

# Synthesis of Solid Epoxy Resins Base on BPC II and Bisphenol A Using Conventional Heating Equipment and Microwave

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Received 4 May 2004; accepted 9 December 2004

DOI 10.1002/app.21904

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** New solid state epoxy resins based on diglycidyl ether of 1,1-dichloro-2,2 bis (4-hydroxyphenyl), ethylene (BPC) and BPA epoxy resins in the reaction with BPC and BPA were developed. Solid epoxy resins were synthesized by the use of two different heating methods: conventional and microwave reactor. The use of microwave radiation as novel heating medium as an alternative to the conventional methods, which provide a quicker and more effective synthesis. The solid epoxies have high melting points higher than 100°C and the polycondensation degree

remains between  $n = 4$ –12. Epoxy value stays low and occurs around 0,02–0,1. BPA epoxy resins and diglycidylether of BPC II were compared in terms of reaction speed. It can be seen that the reaction of BPC diglycidylether occurs approximately 20% quicker given the same reaction conditions of temperature, and balance of catalyst. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3850–3854, 2006

**Key words:** solid-state; epoxy regins; diglycidyl ethers; 1,1-dichloro; 2,2-bis (4-hydroxyphenyl) ethylene

## INTRODUCTION

During the past few years a growing interest in epoxy resins has been observed. They can be characterized by excellent mechanical resistance and thermal stability, with high resistance to atmospheric conditions, which can be seen to have comparatively better properties than phenolic and polyester resins.

These epoxies offer a high chemical resistance and a strong adhesion to a majority of materials. After the addition of the curing agent, the mixture reduces in physical size; however, this reduction in size is insignificant compared with other resins. These advantages have resulted in the adoption of this resin throughout the manufacturing and construction sectors. Due to this large-scale acceptance, many different varieties of epoxies have been manufactured, beginning with liquid composition and finishing with solid-state products.

Current research focuses on the investigations of the synthesis of solid epoxies during the polyaddition reaction of the bisphenol with low-molecular-weight epoxies.<sup>1,2</sup> One of the biggest advantages of this

method is the lack of formation of byproducts, making it possible to avoid the cleaning stage of the final product.<sup>3</sup>

The use of microwave radiation as a novel heating medium as an alternative<sup>4,5</sup> to conventional methods could be expected to provide a quicker and more effective synthesis.<sup>6,7</sup> So far, radiation microwave heating has been used mainly in processing.<sup>8,9</sup>

The solid epoxies have melting points higher than 100°C and the polycondensation degree remains between  $n = 4$  and 12.<sup>10</sup> The epoxy value stays low and occurs around 0.02–0.1. Received direct method or indirectly, which is referred to as fusion process or polyaddition. Preparation is straightforward typically based as in epichlorohydrin and bisphenol A reactions; the mechanism of the reaction is similar to low molecular weight epoxy reactions. The method is based on catalytic fusion of low- or middle-molecular-weight epoxies with a suitable balance of bisphenol resulting in chain prolongation, as seen in Figure 1.

## EXPERIMENTAL

### Materials

Bisphenol A [2,2 bis(*p*-hydroxyphenyl) propane] was commercially available from Blachownia Chemical Works (Poland). Bisphenol II (C) [BPC II -1,1-di-

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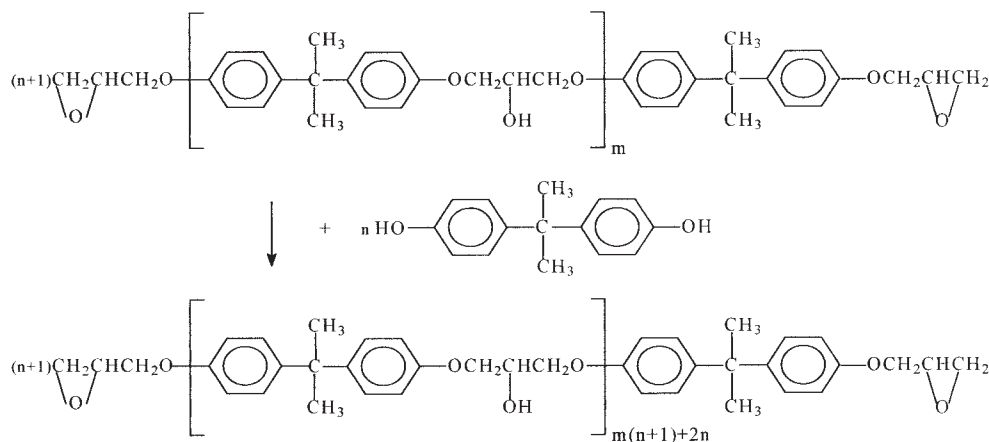


Figure 1 Polyaddition reaction.

chloro-2,2-bis(4-hydroxyphenyl)ethylene] was synthesized in our lab according to the description.<sup>1–3</sup> Three different low molecular epoxy resins were used. Two were of commercial grade: ARALDITE- GY 250 from Ciba Company Austria or Epidian 5<sup>®</sup> from Sarzyna Company (Poland); one was prepared in our lab: DGEBC II [diglycidylether of bisphenol II] (Figure 2).

### Preparation of DGEBC II

The diglycidylether of bisphenol II was prepared with a four-necked round-bottomed flask (1 L) equipped with a reflux condenser, thermometer, dropping funnel, and stirrer, containing 28.1 g (0.1 mol) BPC II and 185.6 g (2 mol) epichlorohydrin by stirring for 3 h at 115°C. During this time sodium methoxide was dropped into the reaction mixture.<sup>2</sup> After the addition of sodium methoxide, the reaction was stirred for another 2 h at boiling temperature. Thereafter the

reaction was filtered to remove the salt (NaCl). The remaining mixture contained methanol and epichlorohydrin, which was separated by distillation. The main product was crystallized from 1 dm<sup>3</sup> methanol : acetone mixture (3 : 2) The efficiency of diglycidyl ether (DGEBC II) was 78 wt %. The melting point was 97–99°C.

Solid-state epoxy was synthesized through the fusion reaction, the base consisted of a selection of low-molecular-weight epoxy resins, which were individually mixed for a homogeneous solution with bisphenol A and bisphenol C (II). The catalyst material used was triphenylphosphin (TTP) from Sigma–Aldrich Company for the epoxy-phenol treatment reaction.<sup>3</sup>

### RESULTS AND DISCUSSION

The main reaction was carried out using the same equipment. Epoxies and curing agents were added,

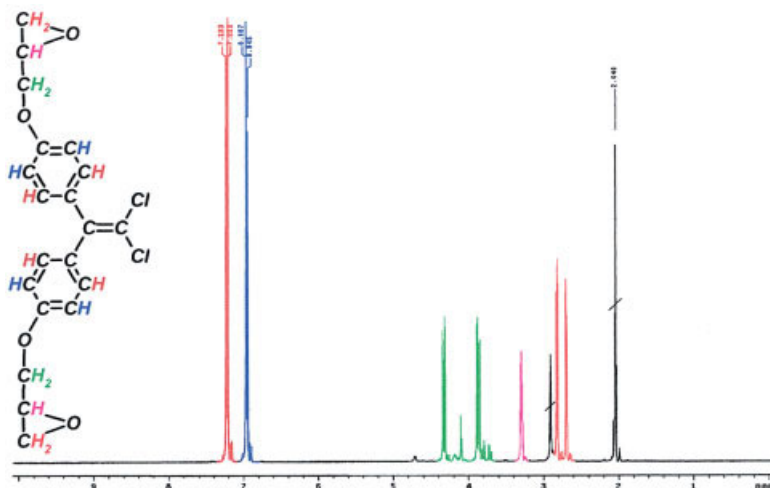


Figure 2 Structure and <sup>1</sup>H-NMR spectrum of DGEBC II. mp = 98°C; <sup>1</sup>H-NMR; 400 MHz (acetone) δ (ppm) = 7222 (d, 4H, ArH), 6956 (d, 4H, ArH), 4100 (m, 4H, O–CH<sub>2</sub>–CH), 3298 (m, 2H, CH–OCH<sub>2</sub>), 2756 (d, 4H, CH<sub>2</sub>O). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE I**  
**The Concentrations of All Reaction Mixtures Calculated Using 25 or 50 g Low-Molecular Epoxy Constant**

Lp.	Bisphenol A [w %]	BPC II [w %]	Rate [g/g] Bisphenol A/BPC II	Temperature [°C]	Time [min] Epidian5/DGEBC II	EN Epidian5/DGEBC II	Mw Epidian5/DGEBC II
Conventional							
1	100	0	17,778/0	120	100/40	0.11/0.098	1818/2048
2	100	0	17,778/0	145	80/40	0.109/0.097	1835/2070
3	100	0	17,778/0	170	60/20	0.1/0.096	2000/2083
4	0	100	0/19,150	120	100/40	0.122/0.100	1639/2008
5	0	100	0/19,150	145	80/40	0.119/0.097	1681/2062
6	0	100	0/19,150	170	30/20	-/0.094	-/2122
7	50	50	8,889/9,575	120	100/40	0.116/0.096	1724/2080
8	50	50	8,889/9,575	145	80/30	0.112/0.095	1786/2092
9	50	50	8,889/9,575	170	60/30	0.107/0.099	1969/2023
10	60	40	10,667/7,660	120	100/40	0.110/0.105	1818/1907
11	60	40	10,667/7,660	145	80/30	0.110/0.099	1818/2019
12	60	40	10,667/7,660	170	60/20	0.109/0.104	1835/1930
13	40	60	7,111/11,490	120	100/40	0.116/0.108	1724/1845
14	40	60	7,111/11,490	145	80/30	0.116/0.108	1724/1854
15	40	60	7,111/11,490	170	60/30	0.114/0.098	1754/2047
16	75	25	13,333/4,788	120	100/40	0.111/0.093	1802/2157
17	75	25	13,333/4,788	145	80/40	0.109/0.103	1835/1946
18	75	25	13,333/4,788	170	60/30	0.104/0.100	1923/1993
19	25	75	4,444/14,363	120	100/30	0.119/0.101	1681/1979
20	25	75	4,444/14,363	145	80/40	0.118/0.096	1695/2083
21	25	75	4,444/14,363	170	60/30	0.117/0.103	1709/1937
Microwave							
1	100	0	8,889/0	170	35	0.110	1818
2	0	100	0/9,575	170	20	—	—
3	50	50	4,445/4,788	170	40	0.12	1667
4	75	25	6,667/2,394	170	40	0.119	1681
5	25	75	2,222/7,182	170	50	0.077	2597

warmed, and mixed together. Two different heating systems were used: conventional electrical and novel, such as the microwave reactor.<sup>7,8</sup>

Several epoxies were heated using the microwave reactor,<sup>9</sup> a Multi-mode Microwave Reactor "Plazmatronika (microwave frequency: 2.45 GHz, maximum of microwave power: 600 W),<sup>11</sup> with connected thermometer. The power of the reactor during synthesis was programmed on constancy level 40% independent from mixture compositions; these reactions were conducted in an atmosphere of argon.<sup>12,13</sup>

Different syntheses were carried out using different epoxies, temperatures (120, 145, 170°C) and varied component concentrations (BPC II from 0 to 100%)<sup>14–16</sup>

The concentrations of all reaction mixtures were calculated using 25 or 50 g low-molecular epoxy constant. The concentration was calculated using the equation below<sup>12</sup> (Table I):

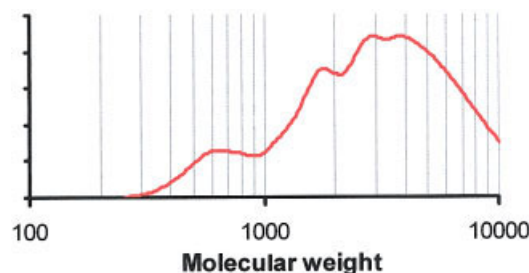
$$\frac{m_B}{m_E} = \frac{M_B(EV_P - EV_k)}{200 + M_B \times EV_k}$$

where  $m_B$  is the mass of bisphenol A (g),  $M_B$  is the molecular weight of bisphenol A (g/mol),  $m_E$  is the mass used for low-molecular-weight epoxy (g),  $EV_P$  is

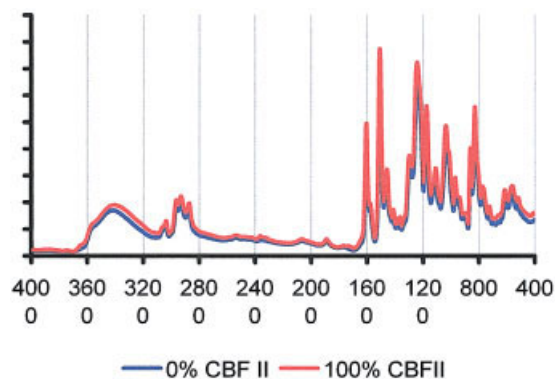
the epoxy value of the used low-molecular-weight epoxy (mol/100 g), and  $EV_k$  is the epoxy value of high-molecular-weight epoxy – ending material (mol/100 g).

Measuring epoxy number controlled the reaction condition. Depending on the reaction conditions the samples were taken every 5 or 10 min.

Using this synthesis method a variety of epoxy resins with different BPC II and bisphenol A concentrations were prepared. The melting point was marked using normalized methods PN –87/C –89,085/04 polydispersion level. The chromatograph GPC (Figure



**Figure 3** GPC of bisphenol A/BPC II : 25/75. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

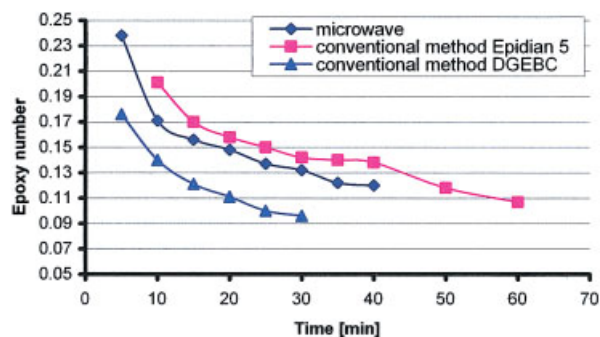


**Figure 4** FTIR: two different epoxies using the same heating method. 778–722 C–Cl<sub>2</sub>; 892 epoxide; ~ 970 C = CCl<sub>2</sub>; 1085,1038,1011 addition to phenol group; 1108 phenyl ether; 1245 ether peak; 1413–1362 C=O, OH; 1460 methyl group; 1509–1607 C=O; 1898–1884 aromatic group; 3037–2871 C–H. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

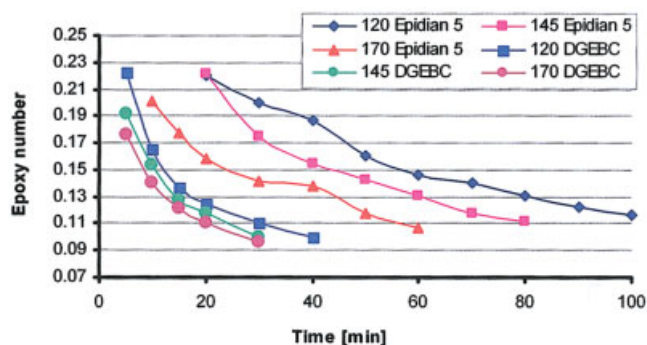
3) was used to visualize the molecular weight dispersion and the spectroscopic FTIR and <sup>1</sup>H-NMR (Figures 2 and 4) were used to investigate the chemical structure. Figure 5 shows comparative graph syntheses of bisphenol A/BPC II : 50/50 for led conventional and microwave method temperature 170°C using commercial epoxy Epidian 5 and DGEBC.

Comparison of these methods shows the best results of the processes occurs with the DGEBC conventional method. However the disparity between the results from commercial epoxy resins using conventional heating and microwave is not that considerable in magnitude. Furthermore it can be seen that there is a sizeable difference between DGEBC and commercial epoxy resin; this can be explained through differences in molecular weight as a function of chloral concentrations.

Figure 6 shows a comparative graph for the synthesis of two different weight relations of bisphenol A/BPC II: 75/25 and 25/75 using the conventional method.



**Figure 5** Bisphenol A/BPC II : 50/50- temp 170°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 6** DGEBC and Epidian 5: conventional method. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

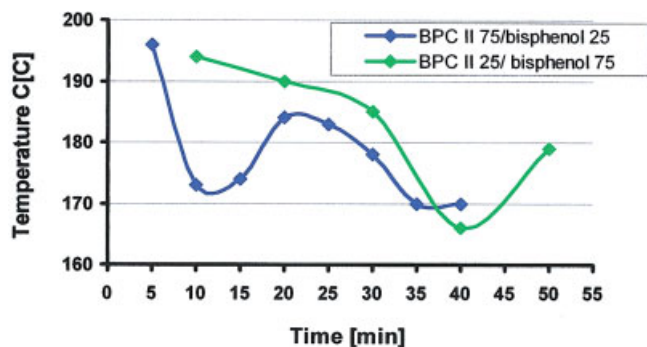
Figure 7 shows a comparative graph for syntheses of two different weight relations bisphenol A/BPC II : 75/25 and 25/75 using the led microwave method process. The graph shows time against mixture temperature, which portrays the changes of temperature occurring in the reactionary mixture, which was registered by the thermometer associated with the computer. The graph shows that the real temperature of the process depends on BPC II concentration

Measurements of viscosity were performed in 20% solutions of epoxy, in dioxane. The results graphed in Figures 8, 9, and 10) show that the viscosity increases when the concentration of bisphenol A increases and is accompanied by a fall in viscosity when the temperature rises.

The measurements can be seen to indicate (Figure 8) an increase in viscosity as well as viscosity shear rate. The largest growth in viscosity can be seen in bisphenol based epoxies: bisphenol addition/BPC II = 40/60%.

## CONCLUSIONS

Solid epoxy resins could successfully be synthesized by the use of two different heating methods: conven-



**Figure 7** Bisphenol A/BPC II : 75/25 and 25/75: microwave method. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

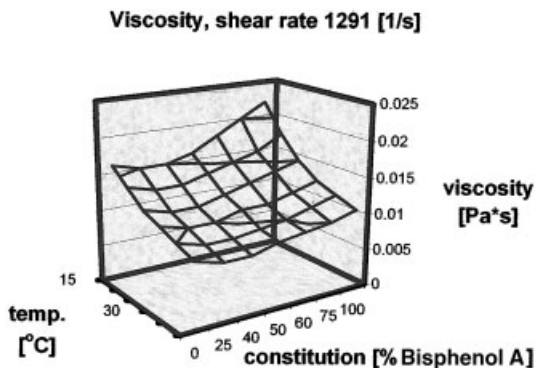


Figure 8 Dependence of viscosity versus temperature and resin.

tional and microwave reactor. It can be seen that the microwave reactor method is quite fast and convenient to use. However, the temperature is dependent on microwave power radiation, making it essential that suitable selections of these parameters are selected for the individual chemical reaction.

Previous work has shown the optimum power selection for the microwave reactor for this reaction type.

It was shown that reduction of the reaction time and a lowering of the reaction temperature resulted in a low epoxy conversion; a temperature that is too high, however, can cause premature solidification and epoxy degradation.

It also was observed, from the BPC II concentration under 75%, that the process temperature 170°C is too high and it would be advantageous to reduce it to a maximum of 145°C. With higher temperatures the reactions runs too furiously. In terms of commercial epoxy it was noted that, as the concentration of BPC II increases, the reaction time has to be increased.

In the case of commercial epoxy, this research shows that the use of microwave radiation decreases

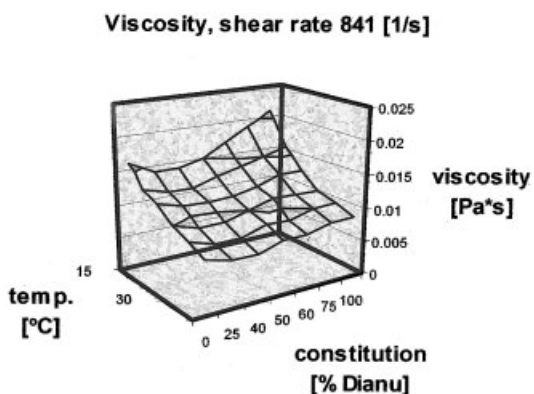


Figure 9 Dependence of viscosity versus temperature and resin content (shear rate 841).

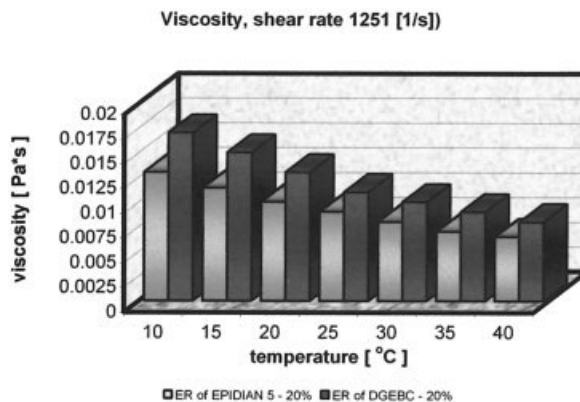


Figure 10 Dependence of viscosity versus resin composition.

the heating time significantly over conventional methods. Through comparison of the molecular weight dispersion from the chromatograph GPC, it was confirmed that these factors are not dependent on the heating medium.

Diglycidylether of bisphenol II base material, compared to commercial epoxies, such as Epidian® 5, is considerably easier to use due to the fact that it remains in solid-state form.

Comparing Epidian® 5 and diglycidylether in terms of reaction speed, it can be seen that the reaction of diglycidylether occurs approximately 20% quicker given the same reaction conditions of temperature and balance of catalyst.

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