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Polymer 44 (2003) 7795–7800

polymer

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Microwave assisted synthesis and determination of chain branching in solid epoxy resins using ^{1}H NMR spectrometry

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Received 25 March 2003; received in revised form 17 October 2003; accepted 22 October 2003

Abstract

The degree of branching in solid epoxy resins (epoxy value EV = 0.11 mol/100 g) prepared under microwave and conventional conditions has been investigated by ^{1}H NMR spectrometry. The applied method involves rapid reaction between trichloroacetyl isocyanate and hydroxyl groups incorporated in the epoxy resin structure. Solid epoxy resins were prepared by polyaddition of Bisphenol A (BPA) to a lower-molecular-weight (L-M) epoxy resin (Rütapox 0162, EV = 0.57) in the presence of 2-methylimidazole (2-MI) as a catalyst. All the microwave reactions were performed in the multimode microwave reactor *Plazmatronika-Poland* with microwave frequency of 2.45 GHz and maximum of microwave power of 600 W. The results show that the degree of branching in resins synthesized under microwave irradiation is comparable with those obtained under conventional heating (i.e. 6–12%) and is not influenced by the reduction of reaction time.

Keywords: Solid epoxy resins; Microwave irradiation; NMR

1. Introduction

Epoxy resins are produced from the beginning of 50-ths. Because of their unique properties, e.g. excellent chemical and electrical resistance, good adhesion to different kinds of materials and heat resistance, they are used in various kinds of everyday life [1]. Solid epoxy resins (EV = 0.25–0.02; $M_n = 1000-10,000$), which are used in industry of varnishes and dyes, are mostly synthesized according to indirect method [2–6]. This method, called *advancement process* is based on polyaddition of Bisphenol A (BPA) to low-molecular-weight (L-M) epoxy resin (EV = 0.58–0.35; $M_n = 370-500$) or middle-molecular-weight (M-M) epoxy resin (EV = 0.30–0.15; $M_n = 500-1000$) in the presence of a catalyst [7–10]. It is possible to synthesize such resins in a batch or continuous process. Recently, we have shown that solid epoxy resins can be prepared under microwave irradiation which reduces the reaction time [11,12].

Schematic reaction of synthesis of high molecular weight epoxy resins is shown in Fig. 1.

As one can see in Fig. 1 each molecule of epoxy resin contains as many aliphatic hydroxyl groups as there are repeated units in the linear structure. These hydroxyl groups are potential branch points, thus for every branch point in a nonlinear structure there is one hydroxyl-carbinol methine pair less in comparison with the linear structure of equal molecular weight (Fig. 2).

The ^{1}H NMR method for determining branch points relies on rapid reaction between trichloroacetyl isocyanate and hydroxyl groups incorporated in the epoxy resin [13–16]. After the reaction, the absorption of carbinol methine proton moves downfield from about 4.2 to 5.5 ppm. In such a way is possible to estimate the number of branch points in macromolecules. For each sample, the ^{1}H NMR spectra are recorded twice i.e. before and after the reaction of hydroxyl group with trichloroacetyl isocyanate. These spectra are shown in Fig. 3.

2. Theoretical calculations

The degree of chain branching estimation proposed by Szczepaniak [17], relies on the calculation of the so-called reduced integration Z_k (1), which is the ratio of the given signal integration value A_k to standard signal integration

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doi:10.1016/j.polymer.2003.10.051

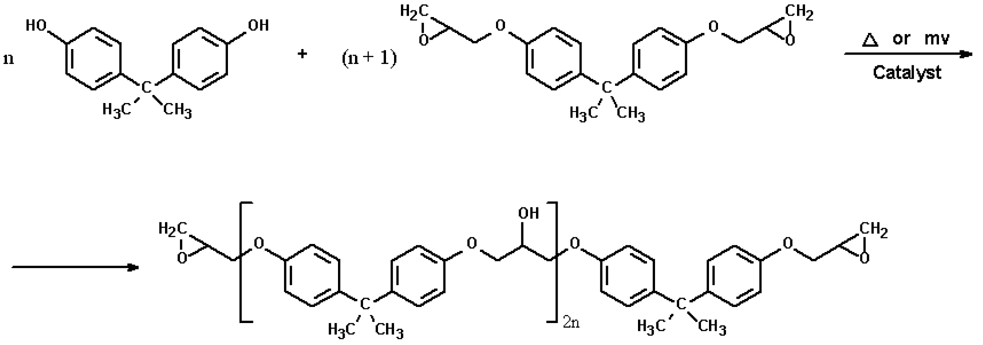

Fig. 1. *Advancement process*—polyaddition of BPA to L-M epoxy resin (e.g. Bisphenol A diglycidyl ether).

value S (2). Z_k can be expressed as follows

$$Z_k = \frac{A_k}{S} \quad (1)$$

$$S = \frac{1}{2}\left(\frac{1}{8}A_{\text{Aromatic}} + \frac{1}{6}A_{\text{Methylene}}\right) \quad (2)$$

where Z_k-reduced integration of 'k' signal, A_k-integration of 'k' signal, A_{Aromatic}-integration of aromatic protons signal (7.0 ppm), $A_{\text{Methylene}}$-integration of methylene protons signal (1.6 ppm). The total number of methine protons Z_{Methine} (3) can be described as a fifth part of sum the reduced integration of methine and methylene signals before reaction

$$Z_{\text{Methine}} = \frac{1}{5}(Z_{4.1} + Z_{4.3}) \quad (3)$$

The number of methine protons in branched molecules Z_{Branched} (4) can be described as a difference between Z_{Methine} and the reduced integration of methine signal after reaction with trichloroacetyl isocyanate

$$Z_{\text{Branched}} = Z_{\text{Methine}} - Z_{5.5} \quad (4)$$

where $Z_{4.1}$-reduced integration of methylene signal before reaction, $Z_{4.3}$-reduced integration of methine signal before reaction, $Z_{5.5}$-reduced integration of methine signal after reaction.

In turn, the degree of branching f (5) can be calculated according to the formula

$$f = \frac{Z_{4.1} + Z_{4.3} - 5Z_{5.5}}{Z_{4.1} + Z_{4.3}} \quad (5)$$

Then it is possible to estimate the number of branch points per molecule r (6) according to the formula

$$r = f\frac{M_n - 340.4}{284.4} \quad (6)$$

Percentage of chain branching can be expressed as a ratio of the number of branch points per molecule r to the number of

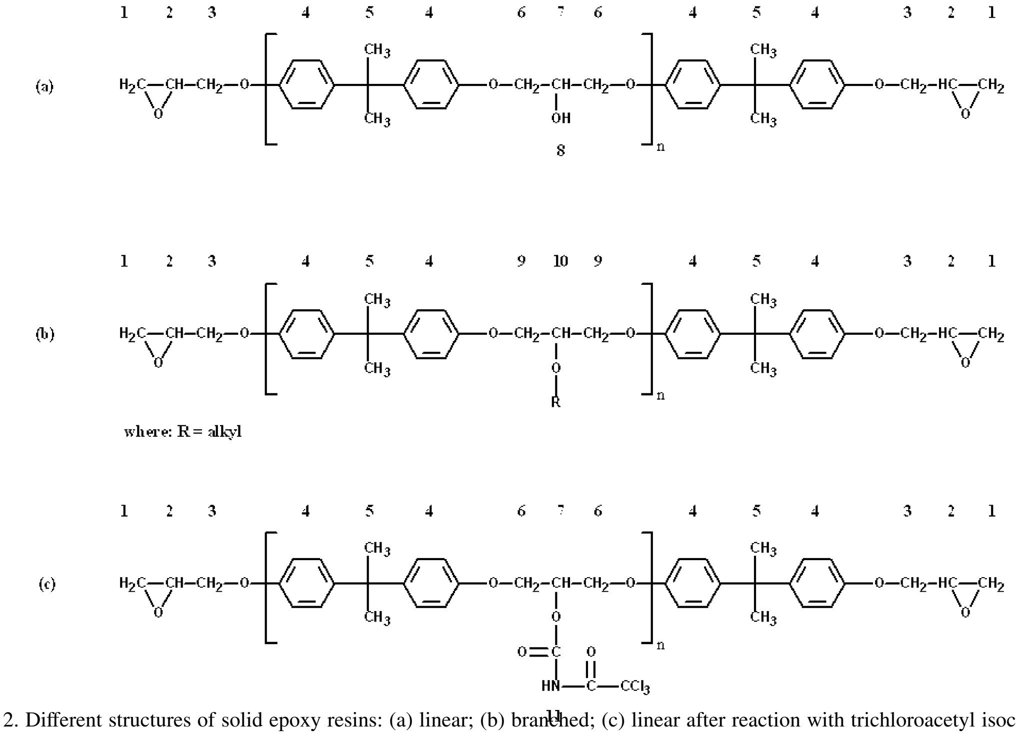

Fig. 2. Different structures of solid epoxy resins: (a) linear; (b) branched; (c) linear after reaction with trichloroacetyl isocyanate.

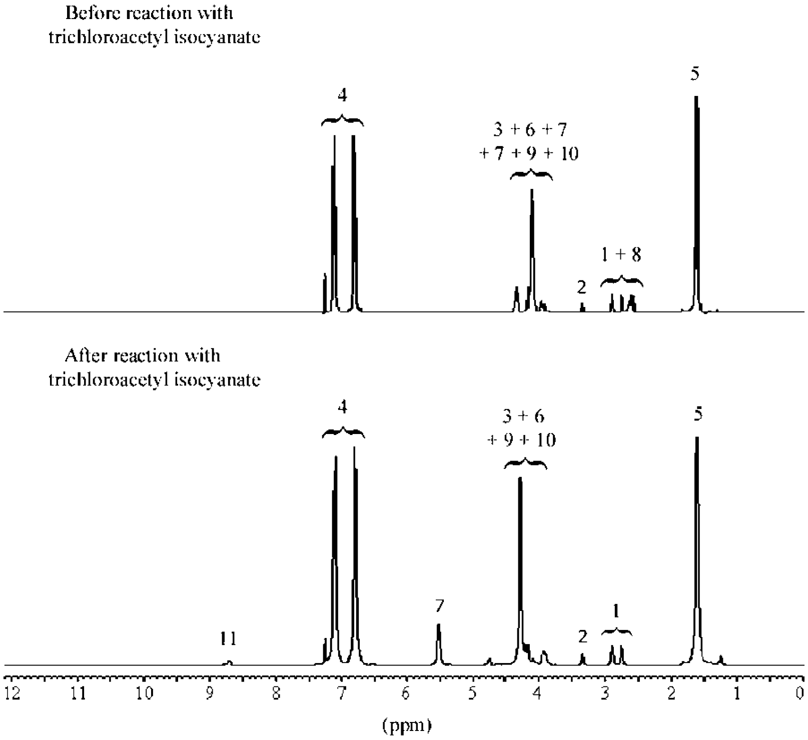

Fig. 3. The ^{1}H NMR spectra of solid epoxy resin before and after reaction with trichloroacetyl isocyanate.

repeat units n (7)

$$n = 2\frac{\mathrm{EEW} - 170.2}{284.4} \tag{7}$$

where EEW-epoxy equivalent weight.

All appropriate data are shown in Table 1.

3. Experimental section

3.1. Materials

Bisphenol A, trichloroacetyl isocyanate and 2-methylimidazole were obtained from Fluka and applied without further purification. L-M epoxy resin Rütapox 0162 (high content of Bisphenol A diglycidyl ether, EV = 0.57) was obtained from Bakelite AG.

3.2. Syntheses of epoxy resins

The general procedure for the syntheses of solid epoxy resins can be described as follows: 11.65 g of BPA was added to 25.0 g of L-M epoxy resin which contained appropriate amount of the catalyst (given in Table 1), to obtain required increase in the molecular weight during the reaction to the desired level. The calculated molar ratio of BPA to L-M epoxy resin was 3:4. To ensure temperature homogeneity, the mixture was stirred with a magnetic stirrer at 140, 160 and 180 °C both under conventional heating (i.e. electric heating mantle) and microwave irradiation (i.e. multimode microwave reactor *Plazmatronika-Poland* with microwave frequency of 2.45 GHz and maximum of microwave power of 600 W), for time necessary to obtain epoxy value about 0.11. The temperature was detected with an infrared pyrometer that is installed in the reactor. The pyrometer was calibrated before use with fiber-optical thermometer produced by *Nortech Technology*, which is characterized by accuracy ± 1 °C. Every 5 min a small sample of epoxy resin was taken from the mixture to determine the EV. After the reaction mixture was cooled down and powdered.

3.3. Measurement and characterization

Epoxy values of the synthesized resins were determined according to the Polish Standard, PN-87/C-89085/13.

All the GPC analyses of final products were performed using GPC chromatograph *Knauer*. A system of three columns was used: *2 × PL-gel Mixed-E* (300 × 7.5 mm; dimension of grains 3 μm) with one precolumn; conditions of measurements: flow rate − 0.8 mL/min, temperature − 30 °C, solvent-tetrahydrofuran (THF). Polystyrene standards were used to calibrate the chromatograph. Results of all the analyses are presented in Table 1. The ^{1}H NMR spectra were recorded on a *Merkury-300 Varian* spectrometer operating at 300 MHz. Deuterochloroform ($CDCl_3$) was used as a solvent.

The general procedure for determination the degree of branching in solid epoxy resins: Approximately 10 mg of high molecular epoxy resin was dissolved in 0.5 mL of $CDCl_3$ in NMR tube. The spectra was scanned and

Table 1
Reaction conditions, results of GPC analyses and determination the chain branching in solid epoxy resins

Sample	Reaction conditions			EV (mol/100 g)	GPC Analyses			Reduced integrations			Branch points/ molecule r	Degree of branching f	Chain branching (%)
	Time (min)	Temp. (°C)	Catalyst content[a]		M_n	M_w	M_n/M_w	$Z_{4.1}$	$Z_{4.3}$	$Z_{5.5}$			
1[b]	150	140	A	0.114	1810	3260	1.80	3.419	0.751	0.753	0.49	0.10	9.8
2[b]	90		B	0.112	1470	2580	1.75	3.478	0.753	0.769	0.47	0.09	9.2
3[b]	25		C	0.110	1950	3780	1.94	3.370	0.737	0.776	0.29	0.06	5.6
4[b]	65	160	A	0.110	2140	3780	1.77	3.416	0.757	0.774	0.38	0.07	7.3
5[b]	40		B	0.113	1850	3390	1.83	3.433	0.782	0.782	0.36	0.07	7.2
6[b]	20		C	0.104	2470	3390	1.83	3.425	0.792	0.775	0.45	0.08	8.1
7[b]	65	180	A	0.109	2380	4340	1.85	3.500	0.765	0.805	0.31	0.06	5.9
8[b]	30		B	0.109	2180	3990	1.83	3.506	0.781	0.804	0.33	0.06	6.3
9[b]	16		C	0.105	2420	4580	1.89	3.528	0.741	0.786	0.44	0.08	8.0
10[c]	280	140	A	0.114	1380	2860	2.08	3.310	0.696	0.706	0.59	0.12	11.9
11[c]	150		B	0.114	2020	3760	1.86	3.490	0.785	0.764	0.53	0.11	10.6
12[c]	55		C	0.113	2170	3640	1.68	3.508	0.787	0.785	0.44	0.09	8.7
13[c]	120	160	A	0.106	1790	3130	1.75	3.440	0.735	0.770	0.43	0.08	7.9
14[c]	80		B	0.111	2180	4000	1.84	3.516	0.761	0.788	0.41	0.08	8.0
15[c]	35		C	0.100	2380	5010	2.10	3.506	0.700	0.749	0.64	0.11	11.0
16[c]	80	180	A	0.101	2180	4000	1.84	3.547	0.776	0.805	0.40	0.07	6.9
17[c]	50		B	0.105	2250	4250	1.89	3.542	0.782	0.794	0.45	0.08	8.2
18[c]	35		C	0.100	2320	4420	1.91	3.531	0.758	0.760	0.66	0.11	11.3

[a] $A = 0.0005$; $B = 0.001$; $C = 0.005$ mol/mol OH in BPA.

[b] Microwave irradiation.

[c] Conventional heating.

integrated. Then 10 mg of trichloroacetyl isocyanate was added to the tube followed by a few drops of D_2O after 5 min. The spectra was recorded and integrated again. The results of all analyses are presented in Table 1. Where branching occurred, it was of the order of 6–12%, the range that might be expected from statistical considerations. Values less than 5% are within an experimental error and the resins were regarded as being linear [13].

4. Results and discussion

For each experiment, the reaction conditions, catalyst content, molecular weights together with epoxy value of epoxy resins are presented in the Table 1.

The analyses of molecular weight distribution by means of GPC show that the solid epoxy resins synthesized under both conventional heating and microwave irradiation have comparable molecular weights, the polydispersities are almost the same. As it can be 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 vs. microwaves), under microwave conditions molecular weights were slightly higher, which can be attributed to faster heating rate under microwave irradiation i.e. the reaction mixtures reached faster desired reaction temperatures.

The results of the chain branching determination in the investigated solid epoxy resins by means of ^{1}H NMR are presented in Table 1, while the relations of the degree of branching in the function of catalyst content, temperature, and reaction time are shown in Figs. 4–6. These relations were prepared on the analyses of results taken from Table 1.

The relation between the degree of branching and catalyst content are shown in Fig. 4. As it can be seen, the degree of branching decreases with the increase of the catalyst content from 0.5×10^{-3} to 5.0×10^{-3} mol at the temperature range of 160–180 °C, whereas, at 140 °C an opposite behavior was observed. It is worth stressing that under microwave conditions, the degree of branching was lower in all the cases, which was desired tendency in the connection with shorter reaction times.

In the next step, we analyzed the relation of degree of branching in the function of the catalyst concentration at different temperatures, and the results are presented in Fig. 5. The degree of branching decreased for the catalyst concentration at the range of 0.5×10^{-3} and 1.0×10^{-3} mol while the reaction temperature increased from 140 to 180 °C. An opposite behavior was observed for the catalyst concentration of 5.0×10^{-3} mol. Therefore, in the connection with the results presented in Figs. 3 and 4, it can be assumed that the catalyst concentration and reaction temperature should be further optimized so that to obtain the lowest possible degree of branching together with shortest reaction time.

Eventually, the comparison of reaction time with the degree of chain branching at the same catalyst levels for

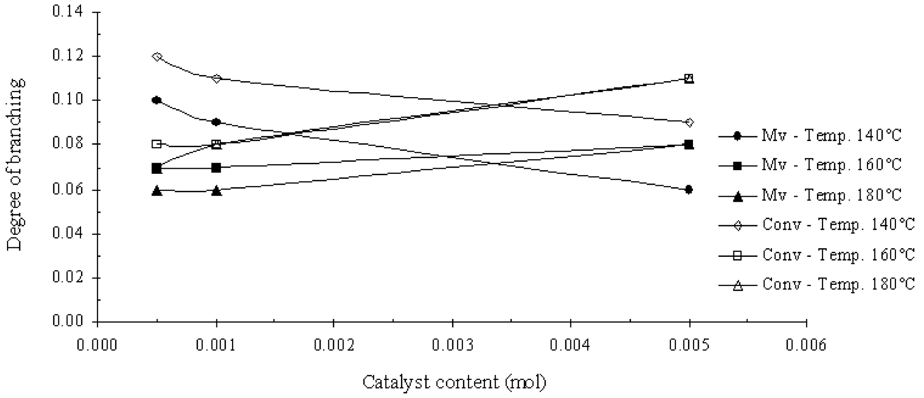

Fig. 4. Degree of branching in solid epoxy resins synthesized under microwave and conventional conditions as a function of the catalyst content.

different temperatures for both microwave and conventional conditions are shown in Fig. 6.

It can be seen again that for the catalyst concentration 0.5×10^{-3} and 1.0×10^{-3} mol the increase of temperature leads to the decrease of the degree of branching, which can be explain by shorter reaction time and, thus, lowering effect of side reactions; however, for the catalyst concentration of 5.0×10^{-3} mol an inverse effect was observed. The later can be explain by high exothermic effect of the reaction (i.e. 74.5 kJ/mol), and higher temperature together with higher catalyst concentration resulted in the increase of chain branching. Moreover, at the higher catalyst concentration we observed fast increase the density of the reaction mixture, which, in turn, caused difficulty with proper stirring and temperature control. Again, it is worth stressing that in all the cases under microwave conditions, the degree of branching was lower, which was desired.

5. Conclusions

In summary, it was demonstrated that it is possible to synthesized solid epoxy resins with a desired epoxy group content applying microwave irradiation (2.45 GHz). In general, all the syntheses under microwave conditions needed shorter reaction time than the syntheses under conventional conditions (i.e. electric heating mantle). Depending on the reaction conditions, the reaction time reduction varies from 20 to 55%, which can be an important economical factor while such syntheses are performed at higher scale. The solid epoxy resins synthesized under both conventional heating and microwave irradiation have comparable molecular weights, and the increase of reaction temperatures resulted in shorter reaction time as well as in the increase of molecular weights. The percentage of chain branching was in the range of 6–12%, and it is consistent with the literature data [13–17]. As it was desired, the final epoxy resins prepared under microwave conditions possessed less chain branching in comparison with those obtained under conventional heating, and the reduction of reaction time did not influence the degree of chain branching. It can be observed that the degree of branching depends on two parameters such as the catalyst content and reaction temperature. On the one hand, the degree of branching increased together with the catalyst content and reaction temperature when they are kept above a certain level. On the other hand, when both catalyst content and reaction temperature are below such a level, the degree of branching decreased together with the catalyst content and reaction temperature.

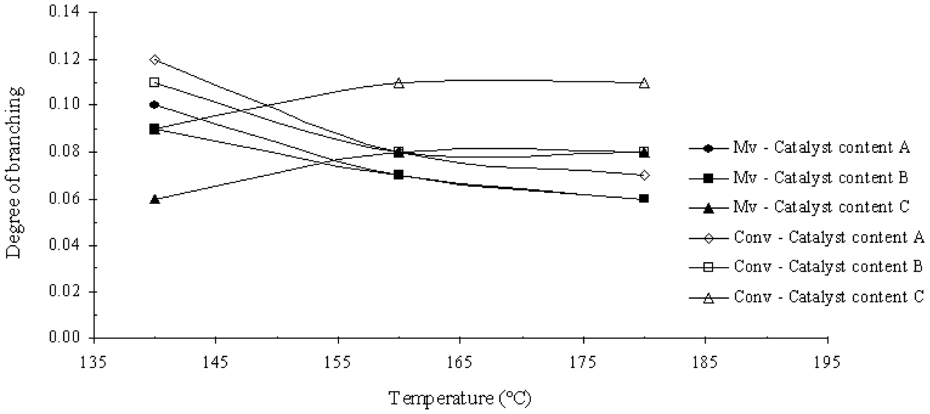

Fig. 5. Degree of branching in solid epoxy resins synthesized under microwave and conventional conditions as a function of the reaction temperature.

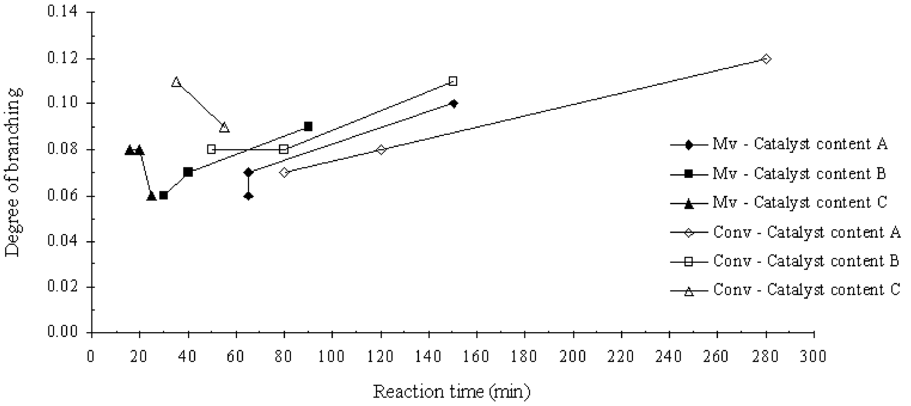

Fig. 6. Degree of branching in solid epoxy resins synthesized under microwave and conventional conditions as a function of the reaction time.

Acknowledgements

The Polish State Committee supported the research for Scientific Research Grant No. 7T09B06521. The authors are grateful to Mr M. Zylewski (Collegium Medicum, Jagiellonian University) for recording the NMR spectra.

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