The structure of novel polyurethanes containing synthetic poly[(*R,S*)-3-hydroxybutyrate]

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Abstract: The aim of the present study was to estimate the structure of new polyurethanes with the potential to be used in medicine. Atactic poly[(*R,S*)-3-hydroxybutyrate], obtained via a ring-opening polymerization, and polycaprolactonediol or polyoxytetramethylenediol were used to built the soft segments. 4,4'-methylene dicyclohexyl diisocyanate and 1,4-butanediol were the components to form hard segments. At FTIR spectra of obtained polyurethanes the bands attributed to -N=C=O groups completely disappeared, similarly as these of -OH groups and the new band characteristic for stretching vibrations of bonded urethane -NH groups appeared. Polyurethanes with low molecular weight were obtained. The observation of FTIR and ^{1}HNMR spectra had been suggested that NH groups form two types of hydrogen bonds: with C=O urethane (possibly with ester group) and ether groups. An addition of poly[(*R,S*)-3-hydroxybutyrate] caused the slight increase in number of urethane-urethane hydrogen bonds. For some of polyurethanes (based on polyoxytetramethylenediol) the allophanate structures were obtained.

Key words: structure, polyurethanes, synthetic atactic polyhydroxybutyrate

Introduction

Poly(3-hydroxybutyrate) (PHB) belongs to the family of biodegradable aliphatic polyesters that can be produced from renewable resources. PHB is an optically active polyester, naturally synthesized by many microorganisms as a resource of carbon and energy. The polymer is fully biodegradable by hydrolytic processes or

microbial activity [1]. Product of its degradation – 3-hydroxybutyric acid - is a common metabolite in human blood.

PHB is a biocompatible material, used as conduits for long-gap repair in peripheral nerves, patch materials for repair of defects in gastrointestine, pericardial substitute after cardiac surgery, or suture material [2].

An alternative method of PHB obtaining is its chemical synthesis via ring opening polymerization of *β*-butyrolactone. An important feature of this strategy is the ability to regulate microstructure of the PHB chain by varying the ratio of *β*-butyrolactone strereoisomers in the monomer feed, leading to atactic, isotactic or syndiotactic PHBs, whereas microbial PHB exists only in isotactic R configuration [3]. It is worthy to note that intracellular native PHB is a mobile and amorphous elastomer and during the recovery process, PHB is denaturated and then becomes crystalline. So synthetic, almost completely amorphous a-PHB, is close to its original state in the cell [1].

The aim of the present study was to estimate the influence of the synthetic atactic poly[(*R,S*)-3-hydroxybutyrate] (a-PHB) on the structure of new polyurethanes (PURs) with the potential to be used in medicine. Telechelic hydroxyterminated atactic poly[(*R,S*)-3-hydroxybutyrate] (a-PHB) and polycaprolactonediol (PCL) or polyoxytetramethylenediol (PTMO) were used to built the soft segments. 4,4'-methylene dicyclohexyl diisocyanate (H_{12}MDI) and 1,4-butanediol (1,4-BD) were the components to form hard segments.

Experimental

Materials

Atactic poly(*R,S*)-3-hydroxybutyrate, a-PHB, (Mn=2000) was obtained in Centre of Polymer and Carbon Materials PAS, Zabrze, by anionic ring-opening polymerization of racemic (R,*S*)-*ß*-butyrolactone in the presence of sodium 3-hydroxybutyrate/18-crown-6 complexes at room temperature [4].

Before the synthesis of polyurethanes a-PHB was dried by heating at 60-70ºC under reduced pressure (1,4 hPa). Polycaprolactonediol, PCL, (Mn=1900) (Aldrich) and polyoxytetramethylenediol, PTMO, (Mn=2000) (Aldrich) were dried by heating at 60-70 ºC or at 90-100 ºC under reduced pressure (1,4 hPa).

4,4'-methylene dicyclohexyl diisocyanate, H_{12}MDI, (Alfa Aesar), was purified via vacuum distillation.

Chain extender 1,4-butanediol, 1,4-BD, (Aldrich) was freed from moisture by an azeotropic distillation with benzene prior to use.

Solvent dimethylformamide, DMF, (Labscan Ltd) was dehydrated over P_2O_5 and distilled under low pressure before synthesis.

Catalyst: dibutyltindilaurate, DBTDL, (Akra Chem.) was used as received.

Polyurethane synthesis and sample preparation

Synthesis of polyurethanes was carried out in a two-step reaction at the vacuum reactor, as described previously [5]. First, the prepolymer was prepared from polyols and H_{12}MDI, in a presence of catalyst (DBTDL), at reduced pressure (1,4 hPa) according to molar ratio of NCO:OH groups indicated in Table 1. Polyols used in synthesis were as follows: a-PHB, or mixture of PCL and a-PHB, or mixture of PTMO and a-PHB (molar ratio of OH groups is indicated in Table 1). For comparison, PURs based only on PCL or PTMO, without a-PHB, where also obtained. The reaction was carried out for 2 h at temperature range 60-70 ºC, when a-PHB was used in polyol mixture, or at range 90-100 ºC, when only PCL or PTMO were used as soft segments.

The prepolymer was then dissolved in DMF to solid mass concentration of 40 %. The chain extender (1,4-BD) was added to obtain equimolar ratio NCO:OH groups and reaction was continued at 60 ºC for 1.5 h.

Solution of polyurethane was poured on Teflon plates and heated at 80 ºC for solvent evaporating. Next, the foils were heated at 105 ºC in vacuum dryer for 5 h.

GPC analysis

Molecular weights of PUR samples were acquired from SpectraPhysics 8800 gel permeation chromatograph (GPC) using tetrahydrofuran (THF) as eluent at a flow rate of 1 mL min^{-1} at 35 ºC. Polystyrene standards with low polydispersity were used as references.

Infrared investigation

Infrared spectra were acquired on a DIGILAB FTS-40A Fourier transform infrared spectrometer in the range of 4000-400 cm^{-1} at a resolution of 2 cm^{-1} and for

an accumulated 32 scans. Samples were analyzed as films obtained after evaporating of chloroform from solutions onto potassium bromide windows.

NMR analysis

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) was recorded using a Varian Unity Iova spectrometer at 300 MHz and a 5-mm sample tube. The ^{1}H NMR spectra were run in dried DMSO, in ambient temperature or at 80 °C, because of insolubility of some polyurethane samples at room temperature. Tetramethylsilane (TMS) was used as an internal standard. The spectra were obtained with 64 scans and a 3.74-s acquisition time.

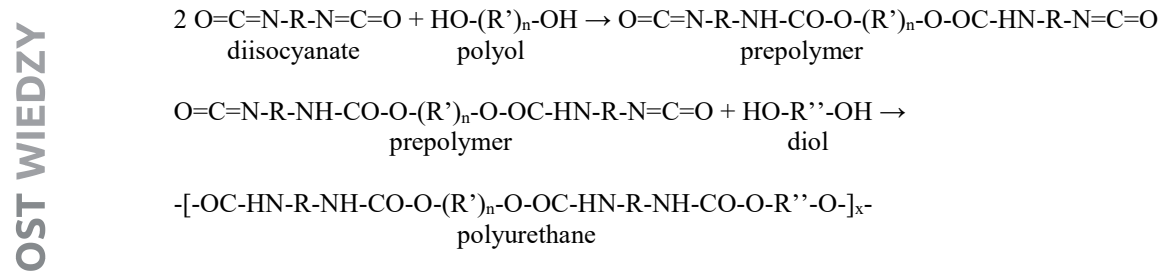
Results and discussion

The different polyols and the molar ratio of polyols, H_{12}MDI and 1,4-BD were altered to obtain the polyurethanes with varied soft segments and varied length of hard segments (Tab. 1). The general scheme of the synthesis of polyurethanes is shown at Scheme 1.

Tab. 1

PUR	Molar ratio of OH groups				Molar ratio of NCO/OH in prepolymer
	PCL	a-PHB	PTMO	1,4-BD	
$PUR_{PTMO/3.7}$	-	-	1	2.7	3.7
$PUR_{PTMO+a-PHB/3.7}$	-	0.23	0.77	2.7	3.7
$PUR_{PCL/3.7}$	1	-	-	2.7	3.7
$PUR_{PCL+a-PHB/3.7}$	0.77	0.23	-	2.7	3.7
$PUR_{a-PHB/3.7}$	-	1	-	2.7	3.7
$PUR_{PTMO/2}$	-	-	1	1	2
$PUR_{PTMO+a-PHB/2}$	-	0.23	0.77	1	2
$PUR_{PCL/2}$	1	-	-	1	2
$PUR_{PCL+a-PHB/2}$	0.77	0.23	-	1	2

Scheme 1



GPC analysis

Molecular weights determined for PURs based on mixed polyols are presented in Table 2.

Tab. 2

PUR	M_n	M_w	M_w/M_n
$PUR_{PTMO+a-PHB/3.7}$	13668	42343	3,10
$PUR_{PCL+a-PHB/3.7}$	7930	20530	2,60
$PUR_{PTMO+a-PHB/2}$	18360	72640	3,95
$PUR_{PCL+a-PHB}$	16040	42990	2,70

All samples showed low molecular weights (ranging from 7930 to 18360) and wide molecular weight distribution (ranging from 2.6 to 3.95).

According to potential application of these polyurethanes as degradable material for medical engineering or in drug delivery system low molar masses can accelerate degradation processes in living body. Thermal properties of obtained polyurethanes [5], indicating on their low crystallinity, suggest their potential degradability [6, 7].

Infrared investigation

Infrared analysis was done for PUR substrates and final products.

At the H_{12}MDI FTIR spectrum the strongest intensity band appears at 2263 cm^{-1} arising from stretching vibrations of N=C=O group. Middle intensity bands corresponding to asymmetric and symmetric stretching vibrations of aliphatic groups are observed at 2932 cm^{-1} and 2854 cm^{-1}, respectively, while these due to the deformation mode at 1449 cm^{-1} (in-plane), 1361 cm^{-1} and 1326 cm^{-1} (wagging).

The bands corresponding to asymmetric and symmetric stretching vibrations of aliphatic groups at the PTMO spectrum appear at 2940 cm^{-1} and 2857 cm^{-1}, 2796 cm^{-1}, respectively, while these of deformation vibrations are observed at 1484 cm^{-1}, 1467 cm^{-1}, 1436 cm^{-1} (in-plane), 1368 cm^{-1} (wagging) and 962 cm^{-1} (rocking). Strong

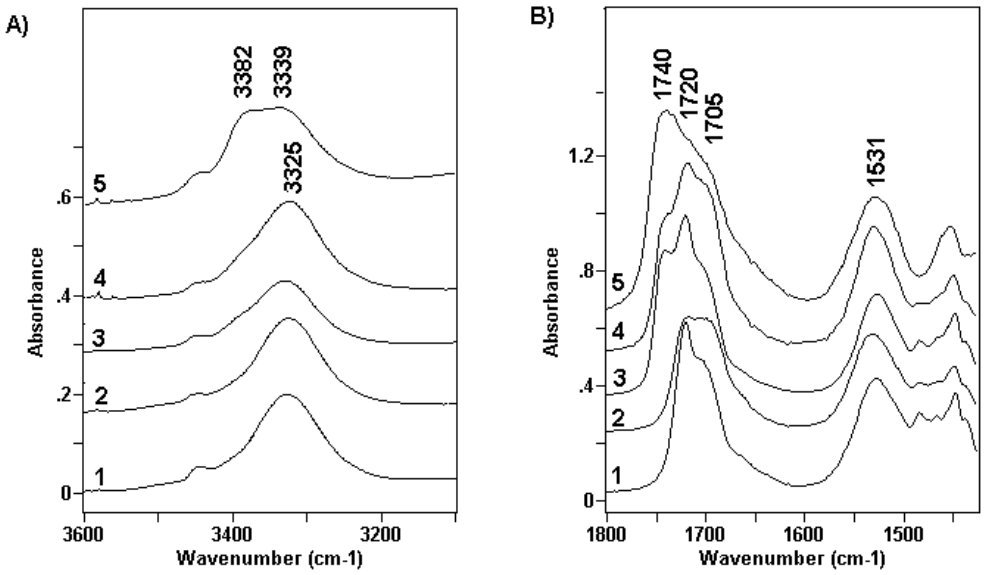
band with maximum at 1114 cm^{-1} arises from the stretching vibrations of C-O ether group. Relatively small intensity band at 3474 cm^{-1} is attributed to the stretching vibrations of OH group, while this at 1015 cm^{-1} could be ascribed to the stretching vibrations of C-OH group.

At PCL spectrum the band ascribed to the stretching vibration of C=O ester group appears at 1726 cm^{-1}, while this of C-O ester group at 1195 cm^{-1}. The bands associated with the stretching vibrations of CH_2 groups are observed at 2946 cm^{-1} and 2867 cm^{-1} and with deformation vibrations at: 1471 cm^{-1} (in-plane), 1368 cm^{-1} (wagging), 1245 cm^{-1} (twisting) and at 733 cm^{-1} (skeletal). Relatively broad and small intensity band at 3533 cm^{-1} corresponds to the stretching vibrations of bonded hydroxyl groups, while sharp one at 3439 cm^{-1} arises from overtone of carbonyl group. The band ascribed to deformation vibrations of O-H group is observed at 1296 cm^{-1} and to stretching vibrations of C-OH groups at 1047 cm^{-1}.

For a-PHB sample the C=O ester groups absorb at 1740 cm^{-1} and due to the literature [8, 9, 10] indicate on the presence of amorphous form. It is also confirmed by the bands at 2985 cm^{-1} and 1186 cm^{-1} characteristic of asymmetric stretching vibration CH_3 groups and rocking vibrations C-O-C, respectively, of in amorphous PHB components [11, 12, 13].

Polymer spectra support the formation of urethane groups during polyaddition reaction. The bands attributed to N=C=O groups completely disappear, similarly as these of OH groups. Simultaneously new bands appear, i.e.: the band characteristic for stretching vibrations of bonded NH (from urethane) groups in the region of 3400-3300 cm^{-1}, the amide I band in the region 1740-1690 cm^{-1} and the amide II band in the region of 1530-1510 cm^{-1}. Due to literature data [14] these two last bands consist mainly of the stretching vibrations of C=O urethane group and deformation vibrations of NH groups, respectively.

Fig. 1.



In the case of polyurethanes obtained from PTMO ($PUR_{PTMO/3,7}$ and $PUR_{PTMO/2}$) in the region ascribed to the stretching vibrations of NH urethane groups one band without any shoulders is observed at 3325 cm^{-1} (Fig. 1A lines 1 and 2). No bands are detected above 3500 cm^{-1}, which suggests that all NH groups are engaged in formation of hydrogen bonds (little intensity shoulder at 3445 cm^{-1} is the overtone of the band at 1720 cm^{-1}). On the other hand, in the region attributed to the amide I bands, i.e. the stretching vibrations of C=O urethane groups, the broad band with some shoulders is recorded (Fig. 1B lines 1 and 2). For $PUR_{PTMO/3,7}$ (polymer obtained at 3.7:1 NCO:OH ratio in prepolymer) two comparable intensity, overlapped bands at 1720 cm^{-1} and 1705 cm^{-1}, are observed, while for $PUR_{PTMO/2}$, polymer obtained at 2:1 NCO:OH ratio, intensity of the band at 1705 cm^{-1} is notably less. An appearance of two bands in that region is interpreted in the literature [8, 10, 15] as a result of presence of free and bonded C=O urethane groups. Thus, the presence in the sample of free carbonyl groups could prove that NH groups form hydrogen bonds not only with C=O urethane groups but also with oxygen in the ether ones. This could be an evidence that some hydrogen bonds appear between hard and soft segments of polyurethanes and diminish the microphase separation what is confirmed by DSC [5]. It could be also found that more bonded C=O (from urethane) groups are present in polymer with greater NCO:OH ratio.

After introducing of a-PHB into polyurethane structure ($PUR_{PTMO+a\text{-}PHB/3,7}$ and $PUR_{PTMO+a\text{-}PHB/2}$) the bands spectra appear due to a-PHB and due to urethane units.

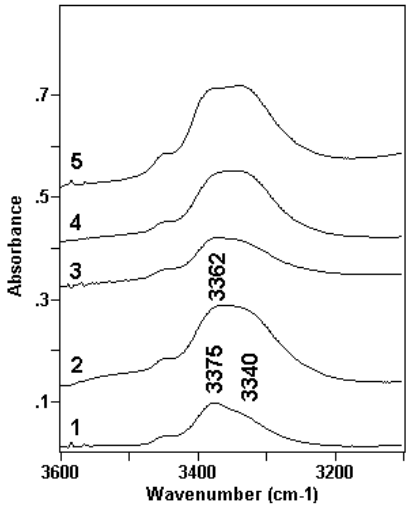
However the obtained spectra are not constituted exactly of the sum of component spectra but some changes are observed. Generally, it could be found that the band ascribed to bonded C=O groups (from urethane) decreases its intensity in comparison to polyurethane without a-PHB (Fig. 1B) and differences are larger for higher NCO:OH ratio in prepolymer ($PUR_{PTMO+a\text{-}PHB/3,7}$). Additionally, characteristic band for stretching vibrations of NH in urethane groups is broader. Simultaneously the little intensity shoulder is detected at about 3380 cm^{-1} for polyurethanes with a-PHB unit.

For polyurethane synthesized with a-PHB (without PTMO - $PUR_{a\text{-}PHB/3,7}$) two overlapped bands with maxima at 3382 cm^{-1} and 3339 cm^{-1} are observed (Fig. 1 line 4). It demonstrates, that NH groups in the presence of the ester ones form hydrogen bonds with C=O from urethane and from ester groups. Consequently, the band at 3382 cm^{-1} corresponds to vibrations of NH groups associated with C=O ester groups, while that at 3339 cm^{-1} - to vibrations of NH groups forming hydrogen bonds with urethane ones.

It could be also noticed that the region characteristic for the stretching vibrations of C=O ester and urethane groups in this case is not quite good for quantitative determination of the relations between free and bonded ester and urethane groups. In spite of the band at 1740 cm^{-1} is attributed to free C=O ester groups, the band due to bonded ones overlap these of urethane groups causing that they are not good separated.

The amide II band for the all four samples (with PTMO or PTMO with a-PHB), similarly as for $PUR_{a\text{-}PHB/3,7}$, appears at 1531 cm^{-1} and any differences are observed in that region.

Fig. 2.



For polyurethanes obtained with PCL at 3.7:1 NCO:OH ratio in prepolymer ($PUR_{PCL/3,7}$) and 2:1 NCO:OH ratio in prepolymer ($PUR_{PCL/2}$) the band ascribed to the stretching vibrations of NH groups appears at 3362 cm^{-1} and 3375 cm^{-1}, respectively (Fig. 2). Simultaneously the shoulder at about 3340 cm^{-1} is also detected. Accordingly to above considerations concerning the polyurethanes from PTMO with addition of a-PHB the bands at higher frequencies corresponds to NH---O=C ester hydrogen bonds while these at about 3340 cm^{-1} to NH---O=C urethane ones. It could be noticed that for higher NCO:OH ratio intensity of the band due to NH---O=C urethane is explicitly higher. After introducing of a-PHB to PUR structure the bands, attributed to the NH---O=C ester hydrogen bonds, shift slightly to lower frequencies and are observed at 3360 cm^{-1} and 3370 cm^{-1}. Whereas intensities of the NH---O=C urethane ones become slightly higher.

The band, attributed to the stretching vibrations of C=O in urethane group (the amide I band), strongly overlaps these of the ester group and is observed as a shoulders at lower frequencies in relation to that of the ester group. Similarly, as for polyurethane based on a-PHB, no quantitative information about the relations between free and bonded ester and urethane groups could be obtained. Simultaneously ester groups absorb at a higher frequency than in pure PCL and a-PHB monomers.

Forming of urethane groups is also proved by appearance of the amide II bands at 1530 cm^{-1}, 1524 cm^{-1}, 1528 cm^{-1} and 1525 cm^{-1} for $PUR_{PCL/3,7}$, $PUR_{PCL/2}$,

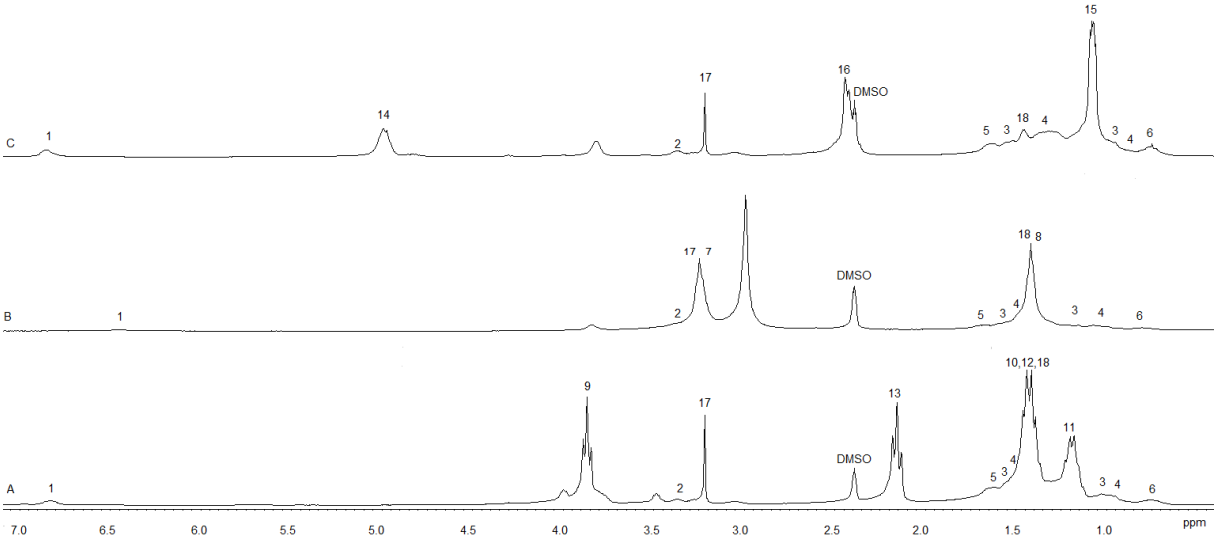
$PUR_{PCL+a\text{-}PHB/3,7}$ and $PUR_{PCL+a\text{-}PHB/2}$, respectively. Thus, the presence of PHB unit causes falling in frequency of the amide II band.

NMR analysis

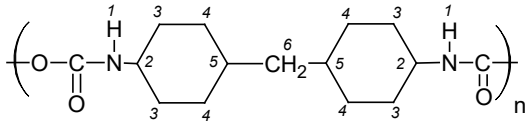
The ^1H NMR spectra of initial compounds and PURs are obtained at room temperature, except spectra of $PUR_{PTMO/2}$ and $PUR_{PTMO+a\text{-}PHB/2}$, which were obtained at 80 °C, because of their insolubility at ambient temperature.

^1H NMR spectra of comonomeric units in polyurethanes are shown in Fig. 3 and correlated data are given in Table 3.

Fig. 3



Tab. 3

Comonomeric units	**Structure**	Group	**Designation of protons in ^1H NMR spectra**
Diisocyanate (R) **H_{12}MDI**		NH CH CH_2 CH_2 CH CH_2	1 2 3 4 5 6
Polyether (R`) **PTMO**	$-O(CH_2CH_2CH_2CH_2-O)_n-$ 7 8 8 7	CH_2 CH_2 CH_2	7 8 9
Polyester (R`) **PCL**	$-(O-CH_2CH_2CH_2CH_2CH_2-CO)_m-$ 9 10 11 12 13	CH_2 CH_2 CH_2 CH_2	10 11 12 13

Polyester (R`) **a-PHB**	-(O-CH(CH$_3$)CH$_2$-CO)$_n$- 14 15 16	CH CH$_2$ CH$_3$	14 15 16
Chain extender (R``) **1,4-Butanediol**	-O-CH$_2$CH$_2$CH$_2$CH$_2$-O- 17 18 18 17	CH$_2$ CH$_2$	17 18

The peaks corresponding to protons of aliphatic groups at the PTMO spectrum are observed as multiple peaks with maximum at 1.48 ppm and at 3.26 ppm for CH_2 attached to high electronegative oxygen atom. The small broad peak of terminal OH group is observed at 4.34 ppm.

At PCL spectrum peaks characteristic for protons of methylene group adjacent to ester group (-OOCC*H*$_2$-) and (-C*H*$_2$OCO-) are observed with maximum at 2.27 ppm and at 3.97 ppm, respectively. Hydrogens due to the -CH_2OH terminal group show the small peaks at 3.59 ppm (-C*H*$_2$OH) and at 4.13 ppm (-CH_2O*H*).

For a-PHB sample the methyl protons are assigned to the intensive bands with maximum at 1.18 ppm (-OCH(C*H*$_3$)CH_2-) on ^{1}HNMR spectrum. The small peaks of protons of terminal groups are observed at 3.95 ppm (HOC*H*(CH$_3$)CH_2-) and at 3.60 ppm (HOC*H*$_2$-). Multiplet at 2.27 ppm is due to methylene protons neighboring to carboxylate group and a broad signal at 5.1 ppm is corresponded to methin proton (-C*H*(CH$_3$)-CH_2-).

Urethane groups are resulting of polyaddition of compounds containing NCO and OH groups in their structure. On ^{1}HNMR spectra of obtained polyurethanes peaks due to NH group are observed in the region of 6.6 – 7.1 ppm. Only NH peaks of $PUR_{PTMO/2}$ and $PUR_{PTMO+a\text{-}PHB/2}$ appear upfield, at 6.4 – 6.7 ppm, what was expected because of an increase of temperature of measurement. According to the literature all of the NH peaks shift to upfield, while other signals (except for water) are independent of temperature [16].

After synthesis signal from protons, corresponding to methin group, which is connected to methylene group between cycloaliphatic rings in H_{12}MDI, shifts upfield (1.72-1,00 ppm). A small peak at 3.45 ppm is ascribed to proton of methin group in cycloaliphatic ring, which is bonded with NH group.

Two peaks: more intensive at 6.97 ppm and very weak at 6.65ppm for $PUR_{PTMO/3.7}$ and 6.56 ppm and 6.45 ppm for $PUR_{PTMO/2}$ are observed on ^{1}HNMR spectra of PURs based on PTMO. Except those mentioned peaks, other weak

signals at 7.08 ppm for $PUR_{PTMO+a\text{-}PHB/3.7}$ and at 6.72 ppm for $PUR_{PTMO+a\text{-}PHB/2}$, after use of a-PHB as a part of soft segments, are observed. It could be explained that the small peaks at 6.65 ppm (or 6.45 ppm) are corresponding to hydrogen bonds formed by NH proton and with C=O urethane groups, but another very weak peak at 7.08 ppm (or 6.72 ppm) could ascribe hydrogen bonding between NH protons and C=O of ester groups, what is confirmed by FTIR observations. On the other hand peaks at 6.65 ppm (or 6.45 ppm) could be related to hydrogen bonding between NH protons and ether oxygen in PTMO [15].

Intensive peaks, in region 1.0 – 1.8 ppm, corresponded to cycloaliphatic protons from H_{12}MDI, are overlapping by methylene protons from PTMO and chain extander 1,4-BD, and are independent on temperature of measurement. The methylene protons from PTMO, attached to atom of oxygen, appear as mutliplets with maximum at 3.32 ppm. Presence of a-PHB in structure polyurethanes caused an appearance of new multiple peaks on spectrum at 5.1 ppm, what is corresponded to methin protons (-C*H*(CH_3)-CH_2-).

On ^{1}HNMR spectra all of PURs containing PTMO in soft segment a very small peak at 9.65 ppm appears, what is probably connected with creating allophanate structures (allophanate bonds are obtained as a result of urethane and isocyanate reaction).

For $PUR_{a\text{-}PHB/3.7}$ ^{1}HNMR spectrum is almost identical as for PURs based on PCL with a-PHB in soft segments. Only peak, assigned to NH proton bonded with oxygen of ester group, is located downfield at 7.15 ppm.

On spectra of PURs based on PCL, PCL+a-PHB, a-PHB, and PTMG a peak at 3.9 ppm is seen. It could be attributed to unreacted OH groups, originated from chain extender. The low molar masses (especially for $PUR_{PCL+a\text{-}PHB/3.7}$ sample) and high molecular weight distribution – mentioned before - suggest that obtained PURs are built with short chains (Table 2) ended with OH groups.

Conclusion

FTIR and ^{1}H NMR spectra support the formation of urethane groups during polyaddition reaction of OH groups of polyols (poly[(*R,S*)-3-hydroxybutyrate], polycaprolactonediol and polyoxytetramethylenediol) and NCO groups of

diisocyanate (4,4'-methylene dicyclohexyl diisocyanate). Polyurethanes with low molecular weight were obtained.

The NH groups, coming from urethane groups, are forming the hydrogen bonds with carbonyl groups of ester and urethane groups and the hydrogen bonds with ether groups.

The greater NCO:OH ratio, the more urethane-urethane hydrogen bonds are formed.

An addition of a-PHB causes the slight increase in number of urethane-urethane hydrogen bonds.

For some of polyurethanes (based on PTMO) the allophanate structures are obtained.

Nomenclature

a-PHB	atactic poly[(*R,S*)-3-hydroxybutyrate]
1,4-BD	1,4-butanediol
DBTDL	dibutyltindilaurate
DMF	dimethylformamide
DMSO	dimethylsulfoxide
FTIR	Fourier transform infrared
H_{12}MDI	4,4'-methylene dicyclohexyl diisocyanate
^{1}H NMR	Proton nuclear magnetic resonance
PCL	polycaprolactonediol
PHB	poly[(*R,S*)-3-hydroxybutyrate]
PTMO	polyoxytetramethylenediol
PUR	polyurethane
TMS	tetramethylsilane

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Legends for figures:

Fig. 1. FTIR spectra of $PUR_{PTMO/2}$ (1), $PUR_{PTMO/3,7}$ (2), $PUR_{PTMO+a\text{-}PHB/2}$ (3), $PUR_{PTMO+a\text{-}PHB/3,7}$ (4), $PUR_{a\text{-}PHB}$ (5).

Fig. 2. FTIR spectra of $PUR_{PCL/2}$ (1), $PUR_{PCL/3,7}$ (2), $PUR_{PCL+a\text{-}PHB/2}$ (3), $PUR_{PCL+a\text{-}PHB/3,7}$ (4), $PUR_{a\text{-}PHB}$ (5).

Fig. 3. ^1H NMR spectra of polyurethanes: A) $PUR_{a\text{-}PHB/3.7}$; B) $PUR_{PTMO/3.7}$; C) $PUR_{PCL/2}$.

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Table 1. Composition of the obtained polyurethanes.

Table 2. Molecular weights of the obtained polyurethanes.

Table 3. Designation of protons in ^1H NMR spectra of comonomeric units in polyurethanes.

Legends for schemes:

Scheme 1. Scheme of synthesis of polyurethanes.