

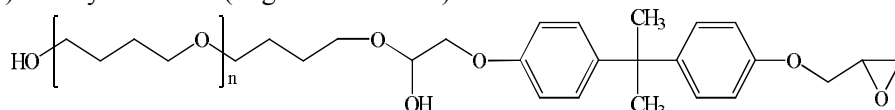
The method demands accurate determination of epoxy groups content, full opening of epoxy groups using sulfuric acid and long-run analysis. This work deals with the method based on IR-spectroscopy to determine the content of hydroxy groups in oligomers obtained *via* chemical modification of epoxy resins by various compounds with the mobile hydrogen atom.

2. Experimental

2.1. Materials

The content of hydroxy groups was determined for the following oligomers:

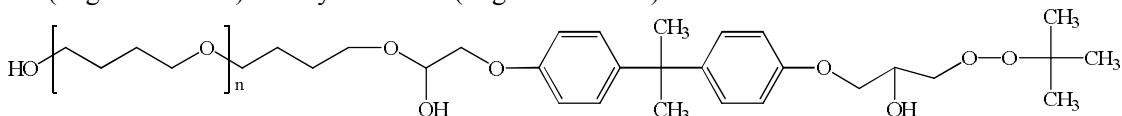
I. Oligomers obtained *via* chemical modification of bisphenol A diglycidyl ether (DGEBA) by 1,4-butanediol (BD) (oligomer HDEO-I) or PolyTHF-2000 (oligomer HDEO-II) of the formula:



where $n = 0$ (HDEO-I) or $n = 26-28$ (HDEO-II)

HDEO-I and HDEO-II were synthesized according to the procedure described in [21]. It was found for HDEO-I: molecular weight (M_n) 420 g/mol; epoxy number ($e.n.$) 11.2 %. For HDEO-II: M_n 2280 g/mol; $e.n.$ 3.3 %.

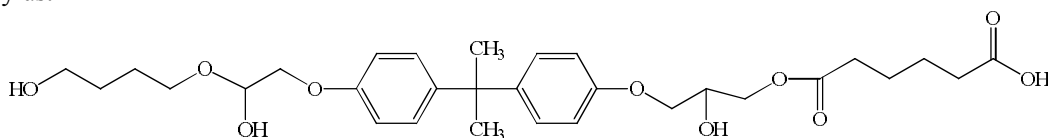
II. Oligomers synthesized *via* reaction between DGEBA peroxy derivative (PO) obtained by the method described in [23] and BD (oligomer HPO-I) or PolyTHF-2000 (oligomer HPO-II) of the formula:



where $n = 0$ (HPO-I) or $n = 26-28$ (HPO-II)

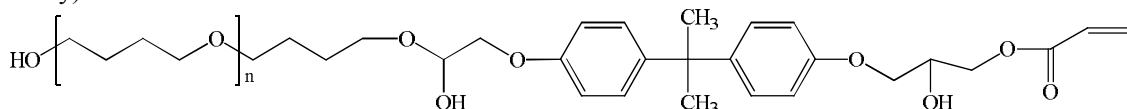
The synthesis procedure for HPO-I is described in [24], HPO-II – [25]. It was found for HPO-I: M_n 507 g/mol; active oxygen content ($[O]_{act}$) 1.91 %. For HPO-II: M_n 2370 g/mol; $[O]_{act}$ 1.03 %.

III. Oligomer HCO was obtained *via* chemical modification of HDEO-I by adipic acid according to the procedure developed by us:



It was found for HCO M_n 565 g/mol.

IV. Oligomers synthesized *via* the reaction between HDEO-I or HDEO-II and acrylic acid (oligomers HAO-I and HAO-II, respectively):



where $n = 0$ (HAO-I) or $n = 26-28$ (HAO-II)

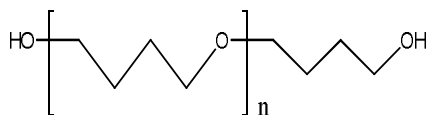
It was found for HAO-I M_n 495 g/mol; for HAO-II – 2350 g/mol.



V. Butanediol (BD) produced by Merck KGaA, Germany:

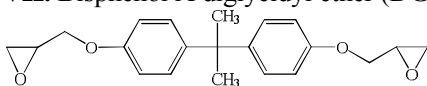
It was found for BD M_n 90.12 g/mol; hydroxy number ($h.n.$) 1230 mg KOH/g.

VI. Oligoether PolyTHF-2000 (BASF Canada Inc., Canada) with M_n 1950 g/mol, $h.n.$ 54.7 mg KOH/g and acid number ($a.n.$) ≤ 0.05 mg KOH/g



$n = 26-28$

VII. Bisphenol A diglycidyl ether (DGEBA) produced by Sigma-Aldrich Co had M_n 340 g/mol; $e.n.$ 24 %, $h.n.$ absent.



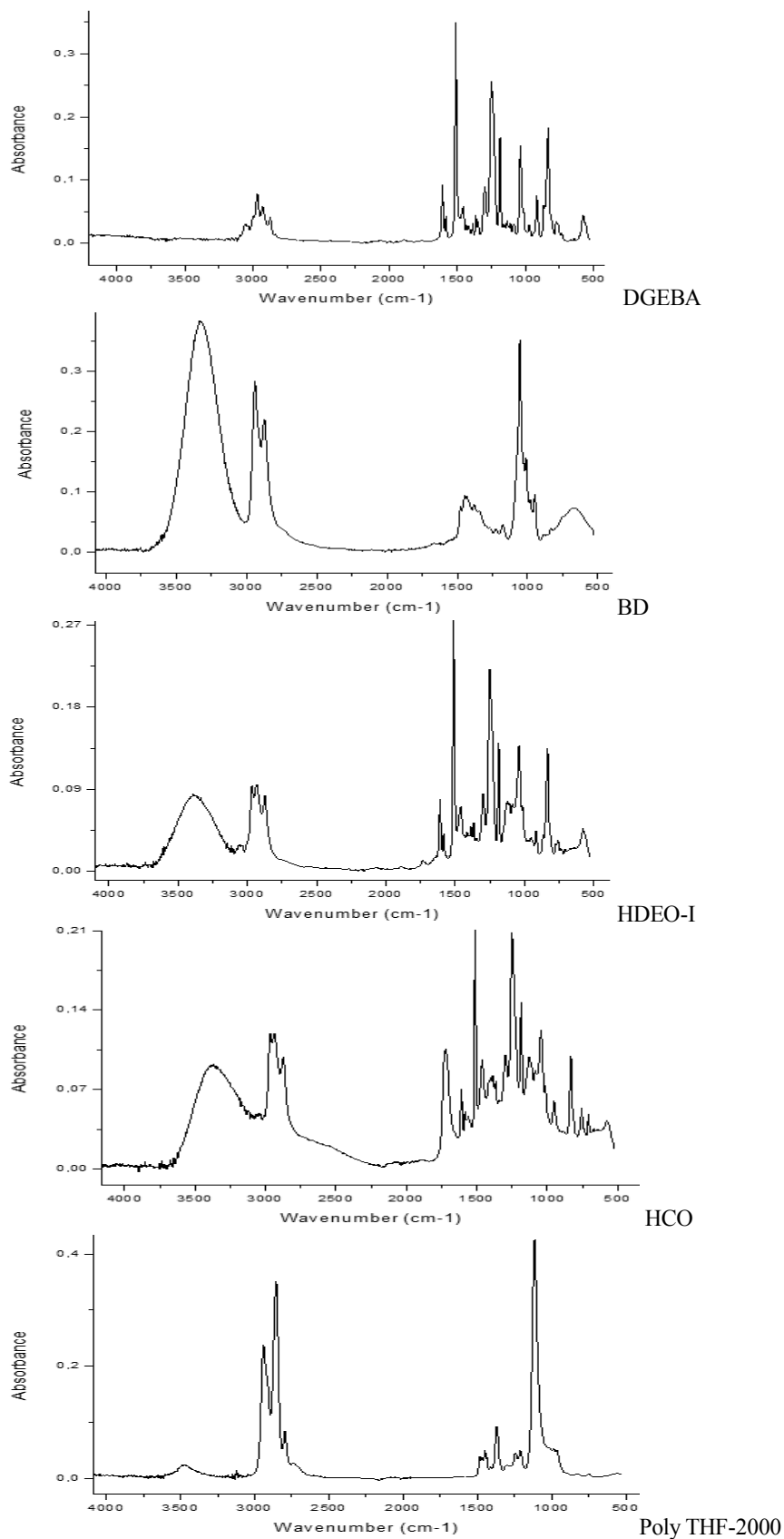


Fig. 1. IR-spectra of some samples



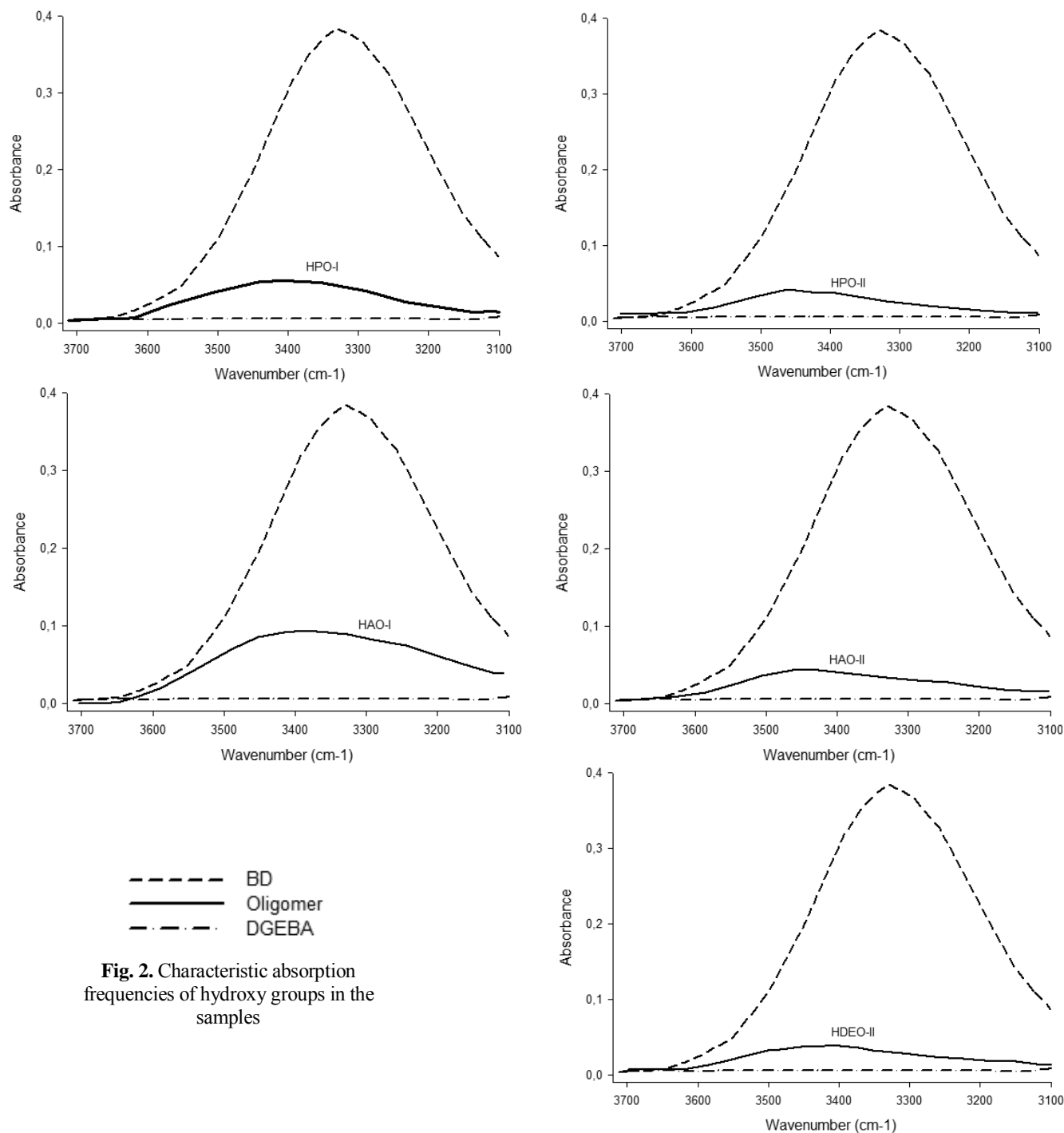
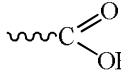


Fig. 2. Characteristic absorption frequencies of hydroxy groups in the samples

While analyzing the data from Table 1 one can see that the values obtained *via* IR-spectroscopy are in agreement with theoretical ones within the error limits. It does not concern the hydroxy number of HCO oligomer. The theoretical *h.n.* for HCO is 292 mgKOH/g and calculated by formula (4) – 373 mgKOH/g. This difference may be explained based on HCO formula. Apart from primary and secondary hydroxyl groups the

HCO contains free carboxy group , consisting of carbonyl and hydroxy groups. Moreover, the stretching vibrations of –OH of carboxy groups are within the range of 3500–3580 cm⁻¹ which is overlapped by hydroxy groups [27]. It means that in such a case the calculated hydroxy number is the sum of absorption bands typical of stretching vibrations of hydroxy group and –OH of carboxy group.

Hydroxy numbers for initial and modified compounds

Compound	S^1 , rel.units	S^2 , %	Hydroxy number					
			IR-spectroscopy		Chemical method		Theoretical value	
			mgKOH/g	%	mgKOH/g	%	mgKOH/g	%
DGEBA	0	0	0	0	0	0	0	0
BD	109.49	100	1230	37.3	1230.0	37.3	1245	37.7
HDEO-I	24.66	22.52	277	8.4	–	–	261	7.9
HPO-I	16.81	15.35	189	5.7	–	–	215	6.5
HCO	33.21	30.33	373	11.3	–	–	292	8.9
HAO-I	31.25	28.54	351	10.6	–	–	335	10.2
Poly THF-2000	4.58	4.18	51	1.55	54.7	1.6	57	1.7
HDEO-II	4.72	4.31	53	1.61	–	–	49	1.5
HPO-II	7.34	6.7	82	2.49	–	–	72	2.2
HAO-II	7.48	6.83	84	2.55	–	–	71	2.1

Note: the theoretical value of hydroxy number for every sample was calculated taking into account its molecular weight and functionality.

4. Conclusions

The content of hydroxy groups was determined *via* IR-spectroscopy in the modified epoxy oligomers containing, apart from hydroxy groups, free epoxy or peroxy, carboxy or acrylic groups. The hydroxy number of investigated oligomers was found to be within 53–373 mgKOH/g. The proposed method allows to determine the content of hydroxy groups with the error lower than 10 %.

References

- [1] Saunders D. and Frish K.: *Khimiya Poliuretanov*, Khimia, Moskva 1968.
- [2] Buist J.: *Compositsyonnye Materialy na Osnove Polyurethanov*. Khimia, Moskva 1982.
- [3] Lyubartovych S., Morozov Yu. And Tretyakov O.: *Reaktsyonnoe Formirovanie Polyurethanov*. Khimia, Moskva 1990.
- [4] Ellis B.: *Chemistry and Technology of Epoxy Resins*. Springer 1993.
- [5] Hetmanchuk Yu. and Bratychak M.: *Khimiya i Technologia Polymerov*. Beskid Bit, Lviv 2006.
- [6] Yu G-E., Heatley F., Booth C. and Blease T.: *J. Polym. Science A*, 1994, **32**, 1131.
- [7] Kubisa P. and Penczek S.: *Progr. Polym. Sci.* 1999, **24**, 1409.
- [8] Wegener G., Brandt M., Duda L. *et al.*: *Appl. Catal.*, 2001, **221**, 303.
- [9] Yasuda K., Yokoyama Y., Matsusta S. and Harada K.: [in:] Goethals E. (Ed.), *Cationic Polymerisation and Related Processes*. Academic Press, London 1984, 329.
- [10] Ionescu M., Zugravu V., Mihalache I. and Mihai S.: [in:] Klempler D. and Frisch K. (Eds.), *Advances in Urethane Science & Technology*. Technomic Publ., Lancaster 1998, 14, 151.
- [11] Barantsevych E. And Ivanchev S.: *Vysokomol. Soed. A*, 1983, **25**, 2019.
- [12] Petrov G. And Likin A.: *Vysokomol. Soed. A*, 1978, **20**, 1203.
- [13] Valuev V., Dmitreva T. And Shlyakhter R.: *Vysokomol. Soed. A*, 1982, **24**, 1168.
- [14] Boiko V. And Hrishchenko V.: *Ukr. Khim. Zh.*, 1982, **45**, 532.
- [15] Reed D.: *Urethanes Techn.*, 2000, **17**, 41.
- [16] Chang W., Baranowski T. and Karalis T.: *J. Appl. Polym. Sci.*, 1994, **51**, 1077.
- [17] Bratychak M., Chervinsky T., Gagin M. *et al.*: *Ukr. Khim. Zh.*, 2005, **71**, 50.
- [18] Bratychak M., Chervinsky T., Astakhova O. and Shyshchak O.: *Chem. Chem. Techn.*, 2010, **4**, 325.
- [19] Bashta B., Bruzdziak P., Astakhova O. *et al.*: *Chem. Chem. Techn.*, 2013, **7**, 413.
- [20] Bratychak M., Iatsyshyn O. and Kochubei V.: *Ukr. Khim. Zh.*, 2012, **79**, 20.
- [21] Bratychak M., Ivashkiv O., Astakhova O. and Haponuk Y.: *Ukr. Khim. Zh.*, 2015, **81**, 59.
- [22] vsegost.com/catalog/43/43983.shtml
- [23] Bazylyak L., Bratychak M. and Brostow W.: *Mater. Res. Innovat.*, 1999, **3**, 132.
- [24] Bratychak M., Ivashkiv O. and Astakhova O.: *Dopov. Nats. Acad. Nauk Ukrainy*, 2015, **5**, 119.
- [25] Ivashkiv O., Astakhova O., Namiesnik J. *et al.*: *Chem. Chem. Techn.*, 2015, **9**, 313.
- [26] Malinovsky M.: *Okisi Olefinov i ikh Proizvodnye*. Goskhimtechizdat, Moskva 1961.
- [27] Kazitsyna L. And Kupletskaia N.: *Primenenie UV-, IR- and NMR-spektroskopiiiv Organicheskoi Khimii*. Vyshaya shkola, Moskva 1971.

ВИЗНАЧЕННЯ ГІДРОКСИЛЬНИХ ГРУП В МОДИФІКОВАНИХ ЕПОКСИДНИХ ОЛІГОМЕРАХ З ДОПОМОГОЮ ІЧ-СПЕКТРОСКОПІЇ

Анотація. Запропоновано визначити вміст гідроксильних груп у модифікованих функційних олігомерах, на основі дигліциділового етеру бісфенолу А, з використанням ІЧ-спектроскопії. Використані для дослідження олігомери крім гідроксильних груп містять епоксидну або пероксидну, карбоксильні чи акрилатну групу.

Ключові слова: гліколь, епоксид, функціональний олігомер, гідроксильне число, ІЧ-спектроскопія.

