

Synthesis and Solubility Properties of Chitin Acetate/Butyrate Copolymers

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ABSTRACT: In this article, syntheses of chitin acetate/butyrate copolymers with different contents of acetyl residue in polymer chain have been described. Chitin copolymers as well as pure diacetylchitin (DAC) and dibutylchitin (DBC) have been obtained in the reaction of shrimp chitin with mixture of acetic and butyric anhydrides used in different proportion. Reactions have been carried out under heterogeneous condition with perchloric acid (PA) used as a catalyst of reaction. Chemical structure of DAC, DBC, and co-(acetate/butyrate) was confirmed in $^1\text{H-NMR}$ as well as in Fourier transform infrared (FTIR) investigations. Results of $^1\text{H-NMR}$ investigation showed that in all cases of chitin esterification carried out at applied conditions, final products with summary degree of substitution (DP) closed to 2 have been obtained. Prepared chitin acetate/butyrate copolymers with high degree

of polymerization (DP) (based on value of intrinsic viscosity) with varying amount of acetyl groups from 0.24 to 1.29 have been formed depending on the mixture composition of acetic and butyric acid anhydrides. All obtained co-(acetate/butyrate) are soluble in organic solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), dimethylacetamide (DMAc) as well as ethanol and form strong transparent films. It was stated that solubility of obtained chitin copolyesters slightly decreases with increase of the acetyl groups content in polymer chain, but it is still high enough to be taken into consideration for eventual production of fibers or scaffolds. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 175–182, 2011

Key words: biopolymers; esterification; FTIR; NMR; polysaccharides

INTRODUCTION

Chitin is the second most abundant polysaccharide, next to cellulose. This naturally renewed polymer with excellent biological properties is composed of β -(1-4)-linked 2-acetamido-2-deoxy-D-glucopyranose units. It occurs as an important constituent of the exoskeleton of many organisms (particularly crustaceans, insects, and mollusks) and in the cell walls of most fungi and some algae. Currently, main source of chitin production is focused on the chitin isolation from marine invertebrates like crab, krill, shrimp, lobster, and others (79%) and fungi (21%).¹ Chitin molecules possess the high hardness and the tendency to the intermolecular association with the formation of high-oriented supramolecular structures. Difficulties related to extraction, purification, and transfer of chitin to a form suitable for processing have restricted the scientific interest to this polymer. The existence in the molecules of chitin reactive hydroxyl groups offers wide possibility for obtaining of new perspective derivatives of chitin based materials. The substitution of hydroxyl groups by hydro-

phobic esters groups might weaken intermolecular hydrogen bonds and increase the solubility of ester derivatives of chitin.

Various acyl derivatives of chitin have been obtained in Japan in 1979–1981 years.^{2,3} Reaction of formylation, propionylation, butyrylation, and acetylation has been carried out using methanesulfonic acid as a solvent as well as a catalyst of reaction and acid anhydrides as acylation agents. Small amounts of chitin esters with different degree of substitution (DP), different yields, and different solubility in organic solvents have been obtained. Diacetylchitin (DAC) has been prepared also under heterogeneous condition in the presence of perchloric acid (PA) as the catalyst of reaction.

Butyryl derivative of chitin with DP 2, known in the literature as dibutylchitin (DBC), is well examined and widely described.^{4–12} Due to its excellent solubility in several popular organic solvents, it was possible to form DBC films, fibers, and nonwoven materials in amounts convenient for practical use. Biological activity of DBC has been confirmed in investigations both *in vitro* and *in vivo*,^{13,14} and in clinical investigations, when ability of DBC to accelerate healing of various wounds has been observed.^{15,16}

The other bioactive ester derivative of chitin—DAC—due to low number of carbon atoms of hydrophobic residues in the side groups of chitin has limited solubility similar to solubility of native

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chitin,^{2,17} therefore this chitin ester does not find practical application.

There is a probability that introduction of two hydrophobic groups—bulky butyrylic and small acetylic as the side groups into macromolecules of chitin esters might result in preparation of new soluble derivatives of chitin with bioactive properties such as induce faster wound healing and stimulate the connective tissue.

There is little information about mixed esters of chitin in the literature. Van Luyen and Rossbach¹⁸ reported about preparation and solution properties of chitin derivatives obtained by acylation chitin with various amounts of butyric (BA) and acetic (AA) anhydrides in methanesulfonic acid. Those chitin derivatives were characterized by infrared (IR) spectroscopy, Differential scanning calorimetry (DSC), elemental analysis, and ¹H-NMR spectroscopy. Mole ratios of AA/BA were taken in limits from 1 : 1.03 to 1 : 2.9. Samples of mixed esters with total DP from 1.52 to 1.84 were obtained. Samples were characterized by improved solubility comparative to pure acetylchitin, but their solubility was still not enough to be dissolved in ethanol, methanol, or acetone like DBC.

Results of chitin acylation with AA and BA carried out under heterogeneous conditions in the presence of PA as the catalyst of reaction were described in 1999 year.¹⁹ Acid anhydrides were used in large excess (*ca* 10 times) to chitin in mole ratio of AA/BA = 1 : 1, reaction was carried out during 4 h at 20°C and 18 h at 0°C. Samples of single chitin esters—DAC and DBC—were obtained also under the same conditions. Mixed esters of chitin as well as DAC and DBC were obtained with yield of 82% to 94% with different solubility in organic solvents: DAC was soluble in formic acid only, DBC in wide assortment of solvents (acetone, methanol, ethanol, dimethylsulfamide, dimethylacetamide, dimethylsulfoxide, chloroform, and methylene chloride). Described mixed chitin esters were fully soluble in dimethylformamide (DMF), dimethylacetamide (DMAc), and dimethylsulfoxide (DMSO), but insoluble in alcohols, chloroform, and methylene chloride. Chemical structure of obtained chitin esters was investigated using Fourier transform infrared (FTIR) spectroscopy and elemental analysis. It was found that in all cases, two-substituted derivatives of chitin were obtained with chemical composition very close to calculated one.

In 2009, article was published describing the results of synthesis of new chitin mixed-acid esters.²⁰ Trifluoroacetic anhydride was used as an effective promoter for the preparation of several single acid esters of chitin and chitin co-(acetate/butyrate) (CAB), chitin co-(acetate/hexanoate), chitin co-(acetate/octanoate), and chitin co-(acetate/palmitate).

Those mixed chitin esters were soluble in DMF at about 95%. Results of physicochemical characterization of obtained products were presented.

In our initial investigation carried out on chitin mixed butyryl/acetyl esters, there has been found increase of mechanical strength of esters films with increase of acetyl group content in polymer chain.²¹ Thus, it could be expected that presence of optimal amount of acetyl groups might improve mechanical properties of fibers spun from chitin co-(butyryl/acetyl) copolymers.

The aim of works undertaken in this paper is synthesis of series of chitin acetate/butyrate copolymers intended for practical use with different contents of acetyl residue in polymer chain, determination of their chemical structure, and investigation of their solubility in several organic solvents.

EXPERIMENTAL

Materials and methods

As a source for chitin copolyesters shrimp shell α -chitin, product of France Chitin, especially prepared for the purpose of European project CHITOMED, realized in 2003–2005, has been used.²² Chitin was characterized by degree of N-acetylation of *ca* 95%, intrinsic viscosity value in DMAc/5% LiCl, 25°C [η] = 23.8 dL g⁻¹, and viscosity average molar mass 574 × 10³ Da.

AA, 98%, POCh Gliwice, Poland; BA, 98%, Aldrich; and PA, 70–72%, Sigma-Aldrich Poland, were obtained from commercial sources and used as received. Organic solvents: DMF, diethyl ether, formic acid (98%), DMAc, DMSO, acetone, methanol, and ethanol of pure grade were also used as received. LiCl, 99%, A.C.S reagent, Sigma-Aldrich Poland, was additionally vacuum dried overnight at 100°C before use. DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid) used as a calibration standard for nuclear magnetic resonance (NMR).

Synthesis of CAB copolymers

CABs have been obtained in the reaction of shrimp chitin with the mixtures of AA and BA used in different proportion. Acylation reaction has been carried out under heterogeneous condition in the presence of PA as a catalyst of reaction. First, the acylation mixture has been prepared: calculated amount of PA was dropped at *ca* -10°C into acetic and butyric anhydrides mixture used with proper molar ratio. Mixture of two anhydrides, two corresponding organic acids and PA, was formed. Organic acids were made due to water present in 70% HClO₄. Next step was realization of chitin acylation reaction. The fresh acylation mixture as above was added slowly to the chitin powder placed in the

agitated glass reactor cooled in ice/NaCl bath. Temperature inside of reactor was kept on the level of *ca* 0°C during first 30 min of reaction and *ca* 25°C later. The five times excess of esterification mixture was used in each reaction. Reagents have been used in the proportion: chitin/(AA+BA)/PA = 1 : 5 : 1, reaction has been carried out during 3 h. Raw products of reaction have been washed three times with small portions of diethyl ether, then several times with distilled water to pH = 7 to remove any traces of acids and dried at 110°C. Final products—pure CABs—have been evolved from the solution of the raw products of reaction in DMF in the processes of filtration of the solution and precipitation of polymers from filtrates with distilled water.

Chitin dibutyrate (DBC) as well as chitin diacetate (DAC) have been obtained as above, when only butyric anhydride and acetic anhydride, respectively, have been used for preparation of acylation mixture. Reagents were used in the proportion: chitin/acid anhydride/PA = 1 : 5 : 1 (mol/mol) (AQ), pure DBC was evolved from the raw product of reaction as above, pure DAC has been evolved as copolyesters where formic acid (98%) was used as a solvent of DAC.

Analyses of obtained products

Intrinsic viscosity of obtained DBC and chitin copolyesters was determined by viscometry method using dilute solutions of polymers in DMAc in range of concentrations from *ca* 0.4 to 0.1 g/100 cm³. Initial solution with the greatest polymer concentration was filtered through a glass G3 filter, further solutions were obtained in the process of controlled dilution of initial solution with solvent. Measurements were performed using Ubbelohde viscometer at 25°C.

Chemical structure and DS of DBC, DAC as well as CABs soluble in DMF were determined by ¹H-NMR spectroscopy analysis on Bruker AM 400 spectrometer using a mixed solvent of DCl and D₂O (20%, w/w) with the presence of DSS as reference.

The DP by butyric and acetic groups (DS_{Bu} and DS_{Ac}) was calculated using the following formula, respectively:

$$DS_{Bu} = \frac{1/3I_{\gamma CH_3}}{1/6I_{H_2-H_6}}$$

$$DS_{Ac} = \frac{1/3I_{\alpha CH_3}}{1/6I_{H_2-H_6}}$$

where $I_{\gamma CH_3}$ is the integral intensity of the signal of methyl protons of butyryl residues at maximum 0.60

ppm, $I_{\alpha CH_3}$ is the integral intensity of the signal of methyl protons of acetyl residues at maximum 2.21 ppm, and $I_{H_2-H_6}$ is the integral intensity in the range 3.0–4.2 ppm of the signals of H₂–H₆ protons of glucosamide residues. IR spectra of initial chitin and soluble products of esterification in form of thin films were recorded using FT-IR Perkin-Elmer System 2000 spectrometer.

Thin films of DBC were cast from dilute acetone solution (*ca* 1 g/100 mL). Films of DAC and mixed copolymers were prepared from solutions of polymers in formic acid (98%) as follows: after dissolution of polymer 5 mL of solution with concentration of 10% was poured out on the Petri dish with diameter of 7.5 cm. The solvent was evaporated off, and thin film was formed, then obtained film was washed with distilled water several times until no traces of formic acid was detected in water and dried.

Films of chitin were prepared from dilute solution of polymer (*ca* 0.04 g/100 mL) in DMAc/5% LiCl. After clearing of the solution from any insoluble substances in the process of filtration, 7 mL of solution was poured out on the Petri dish with diameter of 7.5 cm and let alone till swollen disc of polymer was formed. Disc of polymer was washed with distilled water till full removing of the solvent first and next with ethanol to remove water. Then thin film of chitin was vacuum dried at 60°C.

Films of all samples directly before IR spectra recording were additionally dried at 110°C during 10 min under reduced pressure. IR investigation of DMF-insoluble parts of chitin copolymers was recorded in KBr (1/100) pellets.

RESULTS AND DISCUSSION

Synthesis of chitin esters

In the publications describing synthesis of DBC,^{4,5} there was stated that PA was found as a very effective catalyst of reaction of esterification of chitin, and disubstituted chitin derivative well soluble in popular organic solvents has been obtained with the yield up to 90–95%. Insoluble parts of the raw product of syntheses were found as chitin derivatives with DP less than 2.

During syntheses of mixed chitin copolymers, different amounts of the product soluble in DMF have been obtained depending on the composition of the acylation mixture. Obtained results are collected in Table I.

Solubility properties

DAC is soluble only in acidic solvents, such as formic acid or methanesulfonic acid. DBC is well

TABLE I
Amounts of DMF-Soluble Parts of Chitin Derivatives in the Raw Products of Chitin Esterification

Nr	Ratio of reagents in acylation mixture			Amount of raw product (g)	Amount of DMF-soluble product (g)	Yield of DMF-soluble product (%)	Symbol of DMF-soluble sample	Intrinsic viscosity of the soluble product $[\eta]_{\text{DMAc}}$ (dL g ⁻¹)
	BA	AA	Chitin					
1	1.00	0	0.20	7.76	6.53	85.4	DBC	1.86
2	0.90	0.10	0.20	7.27	6.13	84.2	BA90/AA10	1.88
3	0.80	0.20	0.20	7.13	5.98	83.9	BA80/AA20	2.06
4	0.70	0.30	0.20	6.81	5.62	82.5	BA70/AA30	2.16
5	0.60	0.40	0.20	6.86	5.50	80.2	BA60/AA40	2.25
6	0.50	0.50	0.20	6.79	5.18	76.2	BA50/AA50	2.53
7	0	1.00	0.20	6.52	0	0	DAC ^a	Not determined

^a DAC is insoluble in DMAc.

soluble in great assortment of popular organic solvents: *e.g.*, methanol, ethanol, acetone, DMF, DMAc, DMSO, and also in acidic solvents such as formic acid, methanesulfonic acid, or acetic acid.

All obtained CABs are soluble in DMF, DMAc, DMSO, and ethanol, but they are insoluble in acetone (good solvents for DBC). The samples with up to 50% of acetyl groups are still soluble in methanol and ethanol. Lack of free DBC in acetone used for treating of the products of reaction confirmed that they are copolyesters indeed. Solubility efficiency of obtained chitin copolyesters in DMF slightly decreases with increase of the acetyl groups' content in polymer chain. Increasing of acetyl groups in polymer chain caused the slightly lower transparency of obtained solutions. DAC was stated to be completely insoluble in DMF.

Intrinsic viscosity measurements of all soluble samples have been made for their solution in DMAc at 25°C. In earlier investigations during realization of the tasks of the project CHITOMED,²³ it was found that the intrinsic viscosity value of DBC $[\eta]_{\text{DMAc}} = 1.86$ dL g⁻¹ corresponds to its weight average molar mass, determined by Size Exclusion Chromatography (SEC), M_w equal to 135×10^3 g mol⁻¹, and to degree of polymerization (DP) equal to about 394. Molar masses of obtained copolymers have not been determined in direct measurements, but it could be expected that products of chitin esterification by mixed acid anhydrides obtained under the same conditions like DBC would be characterized by similar DP. However, intrinsic viscosity of obtained chitin copolyesters slightly increases with increase of the acetyl groups' content in polymer chain, probably due to the change of conformation of the polymer chain in the solvent with different amounts of acetic substituent.

Analysis of chitin and products of esterification

Analyses of initial chitin, DAC, and the soluble products of esterification carried out using ¹H-NMR and FTIR spectroscopy yielded in results as below.

In the ¹H-NMR spectrum of chitin (Fig. 1), there are following signals: the separated signal of —CH₃ protons of acetamide group at 2.3 ppm, overlapped signals of H2–H6 protons of polysaccharide chain in the range of 3.2 ÷ 4.1 ppm, and at 4.5 ppm signal of H1 proton of polysaccharide chain.

In the ¹H-NMR spectrum of DBC (Fig. 2), there are following signals of glucosamide chain for the H1–H6 protons: in the range of 3.50–6.00 ppm and the separated signal of —CH₃ protons of acetamide group at 2.2 ppm. Additional signals derived from butyryl groups were detected at 2.52 ppm of α-CH₂— protons, at 1.75 ppm of β-CH₂— protons, and at 1.04 ppm of γ-CH₃ protons.

In the ¹H-NMR spectrum of DAC (Fig. 3), there are following signals glucosamide chain for the H1 to H6 protons: in the range of 3.50–6.00 ppm and the signal at 2.2 ppm of —CH₃ protons of acetamide group. Signal from α-CH₃ protons of additional acetyl groups in chitin ester is overlapped with signal of —CH₃ protons of acetamide group at 2.2 ppm.

In Figure 4, the ¹H-NMR spectrum of the one from obtained CABs is presented. In the spectrum, there are seen two well-separated regions of protons. The region in the range of 0.40–2.70 ppm represents the protons belonging to the acetamide group of chitin and to the ester groups introduced, and the

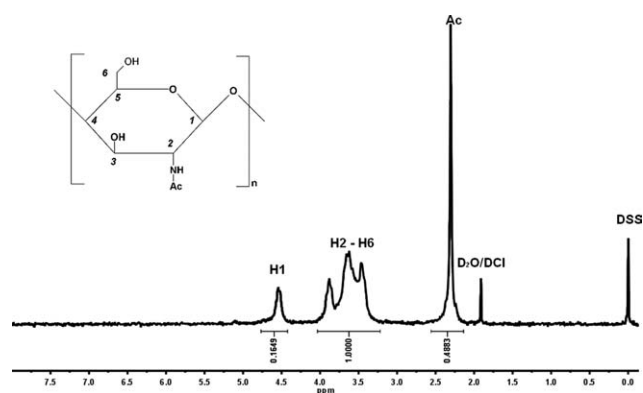


Figure 1 ¹H-NMR spectrum of chitin.

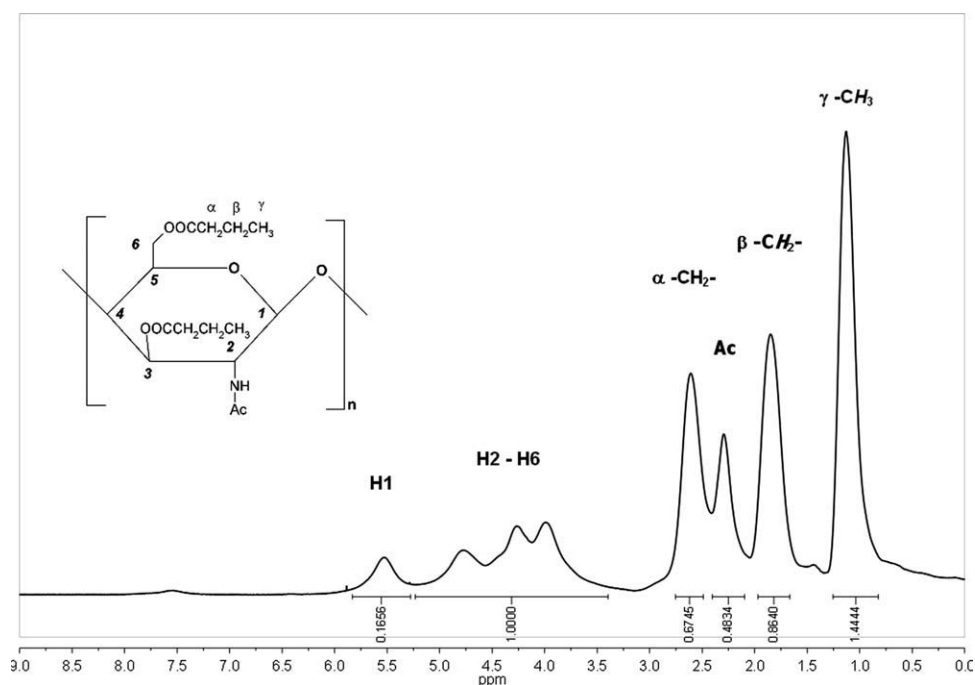


Figure 2 $^1\text{H-NMR}$ spectrum of DBC.

region in the range of 3.00–7.00 ppm belongs to the signals of protons of the polysaccharide residues. At the spectrum of chitin acetate butyrate, there are following signals: $\gamma\text{-CH}_3$ with maximum at 0.60 ppm, $\beta\text{-CH}_2$ with maximum at 1.25 ppm, and $\alpha\text{-CH}_2$ in the range of 2.08–2.18 ppm from the butyrate residues. At the 2.2 ppm signal of $\alpha\text{-CH}_3$, acetamide residues appear. From integration of signals corresponding to -CH_3 of the butyryl group and to the H2–H6 protons at the range of 3.2–4.1 ppm, the DP of butyl groups was calculated. Moreover from inte-

gration of signals corresponding to the -CH_3 of acetamide residues at 2.2 ppm to the H2–H6 protons, the DP of acetyl groups was also calculated.

$^1\text{H-NMR}$ spectra of other DMF-soluble CABs obtained using different molar ratio of anhydrides in the reaction mixture were recorded as before. Calculated values of DP based on the spectra analysis of DMF-soluble DBC, all CABs and DAC soluble in formic acid are listed in the Table II.

Results of $^1\text{H-NMR}$ investigation showed that in all cases of chitin esterification carried out at applied

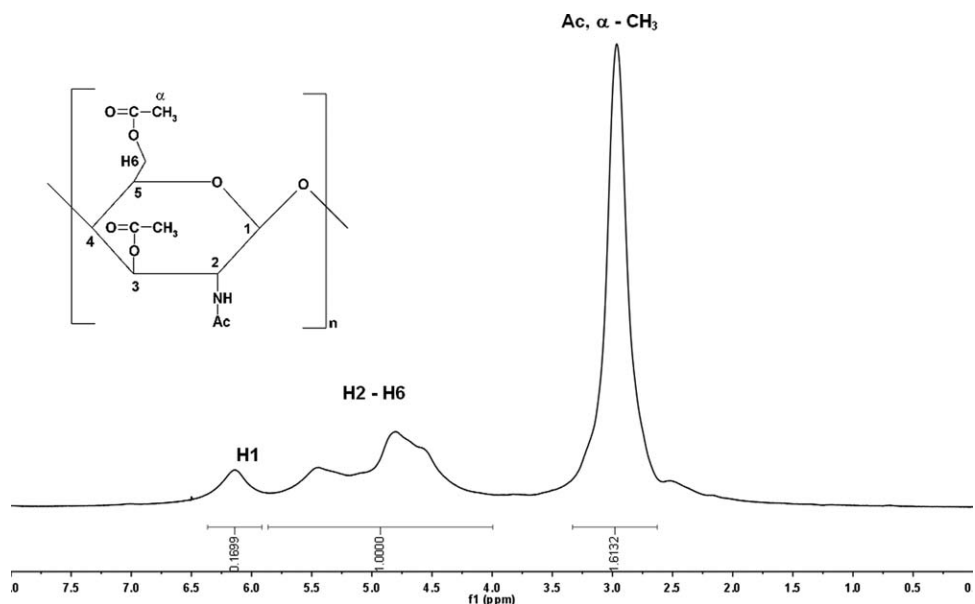


Figure 3 $^1\text{H-NMR}$ spectrum of DAC.

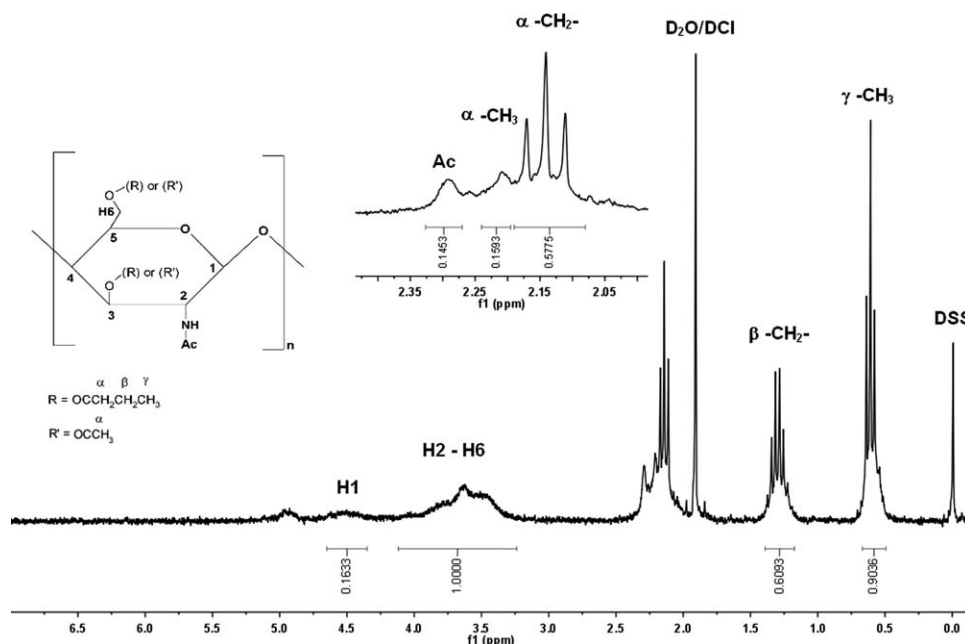


Figure 4 $^1\text{H-NMR}$ spectrum of DMF-soluble chitin co-(acetate/butyrate) with 10/90M ratio of anhydrides in the initial acylation mixture.

conditions in the presence of PA as a catalyst of reaction, final products with summary DP about 2 have been obtained. For some of them, higher DP has been calculated. It is probably due because of measuring error for NMR spectroscopy. During syntheses of chitin ester derivatives, when two acid anhydrides have been used in acylation mixture with five times exceed, products with different chemical structure have been obtained. The contents of acetyl groups in obtained CABs were higher than those calculated from composition of the acylation mixture, probably due to higher reactivity of acetic anhydride. The same phenomenon was observed by Van Luyen and Rossbach.¹⁸ FTIR spectroscopy was used to confirm the structural changes caused by reaction of applied anhydrides with hydroxyl groups of chitin.

To compare the obtained spectra of chitin, DBC, and DAC, an overview of them is given in Figure 5. The IR spectrum of chitin (Fig. 5a) is characterized by large and intense band at $ca\ 3450\ \text{cm}^{-1}$ due to O—H groups, C—H stretching bands at $2783\ \text{cm}^{-1}$ due to the GlcNHAc units, three bands due to amide groups: I – at $1650\ \text{cm}^{-1}$, II – at $1565\ \text{cm}^{-1}$, and III – at $1412\ \text{cm}^{-1}$, band of $-\text{CH}_3$ in acetylamide groups at $1376\ \text{cm}^{-1}$; band of O—H groups at $1262\ \text{cm}^{-1}$; C—O—C band in the glucopyranose ring at $1028\ \text{cm}^{-1}$; and the specific bands of the $\beta(1 \rightarrow 4)$ glycoside bridge at 1153 and $895\ \text{cm}^{-1}$.²⁴ In the FTIR spectrum of DBC (Fig. 5b), there is no absorption at $ca\ 3450\ \text{cm}^{-1}$ due to lack of O—H groups, new absorptions appear at $1740\ \text{cm}^{-1}$ (strong) and at $ca\ 1250\ \text{cm}^{-1}$ (less intensive) due to carbonyl groups $=\text{C}=\text{O}$, and there is seen the larger absorption at $2990\text{--}2850$

TABLE II
Degrees of Substitution by Butyric and Acetic Groups in the Chitin Chain as a Function of Anhydrides Molar Ratio in the Acylation Mixture

Symbol of DMF-soluble sample	DS _c calculated from ratio of anhydrides in acylation mixture		DS _d determined from $^1\text{H-NMR}$ spectroscopy results		Summary DS determined from H-NMR investigations
	DS _{cBu}	DS _{cAc}	DS _{dBu}	DS _{dAc}	
DBC	2.00	0	2.0	0	2.00
BA90/AA10	1.80	0.20	1.81	0.24	2.05
BA80/AA20	1.60	0.40	1.58	0.42	2.00
BA70/AA30	1.40	0.60	1.37	0.68	2.05
BA60/AA40	1.20	0.80	0.94	1.10	2.04
BA50/AA50	1.00	1.00	0.75	1.29	2.06
DAC ^a	0	2.00	0	2.06	2.06

^a Sample soluble in 98% formic acid.

cm^{-1} , 790, and 740 cm^{-1} due to increased content of aliphatic $-\text{CH}_2-$ and $-\text{CH}_3$ groups. The FTIR spectrum of DAC (Fig. 5c) differs from the FTIR spectrum of DBC with lower absorption at $2900\text{--}2800 \text{ cm}^{-1}$ (no content of aliphatic $-\text{CH}_2-$ groups) and much more stronger absorption at $ca 1232 \text{ cm}^{-1}$ due to carbonyl $\text{C}=\text{O}$ in acetyl group.

The FTIR spectra of DMF-soluble CABs registered in the range of absorption from 4000 to 400 cm^{-1} are presented in Figure 6. In all cases, there was observed no absorption at $ca 3450 \text{ cm}^{-1}$, what confirmed the complete substitution of hydroxyl groups in chitin chain? Strong absorption appeared at 1740 cm^{-1} due to carbonyl groups $=\text{C}=\text{O}$ of the esters of fatty acids, and an absorption appeared at $ca 1232 \text{ cm}^{-1}$ due to the carbonyl in acetyl group, which was absent in IR spectrum of DBC. Intensity of that absorption depended on the content of acetyl groups in copolyester chain.

In all IR spectra of obtained chitin derivatives, no changes were observed at 1650 cm^{-1} , 1565 cm^{-1} , and at 1412 cm^{-1} due to amid groups in polymer chain. It means that applied conditions of ester syntheses did not cause changes in degree of deacetylation of initial chitin.

CONCLUSIONS

Several chitin copolymers with different chemical structure have been obtained with high yield in the processes of chitin esterification carried out under heterogeneous condition in the presence of PA as the catalyst of reaction. Applied conditions of reaction resulted in obtaining of CABs with summary DP of about 2, containing from (DS_a 0.24–1.29) % of acetyl groups in polymer chain. Chemical structure of co-(acetate/butyrate) was confirmed in $^1\text{H-NMR}$

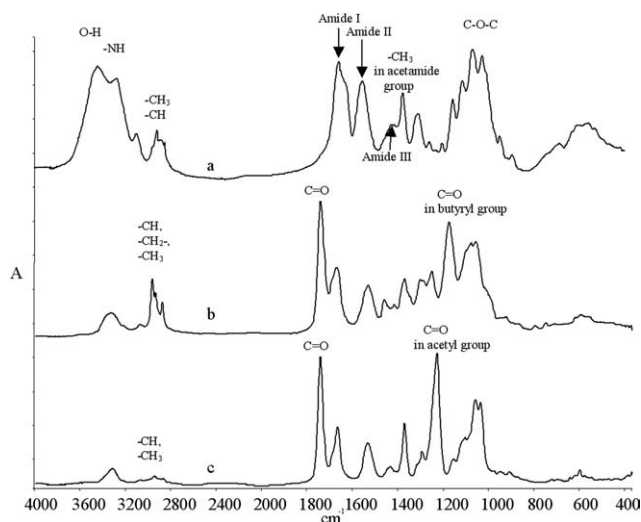


Figure 5 FTIR spectra of chitin (a), DBC (b), and DAC (c) recorded from thin films of polymers.

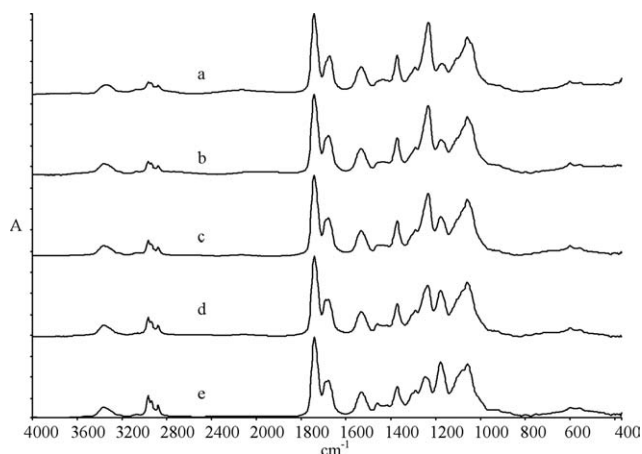


Figure 6 FTIR spectra of DMF-soluble chitin co-(acetate/butyrate): BA50/AA50 (a), BA60/AA40 (b), BA70/AA30 (c), BA80/AA20 (d), and BA90/AA10 (e).

and FTIR investigations. All described co-(acetate/butyrate) received with high yield are characterized with high DP and good solubility in several organic solvents such as DMF, DMSO, DMAc. Obtained copolyesters have film forming properties, which is necessary for fiber formation process. Copolymer BA90/AA10 is soluble in alcohols such as ethanol as well as methanol and forms viscous solutions suitable for fiber spinning, which is the aim of my future investigations. High solubility of chitin copolyesters in several organic solvents allows supposing that they could be used for preparation of various forms of materials for biomedical applications.

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