

## Kinetics Study of Bisphenol A Synthesis by Condensation Reaction

Azam Rahimi\* and Salwa Farhangzadeh

Department of Polymer Science & Catalysts, Iran Polymer Institute, P. O. Box: 14965/115, Tehran, I.R. Iran

Received 15 November 2000; accepted 23 January 2001

### ABSTRACT

Bisphenol A (BPA) is the most important bisphenols, which is used industrially for the manufacture of polycarbonate resins and epoxy resins. These two applications have achieved greatest significance in recent years and consume over 90% of the BPA output. BPA was prepared in our laboratory by condensation reaction of acetone with excess phenol in presence of an acid catalyst and promoter in high yield and high state of purity at optimum conditions of variables. In this paper we discuss the mechanism and kinetics aspects of BPA condensation reaction to acquire a better understanding of the course of the reaction.

**Key Words:** bisphenol A, condensation reaction, kinetics, mechanism, yield

### INTRODUCTION

The importance of bisphenols has increased continually with the growth of the plastics industry. Bisphenol A or 4,4'-isopropylidene diphenol, the most widely used bisphenols, is an important intermediate for high-grade thermosets, thermoplastics and as a raw material in the production of epoxy resins and polycarbonate resins [1]. Bisphenol A is also used as antioxidant for brake fluids and as a stabilizer for PVC-resins, oxo-alcohols and their esters. It is used as fungicide, to a limited extent, in textile and asphalt coverings. Bisphenol A is a solid compound with white to dark tan colour, based on its purity. It has a melting point 157–158 °C and a boiling point 220 °C at 4 mmHg, and phenolic smell.

Various methods were employed to synthesize bisphenol-A. One procedure, for example, involved the use of sulphuric acid or hydrochloric acid, and another improved procedure involved the development of a solid cation-exchange resin catalyst [2]. The kinetics of BPA production has been studied by many researchers. Takenaka [3] has suggested the anionic mechanism for the reaction of phenol and acetone under a low pressure of hydrogen chloride to give BPA. A very similar mechanism has been proposed by Schnell [4]. Schnell has also presented mechanisms for the alkaline condensation of phenol with acetone.

In this paper we discuss the mechanism and kinetics aspects of condensation reaction of acetone with phenol in presence of acid as catalyst and a

(\*) To whom correspondence should be addressed.

suitable promoter.

On the basis of literature studies and kinetics data that we have obtained in our laboratory we have a better understanding of the course of the reaction.

## 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 domestic chemical suppliers. The other materials, which were used in small proportions, were obtained from Merck Chemical Co.

IR Spectra of the product were recorded by a Phillips PU 9712 infra-red spectrophotometer. H NMR Spectra were recorded on a JEOL-PMX 60 MHz 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 (94 g), acetone (12.75 g), HCl catalyst (37.5 g) and thioglycolic acid (0.5 g) promoter were placed in a three necked-round bottom flask equipped with a condenser, mechanical stirrer

**Table 1.** Bisphenol A yield (on the basis of acetone) at different reaction times.

Sample	T (min)	Weight (g)	Yield (%)
1	20	17.22	11.4
2	30	32.46	21.5
3	50	48.92	32.4
4	60	58.22	38.6
5	80	72.18	47.8
6	120	78.95	53.2
7	190	102.98	68.2
8	300	123.45	81.8
9	360	130.01	86.1
10	420	134.54	89.1
11	480	137.56	91.1
12	515	137.95	91.4
13	900	136.20	90.2

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 the given time. Then, the product was washed, dried and weighed. This experiment was repeated with optimum concentrations of reactants, catalyst, and promoter at various temperatures. The purity of each sample was examined by its solidification point, DSC, IR, and H NMR spectroscopy. Then, the yield of the reaction was calculated for each experiment. Table 1 shows the average results at different period of reaction time. Excess phenol was recovered by conventional method.

## RESULTS AND DISCUSSION

### Bisphenol A Synthesis

Bisphenol A is prepared by the condensation of two molecules of phenol with one molecule of acetone in the presence of acid catalyst, and suitable promoter according to the following reaction: Many factors affected the reaction time and yield, such as reaction temperature, phenol/acetone molar ratio, volume of acid catalyst, concentration of promoter.

As a national project supported by the National Center for Scientific Research, bisphenol A was prepared in our laboratory by the reaction of industrial grade acetone and excess phenol using concentrated hydrochloric acid as a condensation agent and organic sulphur compound as promoter.

After purification and drying, the solidification point of the white solid product was found about 156–157 °C. The purity of bisphenol A obtained was determined by IR and NMR spectroscopy and differential scanning calorimetry-thermal gravimetry (DSC-TG).

The results indicate that the product was obtained in high state of purity [5].

Then a series of experiments were carried out at different conditions to evaluate the effect of temperature, catalyst concentrations, reactants, and promoter on the reaction yield. As the results show 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 (Table 1) [6].

### Reaction Mechanism

As it was mentioned above, the condensation reaction of phenol and acetone takes place in presence of an acid, normally hydrochloric acid, and a promoter mostly thioglycolic acid [5]. It appears that the thioglycolic acid reacts readily with acetone to form  $(\text{CH}_3)_2\text{C}(\text{SCH}_2\text{COOH})_2$  which acts as a proper promoter.

This reactive compound form an active intermediate with HCl. Then it attacks in the *para*-position to form the carbonium ion  $p\text{-COC}_6\text{H}_4\text{C}(\text{CH}_3)_2^+$ , which in turn attacks the second molecule [7] of phenol to form BPA.

According to Schnell it was supposed that the first step of the reaction i.e. the formation of *para*-carbinol, 4-(4-hydroxyphenyl)-2-propane-2-ol, to be the rate-determining step. De Jang et al. [8, 9] work confirmed this assumption and explained the preference for *para*-position. They investigated that at 60–90% conversion, when the phenol concentration is constant, the first order reaction in acetone is observed. They also synthesized the *para*-carbinol as white crystals, which react very fast with phenol in toluene and sulphuric acid and give a quantitative yield of bisphenol after 5 min at room temperature.

### Reaction Kinetics

De Jong et al., studied the kinetics of the condensation reaction of stoichiometric amounts of phenol and acetone in the presence of large amount of acid catalyst and a small amount of promoter. They found that the plots of the yield (R%) in the form of:

$$-\log(100-R)/100 = kt \quad (1)$$

This relation gives straight lines in the range of 60–90% conversion in which the phenol concentration is constant, and in this condition a simple kinetics expression for the reaction rate ( $v$ ) of BPA formation was derived and reduced to observed first order reaction in acetone:

$$v = k' [A] \{C_0 + C_T [T]\} \quad (2)$$

where: A and T are the concentration of acetone and thioglycolic acid and  $k'$ ,  $C_0$  and  $C_T$  are constants.

These results confirm the picture of mechanism of bisphenol A formation given above. Gupta et al., [7] investigated the operating conditions for the maximum yield at the optimum conditions of variables and expressed the yield-time relationship for all variables fixed at the maximum yield level as the following equation which is in better agreement with experimental data:

$$X = 1 - (1+0.03t)^{-2.0} \quad (3)$$

where: X is fraction conversion of the limiting component (mol/mol).

In order to understand the course of the reaction, a series of experiments were conducted in our laboratory on the basis of these kinetics studies to obtain the necessary information for designing a pilot plant for industrial production of BPA in Iran. These experiments were carried out at 60 °C for all other variables, such as concentrations of catalyst and reactants, fixed at the maximum yield level. The reaction mixture was quenched after a given period of time and the precipitated product was washed, dried and weighed. The yield of the reaction with acetone base was calculated for each experiment. The plot of yield vs. time is shown in Figure 1.

The plots of the yield (R%) in the form of eqn (1) give a straight line in the range of 60–90% conversion (Figure 2), which is in good agreement with literature data. In these conditions, the rate in relation to acetone is followed as a first order reaction.

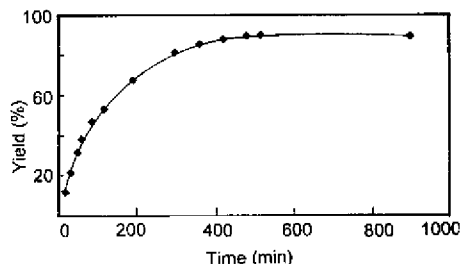


Figure 1. The plot of yield vs time for bisphenol A formation.

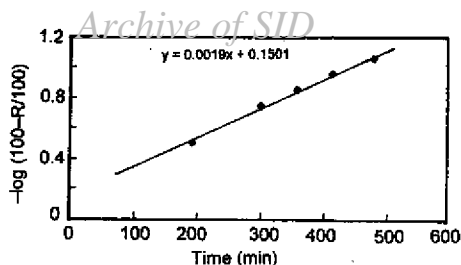


Figure 2. The plot of  $-\log(100-R/100)$  vs time for bisphenol A formation.

## CONCLUSION

The mechanism and kinetics of the condensation reaction of BPA production from industrial starting material were studied. The kinetics data were obtained at 60 °C for all other variables fixed at the maximum yield level. The obtained yield-time relationship was obtained and was in good agreement with literature. It was found that in the range of 60–90% conversion the observed reaction rate in acetone is followed as first order.

## REFERENCES

1. Dabiri H.E., Rahimi A., Farhangzadeh S. and Sajjadi N., "Polycarbonates: synthetic methods and applications", *Iran. J. Polym. Sci. & Tech.*, **7**, 3, 1994.
2. Faler, et al., "Method and catalyst for making bisphenol", US Pat., 4294, 995, Oct. 13, 1981.
3. Takenaka J., Yamamoto T. and Hirano Y., "Preparation of bisphenol A", *Kogyo Kagaku Zasshi*, **70**, 11, 2081–8, 1967.
4. Schnell H. and Krimm H., "Über die bilung und spaltung von dihydroxy-diarylmethan-derivaten", *Angew. Chem.*, **75**, 662, 1963.
5. Rahimi A., Farhangzadeh S. and F. Ziaee, "The effect of temperature, catalyst, and reactants on yield of BPA synthesized from industrial synthetic materials", *Iran. Polym. J.*, **8**, 1, 1999.
6. Rahimi A. and Farhangzadeh S., "Preparation and identification of BPA", *Iran. J. Polym. Sci. & Tech.*, **8**, 2, 1995.
7. Gupta S.R. and Dwivedi M.C., "The manufacture of bisphenol A", *Chem. Age India*, **22**, 6, 1971.
8. J.I. De Jong, "The alkylation of phenol with isobutene", *Recueil*, **83**, 469–476, 1964.
9. De Jong J.I. and Dethmers F.H.D., "The formation of 2,2-bis(4-hydroxyphenyl)-propane (bisphenol A) from phenol and acetone", *Rec. Trav. Chim.*, **84**, 4, 460–464, 1965.