Reactions of Hydroxyalkyl Esters with Phenyl Isocyanate

Renata Lubczak, Jacek Lubczak

Faculty of Chemistry, Rzeszów University of Technology, 35-959 Rzeszów, Poland

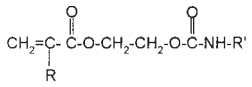
Received 18 June 2004; accepted 13 October 2004
DOI 10.1002/app.21563
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In a reaction between 2-hydroxyethyl methacrylate and phenyl isocyanate (PI), we did not obtain the expected urethane ester monomer but products of its subsequent conversion, namely, ethylene dimethacrylate and ethylene bis(phenylcarbamate). The effects of the structures of various hydroxyalkyl esters on the transformation of the products of their reaction with PI into their respective diesters and alkanediyl bis(phenylcarbamates) were observed with standard spectral methods (IR, ^{1}H-NMR) and chromatographic and classical separation techniques. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1357–1367, 2005

Key words: polyurethanes; structure; synthesis

INTRODUCTION

In the reactions of 2-hydroxyethyl esters of acrylic acid or methacrylic acid (MA) with typical isocyanates, one obtains so-called urethane ester monomers[1] of the general formula:



where R denotes H— or CH_3— and R′ stands for an alkyl or aromatic moiety. The polymerization of these monomers yields polymeric materials applicable as impregnation and adhesion agents, crosslinking agents, nontoxic dentistry materials, coatings, and waveguide protective materials.[2–10] By selecting proper isocyanates, polyetherols, and hydroxyalkyl esters as raw materials in the synthesis of urethane esters one can adjust the properties of the resulting polymers. The data published on these materials, however, are mainly patent descriptions[2–4] with very little basic information on the reaction of hydroxyalkyl with monoisocyanates. The reason might be the well-known course of the reaction between alcohols and typical isocyanates. Also, studies of the reaction between bifunctional isocyanates and 2-hydroxyalkyl acrylates have not revealed any deviations from expected results.[10] In this article, we show that some reactions involving monofunctional isocyanates and hydroxyalkyl esters produce quite unexpected products. In this study, we concentrated on the reactions of phenyl isocyanate (PI) with esters that had different substituents either in their acyl or alkoxyl part.

Correspondence to: J. Lubczak.

Journal of Applied Polymer Science, Vol. 96, 1357–1367 (2005)

EXPERIMENTAL

Materials

Our materials included acetic acid (AA; pure to analysis (p.a.); Chemical Plants Oświęcim, Poland), stearic acid (SA; pure, POCH, Gliwice, Poland), methacrylic acid (MA pure, Sigma-Aldrich, London, UK), cyclohexanecarboxylic acid (CHCA; pure, Sigma-Aldrich), benzoic acid (BA; pure, POCH), *o*-methylbenzoic acid (MBA; pure, Fluka, Buchs, Switzerland), *o*-nitrobenzoic acid (NBA; pure, Sigma-Aldrich), ethylene oxide (EO; pure, Fluka), triethylamine (TEA; pure, Fluka), PI (pure, Sigma-Aldrich) heptane (p.a., POCH), benzene (p.a., POCH), xylene (p.a., POCH), the cation-exchange resin Amberlite IR-120 (Sigma-Aldrich), propane-1,3-diol (pure Sigma-Aldrich), butane-1,4-diol (pure, Merck, Whitehouse Station, NJ), and phenylacetic acid (PA, pure, Sigma-Aldrich).

Unless stated otherwise, all of the reactions were carried out in a typical set consisting of a three-necked flask (100, 250, or 500 cm^3) equipped with a mechanical stirrer, a reflux condenser (with a Dean–Stark head when water was a product), and a thermometer.

Hydroxyalkyl esters

2-hydroxyethyl esters

A three-necked, 500-mL flask equipped with a mechanical stirrer, thermometer, and reflux condenser of special construction was used [to limit losses of low-boiling EO (bp = 14°C), solid CO_2 was placed in the condenser, and the condenser was successively replenished with fresh dry ice as it evaporated]. Carbox-

ylic acid (1 mol) was placed together with an appropriate amount of xylene [specified in parentheses in cm^3 in the following: the carboxylic acids were AA (0), SA (300), phenyloacetic acid (PAA; 220), MA (0), CHCA (0), BA (300), MBA (280), and NBA (350)]. Then, EO was introduced in a few portions, each containing about 15 g (0.33 mol) of EO. After the first portion of EO was introduced, the mixture was heated up to the boiling point and kept at boiling until no EO condensate droplets were seen on the inner walls of the condenser. In reactions where the temperature increase was too slow, TEA was added as a catalyst [the following amounts of TEA were used (mol/mol of acid): 0.025/AA, 0.048/PAA, 0.025/MA, 0.02/CHCA, 0.043/BA, 0.041/MBA, and 0.028/NBA]. The mixture was then cooled down to 10°C, the next portion of EO was introduced, and the procedure was repeated. After all of the EO had been introduced (1 mol) and the mixture reached 100°C, the acid number (AN) was determined by titration with 0.1*M* $KOH_{aqueous}$. When the AN was higher than zero, the lacking amount of oxirane was calculated and added. The addition reaction was continued until AN was 0 (the reaction times were 12.0, 39.5, 18.5, 7.5, 14.5, 11.5, 23.0, and 20.5 h for AA, SA, PAA, MA, CHCA, BA, MBA, and NBA, respectively). Finally, the solvent was removed in a rotary evaporator. 2-Hydroxyethyl methacrylate (HEMA), 2-hydroxyethyl acetate (HEA), 2-hydroxyethyl phenylacetate (HEPA), 2-hydroxyethyl cyclohexanecarboxylate (HECHC), 2-hydroxyethyl *o*-methylbenzoate (HEMB), and 2-hydroxyethyl *o*-nitrobenzoate (HENB) were purified by distillation under reduced pressure (HEMA bp = 59.0–59.5°C/2.4 hPa; HEA bp = 57.0°C/4.0 hPa; HEPA bp = 150°C/15.7 hPa; HECHC bp = 115°C/2.0 hPa; HEMB bp = 152°C/6.9 hPa; HENB bp = 180°C/3.0 hPa). 2-Hydroxyethyl stearate (HES) was crystallized from methanol or heptane, and 2-hydroxyethyl benzoate (HEB) was crystallized from benzene.

HEMA Yield: 96%. ANAL. Calcd for $C_6H_{10}O_3$ (M_{calcd} = 130.1; M_{found} = 129.1): C, 55.38%; H, 7.69%. Found: C, 55.11%; H, 7.28%. ^{1}H-NMR: 6.05, 5.6 (2H, 2s, CH_2═); 4.40 (1H, s, OH); 4.15 (2H, t, CO—O—CH_2); 3.65 (2H, t, C—CH_2—OH); 1.95 (3H, s, CH_3). IR (capillary film): 3320 (OH), 1645 (C═C), 1730 (C═O), 1080 (C—OH). Refractive index ($n^{20}_{D\ ref.}$) = 1.4530;[11] $n^{20}_{D\ found}$ = 1.4528.

HEA Yield: 97%. ANAL. Calcd for $C_4H_8O_3$ (M_{calcd} = 104.1; M_{found} = 107.0): C, 46.15%; H, 7.74%. Found: C, 45.92%; H, 7.52%. ^{1}H-NMR: 4.47 (1H, s, OH), 4.04 (2H, t, CO—O—CH_2), 3.60 (2H, t, C—CH_2—OH), 2.02 (3H, s, CH_3). IR (capillary film): 3320 (OH), 1730 (C═O), 1440 (CH_2), 1380 (CH_3), 1080, 1040 (C—OH). $n^{20}_{D\ ref.}$ = 1.4200;[12] $n^{20}_{D\ found}$ = 1.4190.

HES Yield: 90%. ANAL. Calcd for $C_{20}H_{40}O_3$ (M_{calcd} = 328.5; M_{found} = 324.2): C, 73.12%; H, 12.27%. Found: C, 72.52%; H, 12.95%. ^{1}H-NMR: 4.15 (2H, t, CO—O—CH_2), 3.74 (2H, t, C—CH_2—OH), 3.10 (1H, s, OH), 2.28 (2H, t, —CH_2—CO—O), 1.20 [30 H, m, $(CH_2)_{15}$], 0.74 (3H, s, CH_3). IR (KBr): 3310 (OH); 2900, 2850 (CH_2); 1735 (C═O); 1170 (C—OH and CO—O). $mp_{ref.}$ = 60–61°C;[12] mp_{found} = 59–60°C.

HEPA Yield: 94%. ANAL. Calcd for $C_{10}H_{12}O_3$ (M_{calcd} = 180.2; M_{found} = 182.4): C, 66.65%; H, 6.71%. Found: C, 65.92%; H, 6.98%. ^{1}H-NMR: 7.20 (5H, s, phenylgroup (Ph)), 4.39 (1H, s, OH), 4.05 (2H, t, CO—O—CH_2), 3.65 (2H, t, C—CH_2—OH), 3.42 (2H, s,—CH_2—CO—O). IR (capillary film): 3310 (OH); 3000 (═CH in Ph); 1775 (C═O); 1580, 1490 (C═C in Ph); 1250 (CO—O); 1080 (C—OH); 710, 690 (═CH in Ph).

HECHC Yield: 94%. ANAL. Calcd for $C_9H_{16}O_3$ (M_{calcd} = 172.2; M_{found} = 174.2): C, 62.77%; H, 9.36%. Found: C, 63.28%; H, 9.20%. ^{1}H-NMR: 5.20 (1H, s, OH), 3.95 (2H, t, CO—O—CH_2), 3.45 (2H, m, C—CH_2—OH), 2.2 (1H, m, C_1—H in ring), 1.9–0.9 (10H, m, C_{2-6}—H in ring). IR (capillary film): 3300 (OH), 1735 (C═O), 1450 (CH_2), 1240 (CO—O), 1040 (C—OH). $n^{20}_{D\ found}$ = 1.4745.

HEB Yield: 96%. ANAL. Calcd for $C_9H_{10}O_3$ (M_{calcd} = 166.2; M_{found} = 165.2): C, 64.71%; H, 6.03%. Found: C, 64.01%; H, 6.49%. ^{1}H-NMR: 7.98 (2H, m, *ortho*-2H in Ph), 7.55 (3H, m, C_3—H, C_4—H and C_5—H in Ph), 4.63 (1H, s, OH), 4.10 (2H, t, CO—O—CH_2), 3.71 (2H, t, C—CH_2—OH). IR (KBr): 3300 (OH); 3030 (═CH in Ph); 1740, 1710 (C═O); 1590, 1575 (C═C in Ph); 1270 (CO—O); 1090 (C—OH); 715 (═CH in Ph). $mp_{ref.}$ = 45°C;[12] mp_{found} = 44°C.

HEMB Yield: 91%. ANAL. Calcd for $C_{10}H_{12}O_3$ (M_{calcd} = 180.3; M_{found} = 178.2): C, 66.65%; H, 6.71%. Found: C, 66.05%; H, 7.12%. ^{1}H-NMR: 7.85 (2H, m, *ortho*-2H in Ph), 7.25 (3H, m, C_3—H, C_4—H and C_5—H in Ph), 4.65 (1H, s, OH), 4.25 (2H, t, CO—O—CH_2), 2.45 (3H, s, CH_3). IR (capillary film): 3320 (OH); 3010 (═CH in Ph); 1710 (C═O); 1600, 1570 (C═C in Ph); 1380 (CH_3); 1260 (C—OH and CO—O); 1075 (C—OH); 1165, 1145, 735 (═CH in Ph). $n^{20}_{D\ found}$ = 1.5340.

HENB Yield: 93%. ANAL. Calcd for $C_9H_9NO_5$ (M_{calcd} = 211.2; M_{found} = 209.7): C, 51.19%; H, 4.29%; N, 6.63%. Found: C, 51.14%; H, 4.84%; N, 6.45%. ^{1}H-NMR: 8.10–7.80 (4H, m, H in Ph), 4.45 (1H, s, OH), 4.30 (2H, t, CO—O—CH_2), 3.65 (2H, t, C—CH_2—OH). IR (capillary film): 3320 (OH); 3040 (═CH in Ph); 1725 (C═O); 1530, 1350 (NO_2); 1290 (C—OH and CO—O); 1070 (C—OH); 865, 845 (═CH in Ph). $n^{20}_{D\ found}$ = 1.5365.

2-(2-Hydroxyethoxy)ethyl acetate (HEEA)

To a 500-cm^3 autoclave, 44 g (1 mol) of EO and 72 g (1 mol) of the HEA prepared as described previously were introduced along with 2.5 g of TEA (0.025 mol). The reaction was carried out for 336 h at room temperature and then for 120 h at 40°C until

completion. The product was purified by distillation under reduced pressure (bp = 121–123°C/4.6 hPa).

Yield: 85%. ANAL. Calcd for $C_6H_{12}O_4$ (M_{calcd} = 148.2; M_{found} = 146.3): C, 48.64%; H, 8.16%. Found: C, 49.06%; H, 8.43%. ^{1}H-NMR: 4.45 (1H, s, OH), 4.05 (2H, t, CO—O—CH_2), 3.7–3.3 (6H, m, CH_2—O—CH_2CH_2—OH), 1.95 (3H, s, CH_3). IR (capillary film): 3390 (OH), 1735 (C═O), 1240 (CO—O), 1130 (OH and C—O—C), 1050 (C—OH).

Other hydroxyalkyl esters

In a three-necked, 500-mL flask equipped with a mechanical stirrer, thermometer, reflux condenser, and Dean–Stark head, 30 g (0.5 mol) of AA, 35 cm^3 of benzene or heptane, and 3 g of an acidic form of the cation exchanger Amberlite IR-120 as a catalyst were mixed together. Then, 38 g of propane-1,3-diol or 45 g of butane-1,4-diol were introduced to the mixture, and the flask content was kept at boiling (85–105°C) with vigorous stirring for 5.5 or 3.5 h, respectively. The extent of the reaction was followed by observation of the amount of water collected in the Dean–Stark head. The reaction was considered completed when the amount of water in the head did not change for an hour. The catalyst was filtered off on a Büchner funnel, and the solvent was removed in a rotary evaporator. The product was purified by distillation [3-hydroxypropyl acetate (HPA) bp = 205°C/1013 hPa; 4-hydroxybutyl acetate (HBA) bp = 92–94°C/6.7 hPa].

HPA Yield: 78%. ANAL. Calcd for $C_5H_{10}O_3$ (M_{calcd} = 118.1; M_{found} = 119.4): C, 50.83%; H, 8.53%. Found: C, 51.09%; H, 8.59%. ^{1}H-NMR: 4.25 (1H, s, OH), 4.00 (2H, t, CO—O—CH_2), 3.40 (2H, t, C—CH_2—OH), 1.8–1.5 (2H, m, C—CH_2—C), 1.95 (3H, s,CH_3). IR (capillary film): 3420 (OH), 2957 (CH_2), 1732 (C═O), 1365 (CH_3), 1225 (CO—O), 1050 (C—OH). $n_{D\ ref.}^{20}$ = 1.4231;[12] $n_{D\ found}^{20}$ = 1.4240.

HBA Yield: 74%. ANAL. Calcd for $C_6H_{12}O_3$ (M_{calcd} = 132.2; M_{found} = 134.8): C, 54.53%; H, 9.15%. Found: C, 54.37%; H, 9.25%. ^{1}H-NMR: 4.3 (1H, s, OH), 4.0 (2H, t, CO—O—CH_2), 3.35 (2H, m, C—CH_2—OH), 1.7–1.3 (4H, m, C—CH_2—CH_2—C), 1.95 (3H, s, CH_3). IR 3390 (OH), 1735 (C═O), 1365 (CH_3), 1240 (CO—O), 1050 (C—OH).

4-Hydroxybutyl acrylate (HBAC; pure, Sigma-Aldrich) ANAL. Calcd for $C_7H_{12}O_3$ (M_{calcd} = 144.2; M_{found} = 144.0): C, 58.32%; H, 8.38%. Found: C, 59.12%; H, 8.39%. ^{1}H-NMR: 6.2, 5.8 (2H, 2m, CH_2═); 4.35 (1H, s, OH); 4.05 (2H, t, CO—O—CH_2); 3.35 (2H, m, C—CH_2—OH); 1.8–1.2 (4H, m, C—CH_2—CH_2—C). IR (capillary film): 3360 (OH); 1720 (C═O); 1634, 1616 (C═C); 1271 (CO—O); 1054 (C—OH). $n_D^{20}{}_{ref.}$ = 1.4503;[12] $n_{D\ found}^{20}$ = 1.4503.

Other compounds: anticipated products of the transformation of urethane esters

Alkanediyl diesters

In a three-necked, 250-mL flask equipped with a mechanical stirrer, thermometer, reflux condenser, and Dean–Stark head, 0.25 mol of acid (MA, AA, phenylacetic acid (PA), or BA) and an equimolar amount of 2-hydroxyethyl ester of the respective acid were mixed along with 1 cm^3 of concentrated sulfuric acid as catalyst and 65 cm^3 of heptane as an azeotropic agent. In the case of MA and its ester, 0.5 g of phenotiazine were added to prevent a polymerization reaction. The reactions were carried out with the mixture kept at boiling (108–115°C) with vigorous stirring for about 4 h. The extent of the reaction was followed by the measurement of the amount of water collected in the Dean–Stark head. The reaction was considered completed when the water level in the head did not change for an hour. Heptane was then removed in a rotary evaporator, and the catalyst was neutralized with 10% aqueous potassium bicarbonate and washed with distilled water. The crude ethylene dimethacrylate (EDMA), ethylene diacetate (EDA), and ethylene bis(phenylacetate) (EDPA) were purified by distillation under reduced pressure (EDMA bp = 90–95°C/4 hPa; EDA bp = 182–187°C; EDPA bp = 205°C/12 hPa), and ethylene dibenzoate (EDB) was purified by recrystallization from heptane.

We prepared propane-1,3-diyl diacetate (PDDA), butane-1,4-diyl diacetate (BDDA), and 3-oxapentane-1,5-diyl diacetate (OPDDA) in similar way starting with 1 mol of AA and 0.5 mol of propane-1,3-diol, butane-1,4-diol, or diethylene glycol, respectively, with, alternatively, 0.2 cm^3 of concentrated sulfuric acid or Amberlite IR-120 (2.3 g) as a catalyst and heptane (35 cm^3) as an azeotropic agent. The crude products were purified by distillation under reduced pressure (PDDA bp = 94°C/7.9 hPa; BDDA bp = 102°C/7.2 hPa; OPDDA bp = 138°C/10 hPa).

EDMA Yield: 84%. ANAL. Calcd for $C_{10}H_{14}O_4$ (M_{calcd} = 198.2; M_{found} = 200.1): C, 60.63%; H, 7.07%. Found: C, 59.92%; H, 7.39%. ^{1}H-NMR: 6.0, 5.6 (2H, 2m, CH_2═); 4.35 (4H, s, O—CH_2—CH_2—O); 1.90 (6H, s, CH_3). IR (capillary film): 2990 (CH_2, CH_3), 1730 (C═O), 1640 (C═C), 1150 (CO—O).

EDA Yield: 88%. ANAL. Calcd for $C_6H_{10}O_4$ (M_{calcd} = 146.1; M_{found} = 145.2): C, 49.31%; H, 6.89%. Found: C, 49.01%; H, 6.99%. ^{1}H-NMR: 4.20 (4H, s, O—CH_2—CH_2—O), 1.95 (6H, s, CH_3CO). IR (capillary film): 2920, 2840 (CH_3, CH_2), 1740 (C═O), 1365 (CH_3), 1220 (CO—O). $n_{D\ ref.}^{20}$ = 1.4150;[11] $n_{D\ found}^{20}$ = 1.4160.

EDPA Yield: 85%. ANAL. Calcd for $C_{18}H_{18}O_4$ (M_{calcd} = 298.2; M_{found} = 301.0): C, 72.41%; H, 6.03%. Found: C, 72.01%; H, 6.39%. ^{1}H-NMR: 7.6–6.8 (10H, m, H in Ph), 4.20 (4H, s, O—CH_2—CH_2—O), 3.55 (4H, s, —CH_2COO—). IR (capillary film): 2940 (═CH in Ph,

CH_2); 1730 (C═O); 1595, 1540, 1490 (═CH in Ph); 1215 (CO—O); 755 (═CH in Ph). $n_{D\ found}^{20}$ = 1.5564.

EDB Yield: 88%. ANAL. Calcd for $C_{16}H_{14}O_4$ (M_{calcd} = 270; M_{found} = 269.05): C, 71.11%; H, 5.19%. Found: C, 70.82%; H, 5.29%. ^{1}H-NMR: 7.5–6.9 (10H, m, H in Ph), 4.30 (4H, s, O—CH_2—CH_2—O). IR ($CHCl_3$) 2990 (═CH in Ph, CH_2), 1730 (C═O), 1220 (CO—O), 750 (═CH in Ph).

PDDA Yield: 78%. ANAL. Calcd for $C_7H_{12}O_4$ (M_{calcd} = 160.1; M_{found} = 159.8): C, 52.48%; H, 7.40%. Found: C, 52.01%; H, 7.68%. ^{1}H-NMR: 4.00 (4H, t, O—CH_2—C), 1.8–1.5 (2H, m, C—CH_2—C), 1.90 (6H, s, CH_3). IR (capillary film): 2960 (CH_3, CH_2), 1730 (C═O), 1430 (CH_2), 1365 (CH_3), 1218 (CO—O). $n_{D\ found}^{20}$ = 1.4198.

BDDA Yield: 70%. ANAL. Calcd for $C_8H_{14}O_4$ (M_{calcd} = 174.2; M_{found} = 174.7): C, 55.16%; H, 8.10%. Found: C, 55.71%; H, 7.93%. ^{1}H-NMR: 4.0 (4H, t, O—CH_2—C), 1.7–1.4 (4H, m, C—CH_2—CH_2—C), 1.95 (6H, s, CH_3). IR (capillary film): 2900 (CH_2, CH_3), 1735 (C═O), 1435 (CH_2), 1240 (CO—O).

OPDDA Yield: 68%. ANAL. Calcd for $C_8H_{14}O_5$ (M_{calcd} = 190.2; M_{found} = 188.4): C, 55.16%; H, 8.10%. Found: C, 55.71%; H, 7.93%. ^{1}H-NMR: 4.0 (4H, t, O—CH_2—C), 1.7–1.4 (4H, m, C—CH_2—CH_2—C), 1.95 (6H, s, CH_3). IR (capillary film): 2900 (CH_2, CH_3), 1735 (C═O), 1435 (CH_2), 1240 (CO—O), 1010 (C—O—C)

Alkanediyl bis(phenylcarbamates)

In a three-necked, 100-mL flask equipped with a mechanical stirrer, thermometer, and reflux condenser, 0.1 mol of a diol (6.2 g of ethylene glycol, 7.6 g of propane-1,3-diol, 9.0 g of butane-1,4-diol, or 10.6 g of diethylene glycol) and 23.8 g (0.2 mol) of PI were mixed in a reactor flask. A large amount of heat evolved during the mixture of the components, so the temperature rose in some cases to 170°C. The mixture was then allowed to cool to 60°C, and it was kept at this temperature until all of the isocyanate groups reacted (the content of isocyanate groups was determined by the ammonium method[13]). The reaction products were purified by recrystallization from benzene [ethylene bis(*N*-phenylcarbamate) (EBPC), propane-1,3-diyl bis(*N*-phenylcarbamate) (PDBPC), and 3-oxapentane-1,5-diyl bis(*N*-phenylcarbamate) (OPDBPC)] or from the xylene–dimethyl sulfoxide mixture [butane-1,4-diyl bis(*N*-phenylcarbamate) (BDBPC)].

EBPC Yield: 90%. ANAL. Calcd for $C_{16}H_{16}N_2O_4$ (M_{calcd} = 300.3; M_{found} = 298.5): C, 63.99%; H, 5.37%; N, 9.43%. Found: C, 63.29%; H, 5.33%; N, 9.28%. ^{1}H-NMR: 9.67 (2H, s, NH), 7.75–6.87 (10H, m, H in Ph), 4.28 (4H, t, O—CH_2). IR (KBr): 3350 (NH); 1695 (I amide band); 1595, 1495 (C═C in Ph); 1545 (II amide band); 1230 (III amide band); 1160, 1120 (═CH in Ph); 830 (C—N in amide).

PDBPC Yield: 91%. ANAL. Calcd for $C_{17}H_{18}N_2O_4$ (M_{calcd} = 314.3; M_{found} = 310.1): C, 64.96%; H, 5.77%; N, 8.91%. Found: C, 64.52%; H, 5.71%; N, 9.03%. ^{1}H-NMR: 9.6 (2H, s, NH), 7.6–6.8 (10H, m, H in Ph), 4.10 (4H, t, O—CH_2), 1.90 (2H, m, C—CH_2—C). IR (KBr): 3330 (NH); 1706 (I amide band); 1590, 1495 (C═C in Ph); 1530 (II amide band); 1226 (III amide band); 1084, 1028 (═CH in Ph); 692 (C—N in amide).

BDBPC Yield: 89%. ANAL. Calcd for $C_{18}H_{20}N_2O_4$ (M_{calcd} = 328.3; M_{found} = 325.1): C, 65.84%; H, 6.14%; N, 8.53%. Found: C, 65.19%; H, 6.04%; N, 7.95%. ^{1}H-NMR: 9.55 (2H, s, NH), 7.5–6.8 (10H, m, H in Ph), 4.10 (4H, t, O—CH_2), 2.10–1.75 (4H, m, C—CH_2—CH_2—C). IR (KBr): 3290 (NH); 1700 (I amide band); 1590, 1495 (C═C in Ph); 1525 (II amide band); 1230 (III amide band); 1090, 1070, 1030 (═CH in Ph); 745 [$(CH_2)_4$—O]; 690 (C—N in amide).

OPDBPC Yield: 85%. ANAL. Calcd for $C_{18}H_{20}N_2O_5$ (M_{calcd} = 344.3; M_{found} = 342.0): C, 62.78%; H, 5.85%; N, 8.13%. Found: C, 61.92%; H, 6.15%; N, 7.65%. ^{1}H-NMR: 9.6 (2H, s, NH), 7.6–6.8 (10H, m, H in Ph), 4.15 (4H, t, O—CH_2), 3.60 (4H, t, O—CH_2—C). IR (KBr): 3290 (NH); 1730 (I amide band); 1590, 1495 (C═C in Ph); 1540 (II amide band); 1230 (III amide band); 690 (C—N in amide).

1,2-Diphenylurea (DPU) ANAL. Calcd for $C_{13}H_{12}N_2O$ (M_{calcd} = 212.2; M_{found} = 211.0): C, 73.57%; H, 5.70%; N,13.20%. Found: C, 73.02%; H, 6.10%; N, 12.94%. ^{1}H-NMR: 8.6 (2H, s, NH), 7.5–6.8 (10H, m, H in Ph). IR (KBr): 3250 (NH); 1645 (I amide band); 1590, 1495 (C═C in Ph); 1545 (II amide band); 1230 (III amide band); 690 (C—N in amide).

Reactions of hydroxyalkyl esters with PI

In a three-necked, 100-mL flask equipped with a mechanical stirrer, thermometer, and reflux condenser, equimolar amounts (0.2 mol) of the respective hydroxyalkyl esters and PI were mixed in the reactor flask. A rapid increase in temperature up to about 70°C was usually observed due the exothermic effect. The temperature in the flask was eventually set to 40°C and kept there until the disappearance of isocyanate groups.

In some cases, the temperature in the flask was kept at 30°C, and TEA was used as catalyst.

Urethane ester I: 2-benzoiloxyethyl *N*-phenylcarbamate (BEPC)

Yield: 94%. ANAL. Calcd for $C_{16}H_{15}NO_4$ (M_{calcd} = 285.3; M_{found} = 282.7): C, 67.34%; H, 5.29%; N, 4.52%. Found: C, 67.52%; H, 5.31%; N, 4.52%. ^{1}H-NMR: 9.70 (H, s, NH), 8.1–6.9 (10H, m, H in Ph), 4.50 (4H, s, O—CH_2—CH_2—O). IR (KBr): 3295 (NH); 1745 (C═O); 1725 (I amide band); 1600 (C═C in Ph); 1545

(II amide band); 1230 (III amide band); 760, 710 (C═C in Ph). mp = 110.5–112°C.

Urethane ester II: 2-(*o*-methylbenzoiloxy)ethyl *N*-phenylcarbamate

Yield: 90%. ANAL. Calcd for $C_{17}H_{27}NO_4$ (M_{calcd} = 299.3; M_{found} = 297.1): C, 68.22%; H, 5.72%; N, 6.68%. Found: C, 68.32%; H, 5.69%; N, 4.21%. ^{1}H-NMR: 9.7 (H, s, NH); 7.9, 7.4–6.8 (9H, m, H in Ph); 4.50 (2H, t, CH_2—OCO—NH); 2.55 (2H, t, Ph—CO—O—CH_2—C). IR (KBr): 3400 (NH), 1745 (C═O), 1725 (I amide band),1600 (C═C in Ph), 1540 (II amide band) 1250 (III amide band), 1205 (CO—O), 690 (C—N in amide).

Urethane ester III: 2-(*o*-nitrobenzoiloxy)ethyl *N*-phenylcarbamate

Yield: 92%. ANAL. Calcd for $C_{16}H_{14}NO_4$ (M_{calcd} = 330.3; M_{found} = 328.5): C, 64.43%; H, 4.70%; N, 9.40%. Found: C, 64.55%; H, 4.27%; N, 9.42%. ^{1}H-NMR: 9.75 (H, s, NH), 8.0–6.9 (9H, m, H in Ph), 4.55 (2H, t, CH_2—OCO—NH), 3.70 (2H, t, Ph—CO—O—CH_2—C). IR (KBr): 3280 (NH); 1740 (C═O and I amide band); 1580 (C═C in Ph); 1525 (II amide band); 1350 (NO_2); 1230 (III amide band); 1205 (CO—O); 760, 735 (C═C in Ph); 690 (C—N in amide).

Analytical methods

Reaction course

The course of the reaction between the carboxylic acids and EO, propane-1,3-diol, and butane-1,4-diol was followed by the measurement of the AN in the reaction mixture by titration with $KOH_{aqueous}$. The amount of unreacted isocyanate groups was also determined by titration with the ammonium method.[13]

Isolation of urethane ester transformation products

The mixture obtained by the reaction of the hydroxyalkyl esters with PI was dissolved in benzene at 60°C and cooled to allow the proper *N*-phenylcarbamate or urethane ester crystallize. The precipitate was filtered off on a Büchner funnel and washed with benzene. The filtrates were combined, and the solvent was removed on a rotary evaporator under reduced pressure to isolate the appropriate alkanediyl diesters.

Identification of the products

The molar masses of the esters and products of their reaction with PI were determined cryoscopically in 1,4-dioxane. The melting points were determined with a Boëtuis (hot plate) apparatus. The refractive index was determined with an Abbe refractometer (PZO, Warsaw, Poland). Elemental analyses were made on a Fissons EA 1108 apparatus (Carlo-Erba, Stanford Valencia, CA). IR and ^{1}H-NMR spectra were recorded on a PerkinElmer Paragon 1000 FT machine (Wellensley, MA) (capillary film and KBr pellets) and on FT 80 MHz Tesla BS 587 A (Prague, Czechoslovakia) NMR machine (with d_6—dimethyl sulfoxide or d_6—acetone solutions and a hexamethyldisiloxane internal standard).

The products obtained in the reactions of HEMA, HPA, and HEB with PI were analyzed on a Hewlett-Packard 5890 gas chromatograph with a flame-ionization detector with a 30 × 0.53 × 0.88 μm HP-1 column (Palo Alto, CA). Ethyl acetate was the mobile phase; the temperature was 50–220°C, raised at a rate of 20°C/min. The carrier gas (He) rate was 18.3 cm^3/min, and the sample amount was 0.2 μL. All chromatograms of the substrates and presumed urethane esters were made under the same conditions.

RESULTS AND DISCUSSION

From among many methods for the preparation of 2-hydroxyethyl esters, a method was selected involving the reaction of the respective carboxylic acids with EO. The method provided the highest yield and purest product. Wherever possible, the direct method of esterification with diols was avoided because of their equilibrium character and problems with the removal of water, which was soluble in the resulting ester and vice versa. Furthermore, side products could easily be formed, such as diesters and products of autotransesterification of the resulting 2-hydroxyethyl esters. All of that was avoided when oxiranes were applied because the process was carried out at a much lower temperature than the direct esterification.

The solid carboxylic acids were dissolved in xylene. In the case of AA, no solvent was used.

The structures of the compounds were determined on the basis of the results of elemental analysis, molecular weight determination, IR and ^{1}H-NMR spectra, refractive index, and melting points. The data are presented in the Experimental section.

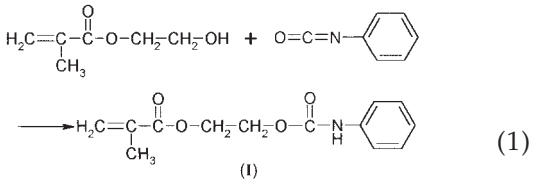
Reactions in the HEMA–PI system

To obtain urethane ester monomer, HEMA was mixed with PI at room temperature. A small exothermic effect was observed (40°C). After the temperature dropped, the amount of isocyanate groups as determined with the ammonium method indicated that the conversion was about 90%. To complete the reaction, 0.25 cm^3 of TEA/mol of HEMA were added (cf. p 4). The mixture was heated to 40°C and kept at this temperature for 30–45 min. Toward the end of the

TABLE I
Elemental Analysis of the Products Obtained in the Reaction of HEMA with PI

Composition	Compound	Content (wt %) C	H	N
Calcd	Urethane ester from HEMA and PI	62.67	6.02	5.62
	EBPC	64.02	5.33	9.33
	EDM	60.63	7.07	—
Found	Crystalline product	63.38	5.53	9.45
	Liquid product	59.78	6.93	—

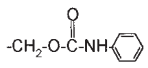
reaction, the presence of a small amount of white crystalline solid was observed. The product crystallized slowly at room temperature. The reaction was faster when it proceeded at a higher temperature (60–80°C). Initially, this product was taken to be the anticipated urethane ester formed according to the following scheme:



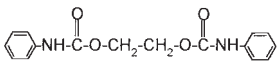
(1)

(I)

The ^{1}H-NMR spectrum of the crystalline product, however, was different than expected. It had a signal from —NH— group at 9.7 ppm from aromatic protons at 6.8–7.6 ppm and one due to —CH_2— group at 4.3 ppm. Their integration ratio was 1:5:2, respectively. The elemental analysis of the compound (Table I) showed that the atomic ratio C:H:N:O was 8:8:1:2, and hence, its simplest formula read $C_8H_8NO_2$. The relevant structure of the fragment is



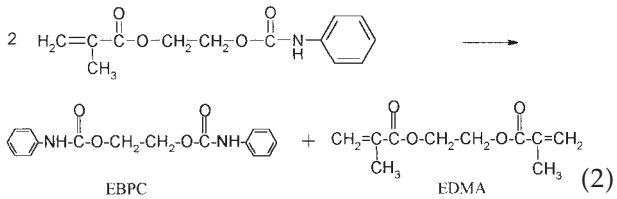
and, when the molecular weight was considered, it was a symmetric compound with the formula $C_{16}H_{16}N_2O_4$, that is, EBPC:



EBPC (II)

This guess was further confirmed by an IR spectrum, where absorption bands characteristic for carbamates could clearly be distinguished (3300, 1715, 1595, 1525, 1075–1090, 750–790, and 690–750 cm^{-1}). The spectrum did not contain methacrylic fragments, including the band at 1645 cm^{-1} due to double bonds.

The formation of EBPC probably could be explained on the assumption that the urethane ester was initially formed, but it rearranged according to the scheme:



EBPC EDMA (2)

This was confirmed by a ^{1}H-NMR spectra of the reaction mixture successively treated with benzene. The extraction resulted in a gradual washing out from the spectra the methacrylic signals without effects on the carbamide fragments [Fig. 1(a,b)]. Finally, pure EBPC was seen in the spectrum [Fig. 1(c)].

EDMA was indeed isolated from benzene filtrate left after crystallization (Fig. 2). By evaporating it at rotary evaporator, we isolated a product that purified by distillation under reduced pressure, yielded a liquid identical with that of EDMA obtained by the reaction of MA with HEMA.

To determine the yield of transformation, the postreaction product obtained from HEMA and PI was analyzed quantitatively by the determination of the content of EBPC and EDMA. The former was isolated by treatment of the postreaction mixture with benzene at 60°C followed by recrystallization of the component again from benzene. Benzene was then distilled off from combined filtrates and weighed before vacuum distillation. This crude EDMA contained some EBPC and benzene; hence, the assay content was estimated from the ^{1}H-NMR spectra of the crude product. Signals from methyl protons in EDMA (at 9.6 ppm) were the diagnostic signals. The content of benzene was calculated from the intensity of the signals at 6.8–7.8 ppm. The estimated yield of EBPC and EDMA was thus about 98%.

In conclusion, in the reaction between PI and HEMA carried out at temperatures from 40°C (reaction temperature) to 60°C (extraction with benzene), we could not obtain the expected urethane ester because it underwent subsequent transformation. The same results were obtained when both the reaction between HEMA and PI and the extraction were carried out at room temperature. Only a much longer time was required. These findings are inconsistent with the results reported by Krishnan et al.,[14] who carried out the reaction in tetrahydrofuran in the presence of tin(II) caprate as a catalyst. They were able to obtain the desired urethane ester capable of subsequent polymerization.[14] By mass spec-

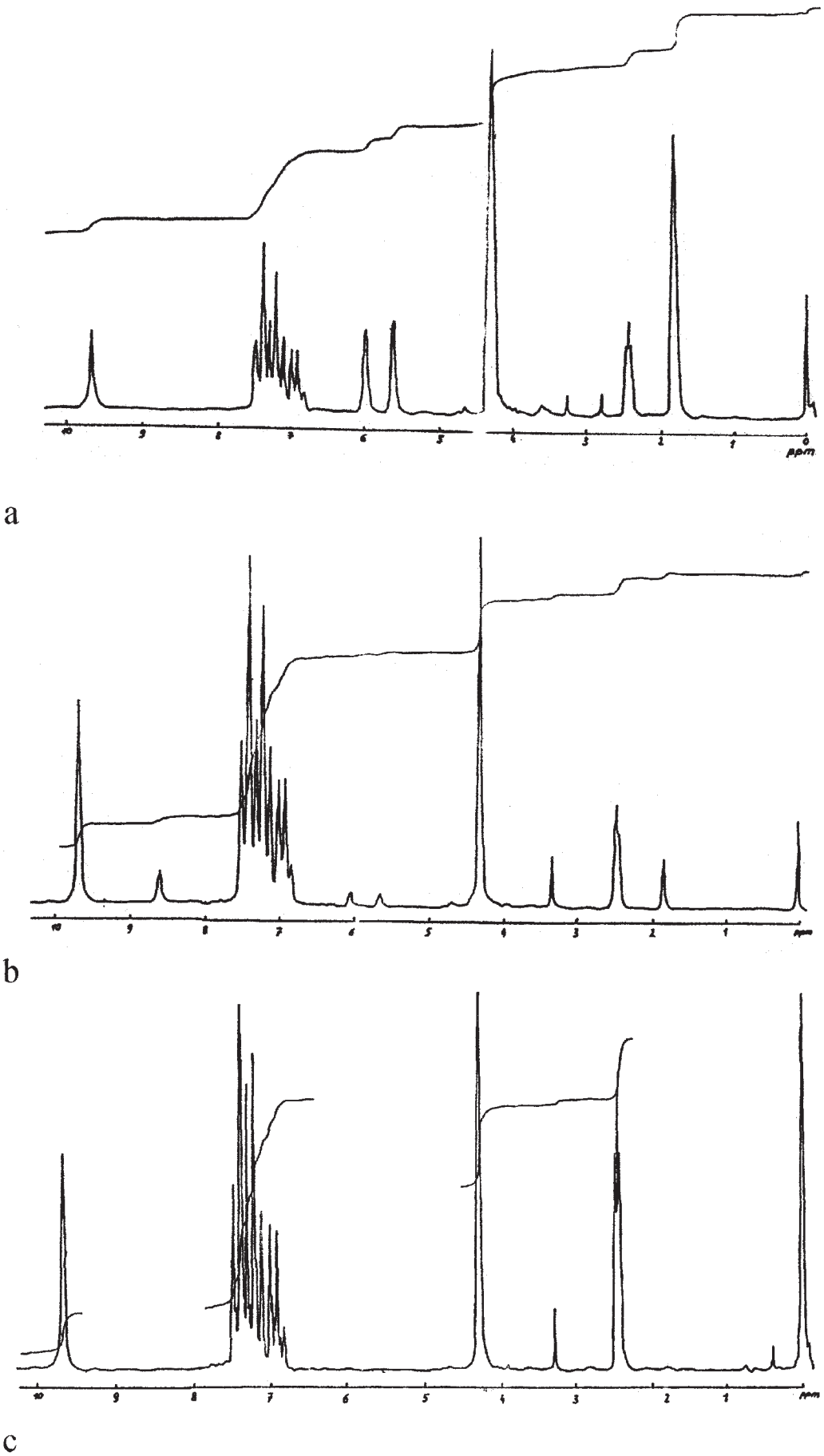


Figure 1 ^{1}H-NMR spectra of the mixtures (a) just after the reaction of 1 mol of HEMA with 1 mol of IP and (b) after washing with benzene and (c) the product after extraction with benzene and recrystallization was completed.

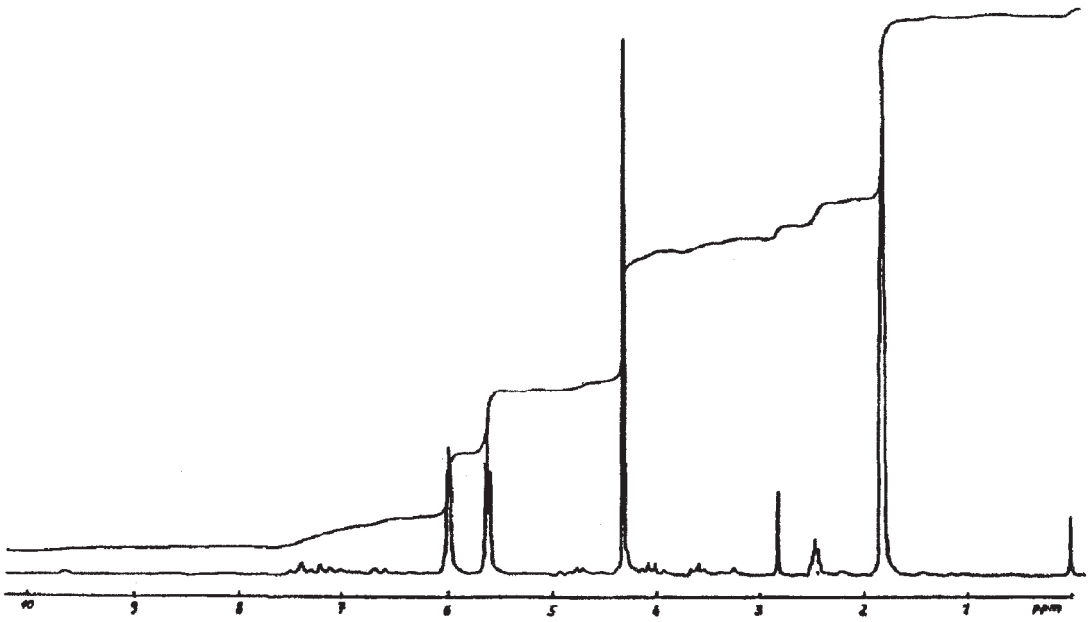
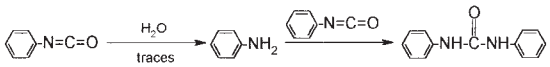


Figure 2 ^{1}H-NMR spectrum of the product isolated from benzene extract (EDMA).

troscopy, they confirmed the molar mass of the product to be 249 g/mol as it should have been.

Gas–liquid chromatography (GLC) analysis of the reaction mixture also revealed that the reaction carried out at 30°C (Table II) undoubtedly produced a mixture of EDMA (retention time = 7.42 min) and EBPC (retention time = 9.19 min); that is, the transformation of urethane ester did occur. To another GLC signal at a retention time 10.84 min, no compound was initially ascribed. This signal was believed to belong to yet unconverted urethane ester. To verify the presumption, the postreaction mixture was left at room temperature or heated to 80°C, and then, GLC analysis was repeated [Fig. 3(a,b)]. In both cases, the size of peak at 10.84 min had a smaller size than in the original mixture. The reason why the authors of ref. 14 were successful follows. The experiment of Krishnan et al.[14] showed that for the reaction carried out at a temperature of 30°C, the product contained urethane ester seen in GLC, but after a few minutes, white EBPC precipitates, and after several hours, the mixture phase separated into EBPC (lower layer) and EDMA (upper layer).

In the GLC chromatogram, there was also another peak at a retention time of 13.16 min. This peak was due to DPU that was apparently also present in the postreaction mixture. Hence, beside the reactions shown in eqs. (1) and (2), the following reaction also took place:



DPU was identified from elemental analysis by the measurement of its boiling point and by analysis of its

TABLE II
Results of the Chromatographic Analyses of the Mixtures Obtained in Reactions of HEMA, HEA, or HEB with PI

Standard	Retention time for standards (min)	Reaction mixture	Found retention times (min)	Identified compounds
HEMA	4.54	HEMA + PI	7.42	EDM
HPA	3.19		9.19	EBPC
HEB	7.97		10.84	Urethane ester
EDM	7.42		13.16	DPU
PDDA	5.73	HEA + PI	5.74	PDDA
EDB	12.63		9.73	PDBPC
EBPC	9.19		10.51	Urethane ester
PDBPC	9.73		13.16	DPU
DPU	13.16	HEB + PI	10.81	BEPC
BEPC	10.81			

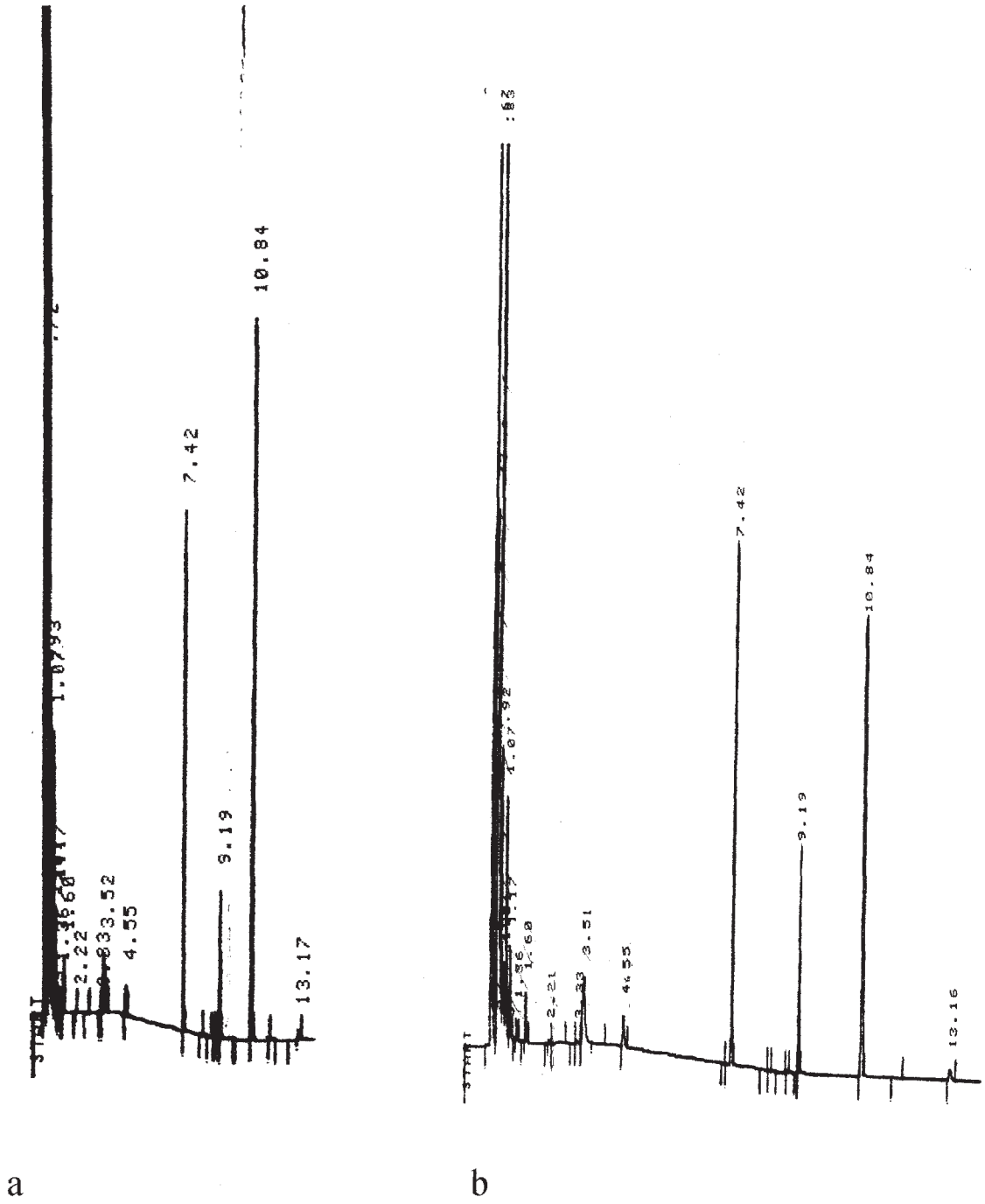


Figure 3 Chromatograms of the reaction mixtures: (a) just after the reaction of 1 mol of HEMA with 1 mol of IP and (b) after further heating at 80°C.

IR and ^{1}H-NMR spectra. We found that the formation of DPU could be avoided by the careful removal of water from hydroxyalkyl ester; with the drying of the hydroxyalkyl ester $MgSO_4$ prior to use, no formation of DPU was observed. The conversion of urethane esters to corresponding diesters and carbamates took place both in the presence and in the absence of TEA. In most of the reactions described hereafter, 2.5×10^{-4} mol of TEA/mol of hydroxyalkyl ester was introduced into the reaction mixture at the end of the reaction between the esters and PI.

Reactions taking place in the systems comprising PI and other hydroxyalkyl esters

To verify whether or not similar transformations took place in reactions of PI and hydroxyalkyl esters of various acyl and alkoxyl groups, a series of experi-

ments was carried out with the following 2-hydroxyethyl esters: HEA, HES, HEPA, HECHC, HEB, HEMB, and HENB. The reactivity of the esters with PI depended primarily on the structure of the acyl group and changed in the order HEA > HEPA > HES > HECHC. This reactivity order seemed to be the result of increasing steric hindrances, that is, the presence of aromatic ring in HEPA and the long aliphatic chain in HES. Furthermore, for *ortho*-substituted fragments in the acyl groups, the bigger the substituent was, the smaller the reactivity of the respective ester with PI was; here also, the steric factor seemed decisive. The reactivity order for aromatic esters was HEB > HEMB > HENB.

In all reactions between PI and the esters selected, white crystalline solid precipitated soon after the reaction started. As we learned later, the solid was either urethane ester or EBPC. To find out where the transformation did take place, the following procedure was applied:

1. In cases where solvent was used, it was first distilled off under reduced pressure, the product of reaction was weighed, and a ^{1}H-NMR spectrum of the whole mixture recorded.
2. The product mixture was dissolved in benzene at 60°C and then cooled. If present in the postreaction mixture, EBPC precipitated off as a fine crystalline powder; it was easy to identify after recrystallization from benzene in the same way as described earlier (elemental analysis, boiling point, IR, and ^{1}H-NMR spectra).
3. From the filtrate left after the operations described in the previous point were made, the solvent was distilled off under reduced pressure and the product, the respective ethylene diester, was identified.

The results follow. In reactions of PI with HEA, HEPA, or HES, no urethane ester was obtained, but a mixture of subsequent products, that is, EBPC and the respective diester, was obtained. Although the ^{1}H-NMR spectra of the postreaction mixture mimicked those of the initially anticipated product, extractions with benzene (similar to those described for HEMA) yielded pure EBPC. From the filtrates freed from benzene excess, the diesters EDA and EDPA were isolated, and their structures were confirmed.

The mixture obtained after the reaction of HECHC with PI left for several days at room temperature separated into two phases. The lower contained crystalline EBPC, whereas the upper contained ethylene bis(cyclohexanecarboxylate).

The reactions of HEB, HEMB, and HENB with PI, on the other hand, yielded the respective urethane esters that precipitated from the respective reaction mixtures and did not transform anymore. This was confirmed by the ^{1}H-NMR spectra of the recrystallized products.

They contained signals from aromatic protons and from ethylene protons, and the ratios of signal intensities agreed with the number of respective protons. Also, the melting points, IR spectra, elemental analysis, and molecular weight determinations confirmed the structures of the urethane esters.

The effect of the position of the hydroxyl group in the alkoxyl part of hydroxyalkyl esters on the readiness of phenyl urethane esters to transform to EBPC was also studied to find whether only hydroxyethyl esters underwent this reaction. The following esters were used: HPA, HBA, HBAC, and HEEA. The esters were reacted with PI as in the previous cases. Here again, the obtained ^{1}H-NMR spectra of the postreaction mixture mimicked the urethane esters, but the extraction with benzene yielded products that were the respective bis(*N*-phenylcarbamates). To verify their identification, we obtained the same products directly by reacting PI with propane-1,3-diol or butane-1,4-diol at a molar ratio 2:1 [cf. the section on Alkanediyl Bis(phenylcarbamates)].

The mixture obtained by the reaction of HEEA did not contain any precipitate. Attempts to separate the products [in this case the respective bis(*N*-phenylcarbamate) and diacetate] consisted of the extraction of the mixture with two solvents of different polarities. The solvents were heptane and DMF at ratios of 4:1 v/v. In the spectrum of the product extracted with heptane, the signals from aromatic protons (6.8–7.6 ppm) as well as that from NH (9.65 ppm) were in a substantial minority compared with signals from methyl group protons (1.95 ppm) due to diacetate. Clearly, OPDDA was present. On the other hand, in the DMF extract, the intensity ratios of signals did not match those expected for the respective urethane ester. The anticipated product of transformation (OPDBPC) was, therefore, prepared separately from diethylene glycol and PI (molar ratio 1:2). The product was a crystalline solid, but it readily dissolved in OPDDA, and this was the reason why the postreaction mixture was homogeneous.

All of these results indicate that the position of the carboxyl group in the alkoxyl moiety had no effect on the possibility of spontaneous transformation of the urethane ester.

For some of the systems, the results were also confirmed chromatographically (GLC). In addition to the system with HEMA described previously, those systems where HPA and HEB were reacted with PI were analyzed. To facilitate identification, the retention times were measured for each substrate, and the possible product that could have been formed from urethane ester was analyzed. Hence, EBPC, PDBPC, EDA, PDDA, and EDB were separately analyzed with GLC.

In the chromatogram of the reaction products of HPA with PI, peaks appeared due to PDDA (5.73 min) and PDBPC (9.73 min). As in the previous case, the signal at 13.16 min due to DPU and a signal at 10.51 min not corresponding to any standard compound, apparently due to urethane ester, was also present. The latter peak had a reduced intensity as the mixture was left at room temperature or slightly heated.

It was again confirmed that in most of the reactions in question, the urethane ester did formed, but it gradually underwent transformation. No further conversion was observed, however, in the case of HEB. In the chromatograms of the products of the reaction of HEB and PI, no peaks due to possible transformation products (EDB or EBPC) were present. The peak due to urethane ester at 10.81 min was present in the chromatogram, and its relative intensity did not change even after heating at 80°C.

In conclusion, urethane ester was stable when its carbonyl group was linked directly to an aromatic ring. The esters with carbonyl groups linked to aromatic ring possessed a larger steric hindrance around the group. The steric hindrance from phenyl made the attack of ester oxygen on carbonyl carbon atom less likely and prevented the transformation. The detailed analysis of the mechanism of the reaction will be reported separately.

CONCLUSIONS

1. In reactions of PI with the hydroxyalkyl esters of carboxylic acids, urethane esters or products of their further conversion were obtained, namely, alkanediyl bis(phenylcarbamates) and their respective diesters.
2. The kind of products probably depended on the steric hindrance in the vicinity the carbonyl carbon atom in the acyl group of the urethane ester. The large steric hindrance was expected to induce the formation of urethane ester instead of its transformation.
3. No effect of the position of hydroxyl group in the alkoxy fragment on the tendency of urethane esters to transform was observed.

References

1. Okhrimienko, J.; Vierkholancev, V. Chemistry and Technology of Film-Forming Substances; WNT: Warsaw, Poland, 1982 (in Polish).
2. Feit, E. D.; Thomson, L. F. U.S. Pat. 4,023,208 (1977).
3. Kazuhiko, I.; Minoru, Y. Jpn. Pat. 207,580 (1992).
4. Tsuneo, I.; Masashi, T.; Junichi, K. Jpn. Pat. 256,446 (1992).
5. Tilak, G. Y. Prog Org Coat 1985, 13, 333.
6. Thomas, J.; Parisi, J. P.; Bouterin, B. Natl Super Chim Polym Bull 1992, 29, 259.
7. Chappelow, C. C.; Byerley, T. J.; Pinzino, C. S.; Millich, F.; Eick, J. D. J Dent Res 1996, 75, 761.
8. Oprea, S.; Vlad, S.; Stanciu, A. Polymer 2001, 42, 7257.
9. Antonucci, J. M.; Brauer, G. M. Dent Med Mater Sect Nadt Bir Stand 1980, 59, 35.
10. Kucharski, M.; Lubczak, J. In Progress in Waveguide Technology; UMCS Editorial Office: Lublin, 1990; pp 376 (in Polish).
11. Handbook of Fine Chemicals and Laboratory Equipment; Sigma-Aldrich: Poznań, Poland, 2003–2004; p 859.
12. Handbook of Chemistry and Physics, 76th ed.; Lide, D. R., Ed.; CRC: Boca Raton, FL, 1995.
13. Kastierina, T.; Kalinina, T. Chemical Analysis of Plastics; WNT: Warsaw, Poland, 1965 (in Polish).
14. Krishnan, P. S. G.; Chouthary, V.; Varma, I. K. Cent Mater Sci Technol 1991, 1, 138.