*, **20**, 12, 40, 1993.

9. Marks M. J., Brewster S. L. and Sekinger J. K., *J. Appl. Polym. Sci.*, **52**, 1809-1814, 1994.
10. Lee P. L., Kowalewski T., Poliks M. D. and Schaefer J., *Macromolecules*, **28**, 2476-2482, 1995.
11. Strehmel V., Eetsel H. and Strehmel B., *J. Appl. Polym. Sci.*, **60**, 1221-1229, 1996.
12. Yong Wang, Dacheng Wu, Xingguang XIE and Ruxia L.; *Polymer J.*, **28**, 10, 896-900, 1996.
13. Blyumenfeld' d Kalugina E. V.; Bolotina L. M. and Sabina M. E., *Inter. Polym. Sci. Tech.*, **20**, 12, PT/45, 1993.
14. Zaldúa A. M., Eugenia Munoz M., Pena, Juan J. Suntamaria A., *Macromol. Rapid Commun.*, **16**, 417-429, 1995.
15. Chol Gi Dae, Kim S. H., Jo W. H. and Rhim M. S., *J. Appl. Polym. Sci.*, **55**, 561-569, 1995.
16. Mitra N. C., Banerjee R. S. and Sarkar A., *J. Appl. Polym. Sci.*, **42**, 2499-2598, 1991.
17. Oliver L.D., SRI, Stanford Research Institute, Sep. 1975.
18. Brydia L.E., *Analytical Chemistry*, **40**, 14, Dec. 1968.