

Synthesis and Characterization of Epoxy Resins Prepared Under Microwave Irradiation

Dariusz Bogdal, Jaroslaw Gorczyk

Department of Polymer Chemistry and Technology, Politechnika Krakowska, ul. Warszawska 24, 31-155 Krakow, Poland

Received 18 March 2004; accepted 20 May 2004

DOI 10.1002/app.21018

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

ABSTRACT: A new microwave-assisted method of synthesis of solid epoxy resins (SER) with desired epoxy-groups content is described. The method is based on the polyaddition of 4,4'-isopropylidenediphenol (BPA) to a lower-molecular-weight epoxy resin [Rütapox 0162, epoxy value (EV) = 0.57 mol/100 g] in the presence of 2-methylimidazole (2-MI), as a catalyst. Analogical syntheses were performed using conventional heating (i.e., electric heating mantle) for the comparison of properties of SER under both conditions. All the microwave reactions were carried out in the multi-mode microwave reactor Plazmatronika (Poland) with microwave frequency of 2.45 GHz and maximum microwave power of 600 W. The main advantage of the microwave

process is twofold reduction of reaction time in comparison to the conventional heating. Values of EV, \bar{M}_n , \bar{M}_w , \bar{M}_w/\bar{M}_n , and degree of branching of the products obtained were determined. It was found that the molecular weight distribution and degree of branching in resins synthesized under microwave irradiation was comparable with those obtained under conventional heating and was not influenced by the reduction in reaction time. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1969–1975, 2004

Key words: addition polymerization; branching; epoxy resins; irradiation; microwave

INTRODUCTION

Solid epoxy resins (SER) [epoxy value (EV) = 0.25–0.02 mol/100 g; \bar{M}_n = 1000–10,000] were introduced to the market in the 1950s.¹ They have found a large variety of applications in adhesives, casting compounds composite materials, electrical laminates, and coatings.² They possess unique properties after hardening, e.g., excellent chemical and electrical resistance, good adhesion and cohesion to different kinds of materials, and heat resistance.³ In industry, SER are manufactured according to the so-called advancement process.⁴ This method is based on the polyaddition of 4,4'-isopropylidenediphenol (BPA) to low-molecular-weight epoxy resin (EV = 0.58–0.35 mol/100 g; \bar{M}_n = 370–500) or middle-molecular-weight epoxy resin (EV = 0.30–0.15 mol/100 g; \bar{M}_n = 500–1,000) in the presence of a catalyst.^{5,6} The most commonly used catalysts are tertiary amines or phosphines, quaternary ammonium or phosphonium salts, and imidazole derivatives. The epoxy groups of low-molecular-weight epoxy resins are used in an excess in relation to active hydrogen atoms in BPA.³ The reaction is carried out for a couple of hours at the temperature range 140–180°C with nitrogen blanket to minimize oxida-

tive degradation reactions.⁷ It is possible to synthesize such resins in the melt,⁸ solvent,⁹ or water dispersion,¹⁰ both in the batch and continuous process.¹¹ Recently, it was shown that a number of polymers and polymeric materials can be successfully prepared, crosslinked, and processed under microwave irradiation.¹² In such applications, the reaction time and energy input were mostly reduced in the reactions that are run for a long time at high temperatures under conventional conditions. Therefore, we decided to investigate and show that SER can be prepared under microwave irradiation with a reduction of the reaction time in comparison with a conventional thermal treatment under strictly similar sets of conditions.¹³

EXPERIMENTAL

Materials

4,4'-Isopropylidenediphenol (BPA), 2-methylimidazole (2-MI), and trichloroacetyl isocyanate (TCAI) were obtained from Fluka and applied without further purification. Low-molecular-weight epoxy resin Rütapox 0162 (high content of the diglycidyl ether of bisphenol A, EV = 0.57 mol/100 g) was obtained from Bakelite AG.

Synthesis of solid epoxy resins

Constant molar ratio of BPA to the low-molecular-weight epoxy resin (3 : 4) was calculated according to the equation¹⁴

Correspondence to: D. Bogdal (pcbogdal@cyf-kr.edu.pl).

TABLE I
The Results of the Molecular Weight Distribution in SER by GPC

Epoxy resin sample	Conditions ^a	Reaction temperature (°C)	Catalyst content (mol×10 ³)	Reaction time (min)	Epoxy value (mol/100 g)	GPC		
						\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
1			0.5	150	0.114	1,810	3,260	1.80
2	MV	140	1.0	90	0.112	1,470	2,580	1.75
3			5.0	25	0.110	1,950	3,780	1.94
4			0.5	65	0.110	2,140	3,780	1.77
5	MV	160	1.0	40	0.113	1,850	3,390	1.83
6			5.0	20	0.104	2,470	3,390	1.83
7			0.5	65	0.109	2,380	4,340	1.85
8	MV	180	1.0	30	0.109	2,180	3,990	1.83
9			5.0	16	0.105	2,420	4,580	1.89
10			0.5	280	0.114	1,380	2,860	2.08
11	Δ	140	1.0	150	0.114	2,020	3,760	1.86
12			5.0	55	0.113	2,170	3,640	1.68
13			0.5	120	0.106	1,790	3,130	1.75
14	Δ	160	1.0	80	0.111	2,180	4,000	1.84
15			5.0	35	0.100	2,380	5,010	2.10
16			0.5	80	0.101	2,180	4,000	1.84
17	Δ	180	1.0	50	0.105	2,250	4,250	1.89
18			5.0	35	0.100	2,320	4,420	1.91

^a MV, microwave irradiation; Δ, conventional heating (i.e., electric heating mantle).

$$m_B = \frac{m_E \times M_B \times (EV_1 - EV_2)}{EV_2 \times M_B + 200}$$

where: m_B is the amount of BPA (g), m_E is the amount of the low-molecular-weight epoxy resin (g), M_B is the molecular weight of BPA, EV_1 is epoxy value of the low-molecular-weight epoxy resin, and EV_2 is the epoxy value of the desired solid epoxy resin (0.11 mol/100 g).

For the general procedure for the synthesis of SER, 11.65 g of BPA was combined with 25.0 g of low-molecular-weight epoxy resin ($EV = 0.57$ mol/100 g) and appropriate amount of the catalyst (given in Table I) at room temperature. To obtain the required increase in the molecular weight ($EV \sim 0.11$ mol/100 g) during the reaction, the mixture was stirred at 140, 160, and 180°C both under conventional heating (i.e., electric heating mantle) and microwave irradiation

TABLE II
The Results of Determination the Chain Branching in SER by ¹H-NMR

Epoxy resin sample	EEW	Number of branch points per molecule, r	Degree of branching, f	Chain branching (%)
1	877	0.49	0.10	9.84
2	893	0.47	0.09	9.23
3	909	0.29	0.06	5.57
4	909	0.38	0.07	7.30
5	885	0.36	0.07	7.15
6	962	0.45	0.08	8.07
7	917	0.31	0.06	5.89
8	917	0.33	0.06	6.27
9	952	0.44	0.08	7.99
10	877	0.59	0.12	11.85
11	877	0.53	0.11	10.64
12	885	0.44	0.09	8.74
13	943	0.43	0.08	7.90
14	901	0.41	0.08	7.97
15	1,000	0.64	0.11	10.95
16	990	0.40	0.07	6.93
17	952	0.45	0.08	8.17
18	1,000	0.66	0.11	11.29

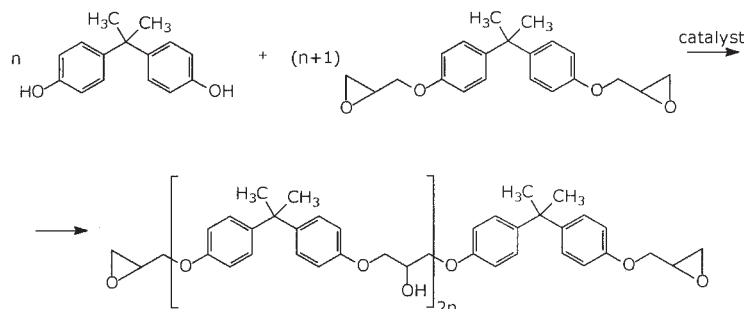


Figure 1 Advancement process: polyaddition of BPA to low-molecular-weight epoxy resin.

(i.e., multimode microwave reactor Plazmatronika (Poland) with microwave frequency of 2.45 GHz and maximum microwave power of 600 W). Small samples of the epoxy resin were periodically withdrawn from the mixture throughout the run to check the reaction progress. After the reaction, epoxy resin was cooled to room temperature and powdered. The properties of SER are given in Tables I and II, while the advancement process of SER is shown in Figure 1.

There are also two possible side reactions that are shown in Figures 2 and 3. These reactions lead to the increase of the degree of chain branching and finally to gelation of the reaction mixture. As a result the final product qualities can be worsened.

Measurement and characterization

Determination of epoxy value

Epoxy value of SER was determined according to the Polish Standard, PN-87/C-89,085/13. The method is based on titration of unreacted HCl (remaining after acid hydrolysis of epoxy group in the HCl/dioxane

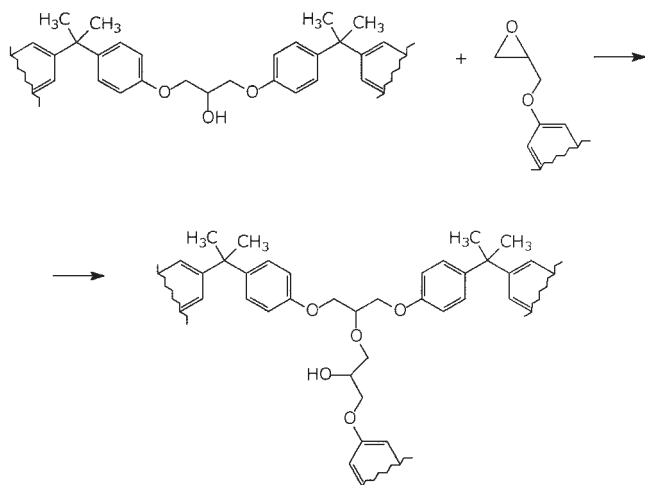


Figure 2 Side reaction: addition of the epoxy group to the secondary hydroxyl group.

mixture) with methanolic NaOH solution. Cresol red was used as an indicator.

Gel permeation chromatography (GPC)

The molecular weight distribution of SER was determined by gel permeation chromatography (GPC-Knauer chromatograph). A system of three columns: 2×PL-gel Mixed-E with one precolumn and refractometer detector was used. Conditions of measurements were flow rate, 0.8 mL/min; temperature, 30°C; and sample concentration, 20 mg/mL. Tetrahydrofuran (THF) dried over metallic sodium wire and distilled was used as an eluent. Polystyrene standards obtained from Waters Associates Inc. were used to calibrate the chromatograph. Results of all the analyses are shown in Table I.

Determination of branching by means of $^1\text{H-NMR}$ spectrometry

The $^1\text{H-NMR}$ method for determining branching relies on rapid reaction between TCAI and the secondary hydroxyl groups.¹⁵⁻¹⁷ After the reaction, the absorption of carbinol methine proton moves downfield from about 4.2 to 5.5 ppm. In such a way it is possible to estimate the number of branch points in macromolecules. Thus, for each sample, the $^1\text{H-NMR}$ spectra were recorded twice, i.e., before and after the reaction of the secondary hydroxyl group with TCAI. The calculation of chain branching in SER was based on the method of estimation proposed by Szczepaniak.¹⁸ The procedure and mathematical calculation were presented in our previous article.¹⁹ The $^1\text{H-NMR}$ spectra

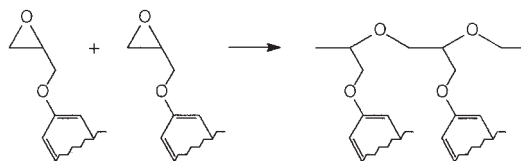


Figure 3 Side reaction: polymerization of epoxy groups.

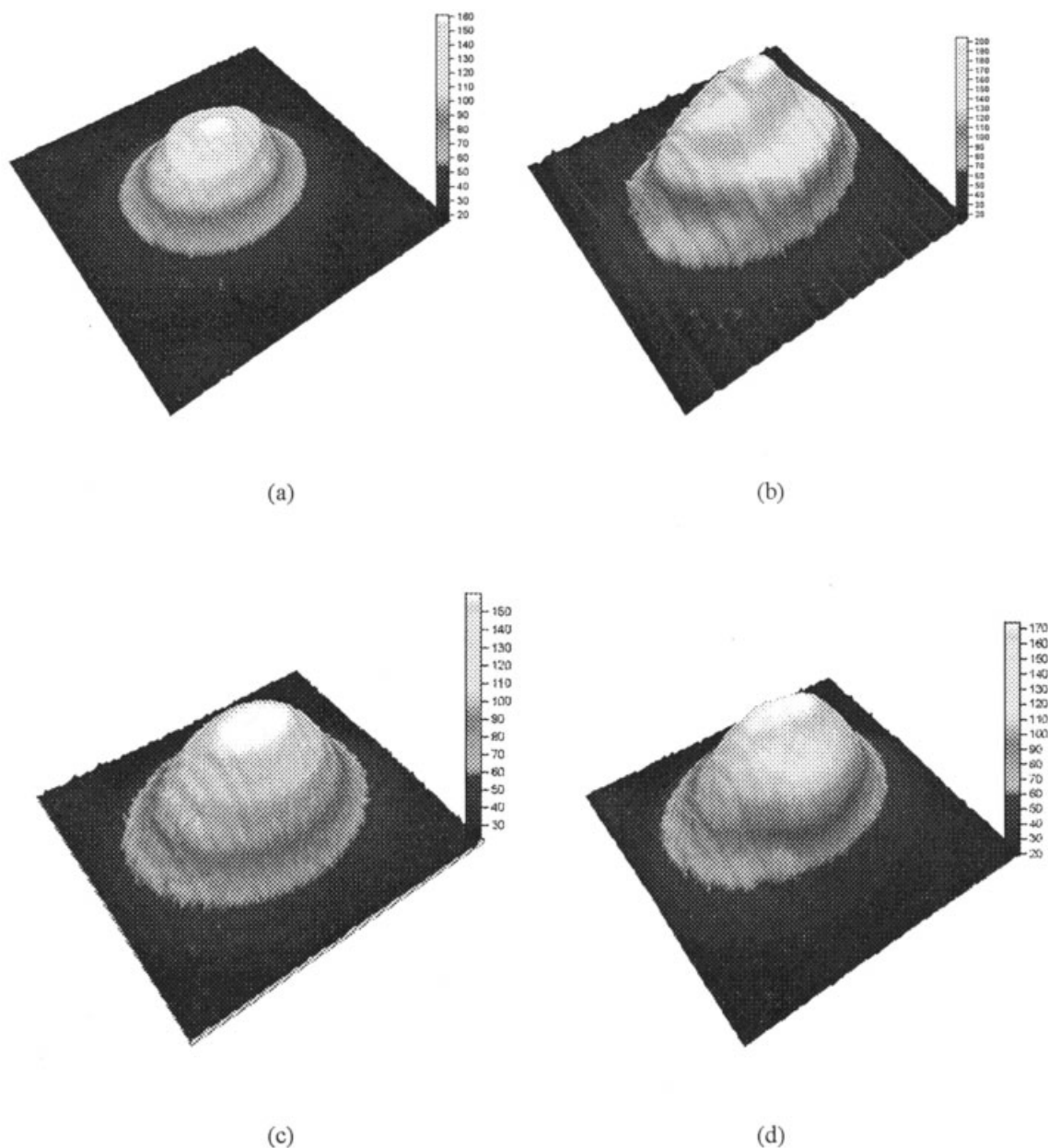


Figure 4 The surface temperature profiles of reaction mixtures recorded by the thermovision camera: (a) microwave stirred mixture; (b) microwave nonstirred mixture; (c) conventional stirred mixture; (d) conventional nonstirred mixture.

were recorded on a Merkury-300 Varian spectrometer operating at 300 MHz. Deuteriochloroform (CDCl_3) was used as the solvent. The results of all analyses are shown in Table II.

Surface temperature profile

The surface temperature profiles of reaction mixtures were recorded by the thermovision camera Vigo V-20E2.

RESULTS AND DISCUSSION

The reaction temperature range from 140 to 180°C was chosen because below 140°C the viscosity of the reac-

tion mixture, which grew during the reaction, was so high that stirring was impossible, while above 180°C the synthesized resin started changing the color from light yellow to deep yellow-brown.

As expected, at the given temperature the longest reaction time was observed in the presence of the lowest catalyst content (0.0005 mol N/mol OH in BPA). On the other hand, when the concentration of the catalyst is too high, the reaction is difficult to control since it is accompanied by a strong exothermic effect. It was found that the catalyst concentration above 0.005 mol N/mol OH in BPA caused a rapid gelation of the reaction mixture.

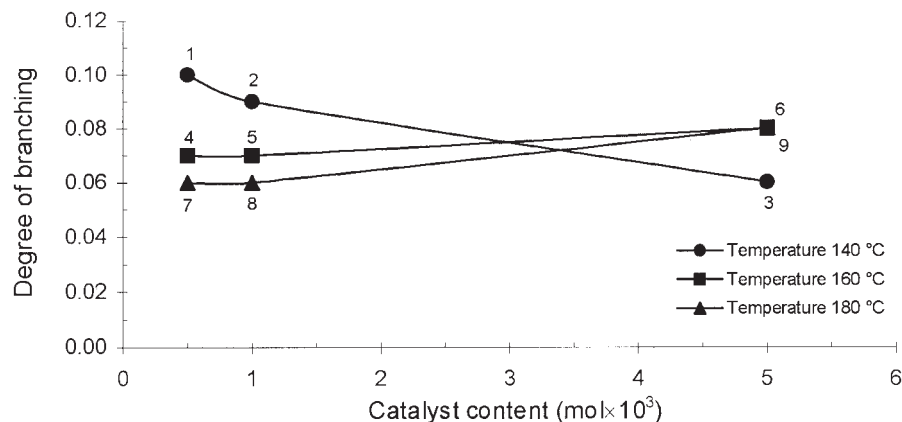


Figure 5 Degree of branching in SER synthesized under microwave irradiation as a function of the catalyst content.

The GPC analyses show that the SER synthesized under both conventional heating and microwave irradiation have comparable molecular weight distributions. As expected, the increase of reaction temperatures resulted in shorter reaction time as well as in the increase of molecular weights, but both (reaction time and molecular weights) were even more influenced by the catalyst content. At every pair of experiments (conventional versus microwave), under microwave conditions molecular weights were slightly higher, which can be attributed to faster heating rate (under microwave irradiation) to the desired reaction temperatures.

The differences in the surface temperature homogeneity that were recorded by means of a thermovision camera under microwave and conventional conditions for both stirred and nonstirred reaction mixtures are presented in Figure 4. The experiments were carried out at 160°C for the time necessary to obtain SER with the required EV (Table I). As expected for an exothermic reaction, the highest temperatures were observed in the center of the reaction vessel for all the processes [Fig. 4(a)—(d)]. Furthermore, for both microwave and

conventional processes, the stirring of the reaction mixture resulted in more uniform temperature profiles [Fig. 4(a) and (c), respectively], while for the nonstirred reaction mixture the maximum surface temperature under microwave irradiation was much higher (~ 200°C) than the bulk temperature. Moreover, for the nonstirred samples prepared under microwave irradiation, high temperature heterogeneity was observed [Fig. 4(b)], which, in turn, often led to crosslinking of resins. It was opposite to the reaction under conventional conditions, in which the temperature for the nonstirred reaction mixture was, however, more inhomogeneous than for the stirred mixture, but the maximum surface temperature reached only 170°C [Fig. 4(d)]. It leads to a conclusion that, in case of viscous reaction systems such as the mixture of low-molecular-weight epoxy resin with BPA, in some parts of a sample local temperature under microwave irradiation can be higher than the overall bulk temperature, and, therefore even pyrometers as well as fiber-optic thermometers are not capable of giving correct information about temperature. Moreover, in case of a high temperature gradient of processed ma-

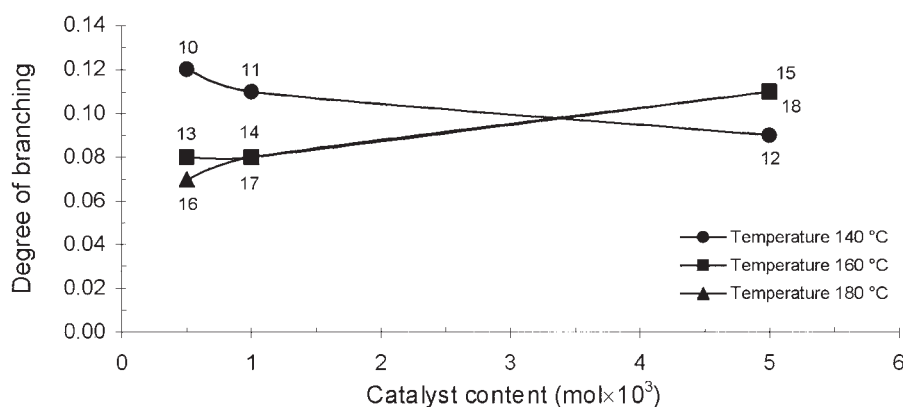


Figure 6 Degree of branching in SER synthesized under conventional heating as a function of the catalyst content.

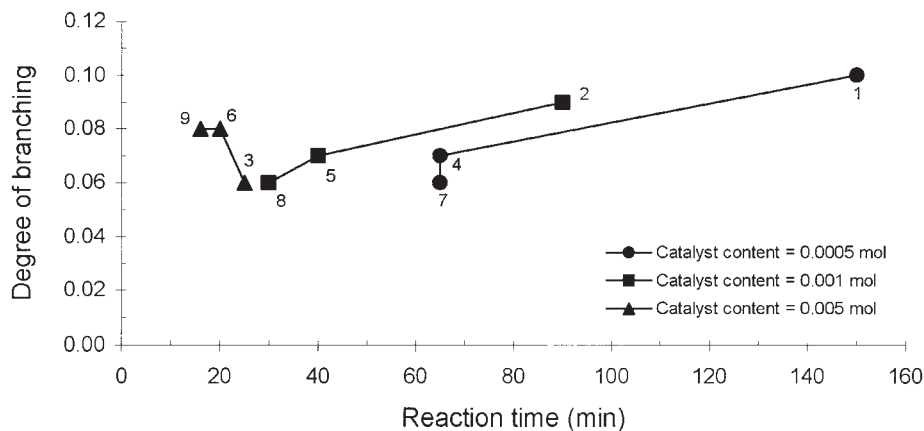


Figure 7 Degree of branching in SER synthesized under microwave irradiation as a function of the reaction time.

terial that can be observed with the maximum temperature at the center of the sample it is hard to say which is the bulk temperature of the reaction mixture. Eventually, a higher temperature of some parts of a material (hot spots) can be a reasonable explanation for higher rates and yields of number of reactions under microwave irradiation, which has been attributed to the so-called microwave effect, i.e., an increase of reaction rates that cannot be explained by an increase of temperature of reaction medium.

The results of the chain branching determination in the investigated SER by means of $^1\text{H-NMR}$ are presented in Table II. The percentage of branching was in the range of 6 to 12%, and it is consistent with the literature data.¹⁷ It is worth stressing that, under microwave conditions, the degree of branching was lower in all cases, which was the desired tendency in connection with shorter reaction times.

The relation between the degree of branching and catalyst content (results taken from Table II) is shown

in Figures 5 and 6. As seen, the degree of branching decreases with the increase of the catalyst content from 0.5×10^{-3} and 5.0×10^{-3} mol at the temperature range of 160 to 180°C, whereas at 140°C the opposite behavior was observed. It can be explained by shorter reaction time and, thus, lowering effect of side reactions. However, the low catalyst concentration i.e., 0.5×10^{-3} mol and long reaction time in lower temperature causes the inverse effect.

In the next step, we analyzed the relation of reaction time with the degree of branching at the same catalyst levels for different temperatures for both microwave and conventional conditions. The results are presented in Figures 7 and 8. It can be seen again that, for the catalyst concentrations 0.5×10^{-3} and 1.0×10^{-3} mol, the increase of temperature leads to the decrease in the degree of branching, which can be explained by shorter reaction times and, thus, the lowering effect of side reactions; however, for the catalyst concentration of 5.0×10^{-3} mol, an inverse effect was observed. The

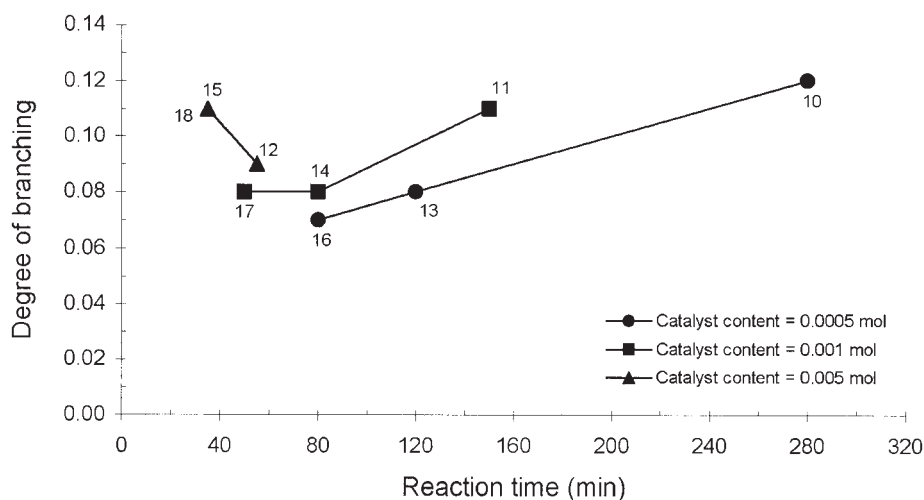


Figure 8 Degree of branching in SER synthesized under conventional heating as a function of the reaction time.

latter can be explained by the high exothermic effect of the reaction (i.e., 74.5 kJ/mol)⁵ and the higher temperature together with the higher catalyst concentration resulting in the increase of chain branching. Moreover, at the higher catalyst concentration, we observed a fast increase of the reaction mixture density, which, in turn, caused difficulty with proper stirring and temperature control.

CONCLUSION

It was demonstrated that it is possible to obtain SER with a desired epoxy group content applying microwave irradiation (2.45 GHz) to heat up the reaction mixture. The characterizations of the final products show that the epoxy resins prepared under microwave conditions have similar molecular weight distribution but possess less chain branching in comparison with those obtained under conventional heating. In general, all the syntheses performed in a microwave reactor needed a shorter reaction time than the syntheses under conventional conditions. The reaction time reduction varied from 20 to 55%, which can be an important economical factor when such syntheses are performed at a higher scale.

The Polish State Committee supported the research for Scientific Research Grant No. 7T09B06521.

References

1. Muskopf, J. W.; McCollister, S. B. *Epoxy Resins in Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2002.
2. Lee, H.; Neville, K. *Handbook of Epoxy Resins*; McGraw Hill Book Co.: New York, 1967.
3. Czub, P.; Boncza-Tomaszewski, Z.; Penczek, P.; Pielichowski, J. *Chemia i Technologia Żywic Epoksydowych*; WNT: Warszawa 2002.
4. Bryan, E. *Chemistry and Technology of Epoxy Resins*; Chapman and Hall: London, 1994.
5. Alvey, F. B. *J Appl Polym Sci* 1969, 13, 1473.
6. Rejdych, J.; Szczepaniak, B. *Polimery (Warsaw)* 1982, 27, 236.
7. Szczepaniak, B.; Penczek, P.; Rejdych, J. *Polimery (Warsaw)* 1998, 43, 732.
8. US Patent 3 006 891, 1961; US Patent 3 006, 892, 1961.
9. US Patent 4 212 781, 1980.
10. US Patent 4 122 067, 1978; EP Patent 0 577 958 A2, 1994.
11. US Patent 6 262 189 B1, 2001.
12. Bogdal, D.; Pielichowski, J.; Penczek P.; Prociak A. *Adv Polym Sci* 2003, 163, 193.
13. Bogdal, D.; Pielichowski, J.; Penczek, P.; Gorczyk, J.; Kowalski, G. *Polimery (Warsaw)* 2002, 47, 90.
14. Penczek, P.; Szczepaniak, B. *Acta Polym* 1991, 42, 112.
15. Rogers, M. D. *J Appl Polym Sci* 1953 1972, 16.
16. Batzer, H.; Zahir, S. A. *J Appl Polym Sci* 1975, 19, 585.
17. Batzer, H.; Zahir, S. A. *J Appl Polym Sci* 1975, 19, 601.
18. Szczepaniak, B. PhD Dissertation; Industrial Chemistry Research Institute: Warszawa, 1996.
19. Gorczyk, J.; Bogdal, D. Determination of Chain Branching in Solid Epoxy Resins Using ¹H NMR Spectrometry; Proceedings of ECSOC-6, The Sixth International Electronic Conference on Synthetic Organic Chemistry: September 1–30, 2002.