

INCORPORATION OF CO₂ INTO VARIOUS TERMINAL AND INTERNAL EPOXIDES

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Dedicated to Professor Štefan Toma, Comenius University in Bratislava, on the occasion of his 70th birthday.

Carbon dioxide was incorporated into various oxirane-containing compounds. The starting materials include natural products with epoxy groups (1–4), glycidyl compounds (5–9) and epoxidized polymers (9, 10). It could be shown that the crosslinking side reaction is not significant for internal epoxides but important for terminal glycidyl compounds.

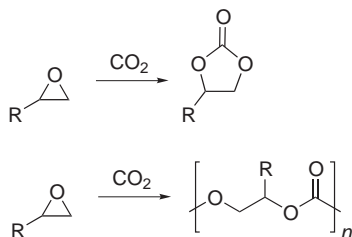
Keywords: Carbon dioxide fixation; Oxiranes; Cyclic carbonates; Crosslinking; Polymer backbone modification; Polycarbonates; Copolymers; Epoxidized polymers.

Carbon dioxide as a C₁ building block is important for a wide range of industrial uses. It is a major emission product of many industrial processes and human activities. For this reason it is very interesting as a raw material for sustainable chemistry^{1,2}.

From the economical point of view, carbon dioxide is abundant which makes it inexpensive. Because of its incombustibility, CO₂ is a good carbon source. From the ecological and social points of view it is desirable to replace more dangerous carbon sources such as carbon monoxide, phosgene or isocyanates by CO₂ if viable. Carbon dioxide is also one of the most important greenhouse gases and so its industrial use could be a method of fighting with the greenhouse effect. For all these reasons the efficient transformation of CO₂ into useful chemicals has received much attention in the last decades and many ways of its chemical use were reported^{3,4}.

One of the most interesting methods in this line of research is the reaction between carbon dioxide and oxiranes, which leads to polycarbonates

on the one hand⁵⁻⁷ and five-membered cyclic carbonates on the other^{8,9} (Scheme 1).



SCHEME 1

Formation of cyclic carbonates and polycarbonates

Both reactions can be effectively catalyzed with metal complexes like chromium salen complexes or manganese metalloporphyrins¹⁰⁻¹² as well as with organic or inorganic salts^{7,13-17}. Because of their low prices in particular salts like LiBr, NaI and tetrabutylammonium bromide (TBAB) are advantageous. In this case the CO₂ fixation takes place via an ionic route. Because of their interesting chemical and physical properties, cyclic carbonates are used in many industrial processes, e.g. as a high-boiling solvent. With the focus on the formation of cyclic carbonates, we investigated in this study the structural influence of epoxides which can support the cross-linking side reaction. Therefore, we compared the reaction of carbon dioxide with glycidyl compounds, having terminal oxirane groups, with some natural and synthetic polymers containing epoxy groups in their skeleton. All used educts are summarized in Table I.

EXPERIMENTAL

Materials

The epoxidized soybean oil (**1a**) was purchased from Arkema and was used as received. The natural products (**2-4**) were purchased from Aldrich Chemical Company and were epoxidized first. The glycidyl compounds (**5-8**) and the glycidylated polymer (**9**) were purchased from Aldrich Chemical Company with good purity, and were used as received. Poly(acrylonitrile-*co*-butadiene) (**10**) from ZEON was also epoxidized first.

Methods

¹H and ¹³C NMR spectra were recorded on a Bruker Avance 200 and 400. ¹H and ¹³C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ -scale) with

the solvent resonance (CDCl_3) as internal standard. IR data (wavenumbers, cm^{-1}) were collected on a Perkin-Elmer Spectrum 100 FT-IR spectrometer using CHCl_3 solutions and a KBr cell ($d = 0.064$ cm). The carbonate formation rates were determined by quantitative Lambert-Beer-Analysis using also a CHCl_3 solution and a KBr cell ($d = 0.064$ cm). SEC (size exclusion chromatography) was measured on a Jasco system with a Jasco PU 980 pump, a Jasco RI 930 refractive index detector and a PSS 10E6 + VSne column using THF as eluent.

Epoxidation of 2, 3 and 4

To a solution of an olefin (1 mol) in CHCl_3 (100 ml) formic acid (0.5 mol) was added. The mixture was stirred and heated up to 40 °C. A 35% H_2O_2 (1.5 mol) solution was added slowly. The temperature increased up to 60 °C. The mixture was kept at 40 °C for 4 h. The reaction mixture was neutralized by adding a saturated solution of potassium carbonate. After washing the product solution with water, the solvent was evaporated in vacuum. The degree of epoxidation was determined by titration with an anhydrous solution of hydrogen bromide in glacial acetic acid.

2a: IR (KBr cell, CHCl_3): 3683, 3620, 3017, 2929, 2856, 2400, 1737, 1653, 1518, 1463, 1378, 1218, 1167, 1099, 928, 877, 849, 755, 669.

3a: IR (KBr cell, CHCl_3): 3683, 3622, 3518, 3018, 2930, 2856, 2400, 1727, 1660, 1519, 1465, 1394, 1375, 1348, 1301, 1218, 1116, 1096, 1033, 928, 877, 852, 752, 668.

4a: IR (KBr cell, CHCl_3): 3683, 3621, 3468, 3019, 2970, 2917, 2855, 2400, 1666, 1521, 1444, 1383, 1332, 1215, 1108, 1046, 985, 928, 877, 849, 760, 669.

TABLE I

Used educts for the CO_2 fixation, their oxirane rates (OR) (mol oxirane per mol compound) and if appropriate their epoxidation yields

	Educts		Yield, %	OR
Natural compounds	1a epoxidized soybean oil	1a	–	4.2
	2 linseed oil	2a	62	3.1
	3 ethyl linoleate	3a	65	1.3
	4 squalene	4a	26	1.6
Glycidyl compounds	5a 4,4'-methylenebis(<i>N,N</i> -diglycidylaniline)	5a	–	4
	6a hydrogenated Bisphenol A diglycidyl ether	6a	–	2
	7a <i>N,N</i> -diglycidyl-4-(glycidylloxy)aniline	7a	–	3
	8a 1,4-cyclohexanedimethanol diglycidyl ether	8a	–	2
Polymers	9a glycidylated poly(Bisphenol A- <i>co</i> -epichlorohydrine)	9a	–	2
	10 Poly(acrylonitrile- <i>co</i> -butadiene)	10a	8	14

Epoxidation of Poly(acrylonitrile-*co*-butadiene)

To a solution of poly(acrylonitrile-*co*-butadiene) (15 g, 3.66 mmol) in CHCl₃ (100 ml), a 0.01 M NaOH solution (10 ml) and 35% H₂O₂ (366 mmol) were added. The reaction mixture was stirred at room temperature for 24 h. After washing the product solution with water, the solvent was evaporated in vacuum. The degree of epoxidation was determined by titration with an anhydrous solution of hydrogen bromide in glacial acetic acid. IR (KBr cell, CHCl₃): 3774, 3683, 3620, 3497, 3019, 2977, 2934, 2867, 2434, 2400, 2241, 1726, 1641, 1601, 1520, 1475, 1453, 1384, 1288, 1219, 1107, 1046, 971, 928, 878, 849, 789, 669. ¹H NMR (CDCl₃): 0.88 (m, CH₃), 1.27 (m, CH₂), 1.42 (s, CH₂), 1.66 (m, CH₂), 2.04 (s, CH₂), 2.1 (m, CH₂), 2.27 (m, CH₂), 2.58 (m, epoxy), 5.1 (m, C=C), 5.36 (m, C=C), 5.54 (m, C=C), 6.69 (s, NH₂). ¹³C NMR (CDCl₃): 29 (m, CH₃), 31 (m, CH₂), 34 (m, CH₂), 39 (m, CH₂), 55 (m, CH), 79 (m, epoxy), 121 (m, C=C), 124 (m, C=C), 139 (d, CN), 190 (s, CONH₂).

Fixation of CO₂ in the Epoxy Compounds

The compound was poured into a 100-ml high-pressure reactor vessel (Berghof, HR-100) and 5.0 mole % of the catalyst relative to the oxirane content was dissolved in it. The reactor was pressurized with CO₂ to 20 bar and heated with a heating block (Berghof, DAH-3) up to 100 °C. The reaction mixture was stirred at this temperature for 24 h. To purify the product and separate it from the catalyst, the reaction mixture was dissolved in CHCl₃ and washed with water. The solvent was removed in vacuum. The degree of CO₂ fixation was determined by quantitative IR analysis.

1b: IR (KBr cell, CHCl₃): 3683, 3620, 3475, 3019, 2929, 2857, 2400, 1801, 1737, 1522, 1466, 1378, 1215, 1176, 1050, 928, 877, 848, 752, 668.

2b: IR (KBr cell, CHCl₃): 3684, 3620, 3470, 3019, 2929, 2856, 2400, 1797, 1737, 1520, 1464, 1378, 1215, 1166, 1098, 1047, 928, 877, 849, 750, 669.

3b: IR (KBr cell, CHCl₃): 3683, 3621, 3475, 3019, 2930, 2858, 2400, 1793, 1725, 1718, 1466, 1376, 1216, 1095, 1034, 928, 877, 849, 756, 668.

4b: IR (KBr cell, CHCl₃): 3683, 3621, 3468, 3019, 2970, 2917, 2855, 2400, 1797, 1666, 1521, 1444, 1383, 1332, 1215, 1108, 1046, 985, 928, 877, 849, 760, 669.

5b: IR (KBr cell, CHCl₃): 3683, 3619, 3474, 3019, 2922, 2400, 1809, 1614, 1567, 1517, 1479, 1439, 1384, 1335, 1217, 1082, 1047, 974, 952, 930, 909, 877, 750, 668.

6b: IR (KBr cell, CHCl₃): 3684, 3620, 3019, 2972, 2937, 2870, 2400, 1797, 1519, 1477, 1446, 1388, 1370, 1334, 1305, 1214, 1170, 1131, 1103, 1062, 928, 877, 849, 755, 669.

7b: IR (KBr cell, CHCl₃): 3683, 3618, 3019, 2974, 2927, 2400, 1801, 1612, 1581, 1512, 1479, 1456, 1424, 1384, 1561, 1212, 1170, 1081, 1058, 955, 928, 877, 752, 627.

8b: IR (KBr cell, CHCl₃): 3683, 3618, 3020, 2922, 2800, 2400, 1797, 1522, 1479, 1451, 1393, 1360, 1335, 1307, 1217, 1171, 1168, 1104, 1052, 953, 928, 878, 848, 752, 668.

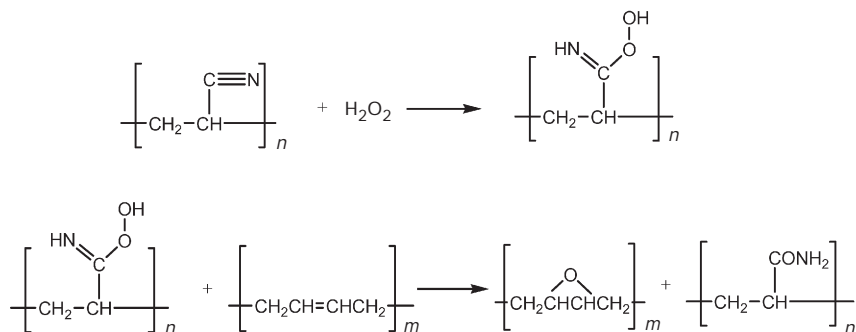
9b: IR (KBr cell, CHCl₃): 3683, 3621, 3019, 2974, 2930, 2400, 1802, 1607, 1582, 1509, 1475, 1426, 1386, 1363, 1344, 1296, 1212, 1184, 1133, 1040, 972, 828, 831, 753, 669, 627, 573, 493.

10b: IR (KBr cell, CHCl₃): 3684, 3618, 3019, 2961, 2440, 2400, 2241, 1801, 1714, 1602, 1522, 1431, 1377, 1214, 1050, 972, 928, 877, 849, 752, 669.

RESULTS AND DISCUSSION

The natural products containing double bonds (**2–4**) as well as poly(acrylonitrile-*co*-butadiene) (**10**) were epoxidized at first for their further use. We used the well investigated formic acid/hydrogen peroxide method^{18,19}. The yields of the epoxidation were determined by titration with an anhydrous solution of hydrogen bromide in glacial acetic acid. Up to 62% of the double bonds (linseed oil, 3.1 mol oxirane per mol of the compound) could be epoxidized in the case of the natural products.

The low epoxidation rate of epoxidized squalene can be assigned to its sterically hindered double bonds. All yields and the corresponding epoxidation rates are summarized in Table I. In the case of poly(acrylonitrile-*co*-butadiene) we could use the intermediary formation of peroxyimino acid and subsequent epoxidation of the backbone (Scheme 2). This was carried out using only a hydrogen peroxide solution under basic conditions. The epoxidized poly(acrylonitrile-*co*-butadiene) (**10a**) was studied by IR, ¹H and ¹³C NMR spectroscopy.



SCHEME 2

Epoxidation of olefins via iminoperoxy acid

The formation of the expected carboxamide could be shown by the appearance of a band at 1726 cm^{-1} . Other new bands at 2900 and 1384 cm^{-1} also indicate the formation of this by-product. The formation of epoxides could be proved by their typical chemical reaction with hydrogen bromide and by ¹H NMR spectra where new signals appeared at 2.7 and 2.8 ppm. On average, 8% of the double bonds could be convert into epoxides (14 mol epoxide per mol polymer).

A similar method for the epoxidation of 2-allylcyclohexanone with benzonitrile and hydrogen peroxide was reported by Payne et al.²⁰, but as

far as we know this is the first time it was successfully used in polymer chemistry.

The syntheses of cyclic carbonates were carried out at 100 °C with 5 mole % catalyst per oxirane moiety and a reaction time of 24 h. The fixation of CO₂ was carried out in a 100-ml high-pressure reaction vessel, at a CO₂ pressure of 20 bar at room temperature. At this pressure we reached a minimal molar ratio between epoxides and CO₂ 1:1.2. No solvent was used. Because of good solubility of the catalysts in water and insolubility of cyclic carbonates in it, all catalysts could be easily removed by washing the reaction mixture with water. This method allows the possible reuse of the catalysts. All fixation products were studied by IR spectroscopy. The exemplary IR spectra of the 3 steps of the poly(acrylonitrile-*co*-butadiene) reactions clearly show the conversion of the polymer into the epoxide and finally into the cyclic carbonate of poly(acrylonitrile-*co*-butadiene) (Fig. 1).

The apparent indication of the formation of cyclic carbonate (**10b**) is an additional absorption band at 1801 cm⁻¹. This is associated with the C=O stretching vibration of the formed carbonyl group. This very significant and typical band also allows the determination of the CO₂ fixation rate by quantitative IR analysis. The necessary calibration of the method was carried out using ethylene carbonate. The degrees of the CO₂ fixation for the oxirane compounds with the used catalysts are summarized in Table II.

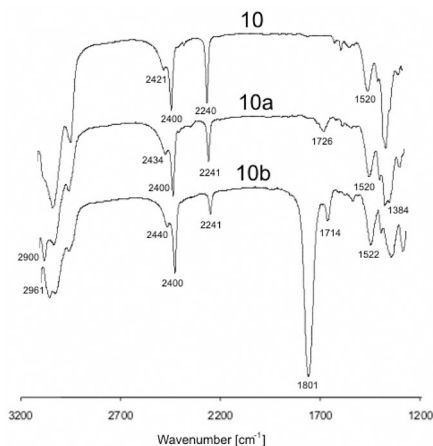


FIG. 1
IR spectra of untreated (**10**), epoxidized (**10a**) and the cyclic carbonate of poly(acrylonitrile-*co*-butadiene) (**10b**)

The described method for the CO₂ fixation in oxiranes can be used for a wide range of natural or synthetic products with good results. For the first time we could successfully incorporate carbon dioxide in the backbone of a polymer. So far only CO₂ fixation in side-chains of polymers have been reported^{21,22}.

In the case of the natural products, TBAB seems to be the most effective catalyst, although LiBr and NaI also show good results. Once more, the low degree of conversion of epoxidized squalene can be assigned to sterically hindered double bonds. In the case of epoxidized poly(acrylonitrile-*co*-butadiene) only TBAB shows catalytic activity.

We also investigated the scale on which the cross-linking side reaction takes place. This was done by SEC. In the cyclic carbonates obtained from natural products as well as in the cyclic carbonate of poly(acrylonitrile-*co*-butadiene) (**10b**), no significant crosslinking took place. In Fig. 2 the SEC profile for the poly(acrylonitrile-*co*-butadiene) with fixed CO₂ (**10b**) is shown.

TABLE II

Fixation of CO₂ by epoxides, their carbonate formation rates (CR) (mol carbonate per mol compound) and their yields by IR for all used catalysts (100 °C, 20 bar, 24 h reaction time and 5 mole % catalyst)

Products	TBAB		LiBr		NaI	
	CR	yield, %	CR	yield, %	CR	yield, %
1b	1.680	40	1.134	27	1.470	35
2b	1.178	38	0.744	24	1.116	36
3b	0.806	62	0.624	48	0.585	45
4b	0.048	3	0.064	4	0.048	3
5b	1.800	45	2.040	51	1.840	46
6b	0.800	40	0.820	41	0.780	39
7b	0.570	19	0.750	25	0.420	14
8b	0.740	37	0.420	14	0.920	46
9b	0.670	38	0.900	45	0.880	44
10b	6.300	45	0.280	2	0	0

The figure shows a unimodal behavior with the highest concentration of products of $M_w = 4450$. Compared with the starting material ($M_w = 4090$), no significant changes took place. In Fig. 2 the SEC profile of the cyclic carbonate of 4,4'-methylenebis(*N,N*-diglycidylaniline) (**5b**) is also shown. Compared with the unimodal behavior of the starting material we can see a second area with products of higher molecular weight. All of the investigated glycidyl compounds show a similar behavior. In some cases, e.g. *N,N*-diglycidyl-4-(glycidyoxy)aniline, a second product fraction occurred. The products of this fraction are insoluble in chloroform in contrast to all main products. This indicates highly crosslinked structures.

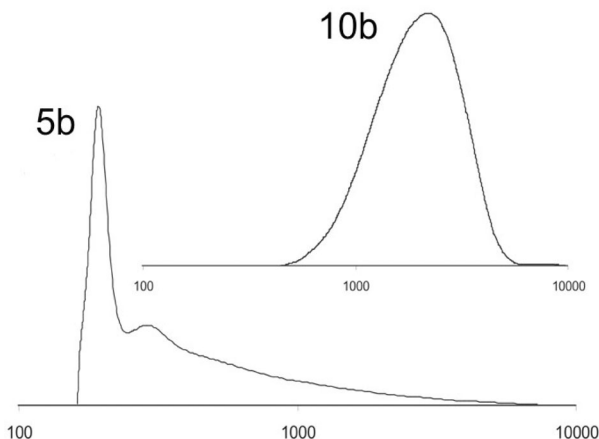


FIG. 2

SEC profiles of cyclic carbonates of poly(acrylonitrile-*co*-butadiene) (**10b**) and 4,4'-methylenebis(*N,N*-diglycidylaniline) (**5b**)

CONCLUSIONS

Carbon dioxide could be incorporated into various oxirane-containing compounds by an easy and inexpensive solvent-free process. In all cases a five-membered cyclic carbonate could be obtained. In this context we could successfully incorporate carbon dioxide in the backbone of polymers. During the CO₂ fixation the viscosity of all products increased. This can be assigned to higher intermolecular forces caused by higher polarity. In the case of internal epoxy compounds, no significant side reactions took place, but for glycidyl compounds crosslinking reactions were observed which lead to a bimodal distribution of the SEC profile, and in most cases to a second insoluble product fraction. This crosslinking can be assigned to the formation of polycarbonates.

We could also demonstrate, that the double bonds of poly(acrylonitrile-co-butadiene) can be oxygenated by a hydrogen peroxide solution under basic conditions. This reaction takes place by the intermediary formation of peroxyimino acid and subsequent epoxidation of the double bonds.

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REFERENCES

1. Song C.: *Catal. Today* **2006**, *115*, 2.
2. Shi M., Shen Y. M.: *Curr. Org. Chem.* **2003**, *7*, 737.
3. Gibson D. H.: *Chem. Rev.* **1996**, *96*, 2063.
4. Froehlich J., Berger S.: *Synlett* **2005**, *16*, 2522.
5. Ochiai B., Endo T.: *Prog. Polym. Sci.* **2005**, *30*, 183.
6. Tomishige K., Yasuda H., Yoshida Y., Nurunnabi M., Li B., Kunimori K.: *Catal. Lett.* **2004**, *95*, 45.
7. Motokucho S., Sudo A., Sanda F., Endo T.: *J. Polym. Sci.* **2004**, *42*, 2506.
8. Nüchter M., Ondruschka B., Hoffmann J., Tied A.: *Stud. Surf. Sci. Catal.* **2004**, *153*, 131.
9. Yoshida M., Ihara M.: *Chem. Eur. J.* **2004**, *10*, 2886.
10. Coates G. W., Moore D. R.: *Angew. Chem.* **2004**, *116*, 6784.
11. Kruper W. J., Dellar D. V.: *J. Org. Chem.* **1995**, *60*, 725.
12. Darensbourg D., Mackiewicz R., Phelps A., Billodeaux D.: *Acc. Chem. Res.* **2004**, *37*, 836.
13. Kihara N., Hara N., Endo T. J.: *J. Org. Chem.* **1993**, *58*, 6198.
14. Doll K. M., Erhan S. Z.: *Green Chem.* **2005**, *7*, 849.
15. Doll K. M., Erhan S. Z.: *J. Agric. Food Chem.* **2005**, *53*, 9608.
16. Tamami B., Sohn S., Wilkes G. L.: *J. Appl. Polym. Sci.* **2004**, *92*, 883.
17. Huang J. W., Shi M.: *J. Org. Chem.* **1993**, *58*, 6198.
18. Schmits W. R., Wallace J. G.: *J. Am. Chem. Soc.* **1954**, *31*, 363.
19. Tanrattanakul V., Wattanathai B., Tiangjunya A., Muhamud P.: *J. Appl. Polym. Sci.* **2003**, *282*, 40.
20. Payne G. B.: *Tetrahedron* **1962**, *18*, 763.
21. Kihara N., Endo T.: *Macromolecules* **1992**, *25*, 4824.
22. Ochiai B., Iwamoto T., Endo T.: *Green Chem.* **2006**, *8*, 138.