

Studies upon the Fine Structure and Selected Physical and Physicochemical Properties of Butyrylchitin Membranes

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SYNOPSIS

The effect of varying the molecular weight of butyrylchitin membranes cast from methylene chloride on their properties has been investigated. Characterization analyses include X-ray, scanning calorimetry and tensile stress-strain. The crystal structure of the butyrylchitin was shown to consist of fringed micelles, irrespective of the molecular weights examined, and of lower crystal volume fraction than usually found for chitin membranes, 0.3 versus 0.5, respectively. The membranes exhibit greater ductility and less swelling in physiological salt solution with increasing molecular weight. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Butyrylchitin, one of the main chitin derivatives, is awakening a growing interest as an effective bioactive natural polymer.¹⁻³ This interest is not, however, founded on a comprehensive recognition of the structure and properties of butyrylchitin. Taking this situation into account, an attempt was made to gain information about the fine structure and some selected physical and physicochemical properties of membranes made of butyrylchitin with different molecular weights. The presented results of investigations concern the following topics:

- Crystalline structure of membranes (assessment of the crystal system and geometrical perfection of the lattice, parameters of the lattice unit cell, crystalline and amorphous density, degree of crystallinity, and average lateral crystallite size).
- Morphological structure of membranes (recognition of the presence of spherulites and assessment of the homogeneity of the crystalline-amorphous structure).
- Peculiarities of the membranes' molecular structure (analysis of specific features as com-

pared to chitin and chitosan membranes in connection with their crystallization ability).

- Selected physical properties of the membranes (thermal, electrical, mechanical, and optical).
- Selected physicochemical properties of the membranes (solubility in typical organic solvents and swelling ability in physiological salt solution).

EXPERIMENTAL

Materials

Membranes that have been prepared at the Institute of Man-Made Fibers of the Technical University of Lodz comprising three different molecular variants of butyrylchitin: high molecular, revealing intrinsic viscosity (η) = 1.3; medium molecular weight with (η) = 1.04; and low molecular with (η) = 0.54. The butyrylchitin applied to manufactured membranes was achieved by esterification of krill chitin (*Euphausia Superba*) (from which remnants of calcium carbonate have been removed) using butyric anhydride in the presence of perchloric acid (70%) as a catalyst of the esterification reaction.⁴

The compliance of the result of chemical elemental analysis with the theoretical chemical structure and the stated lack of OH group absorption bands in IR spectrograms confirmed that the addition of butyl groups during esterification was completed and dibutyrylchitin was achieved.

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The chromatography evaluation of the molecular weight distribution has shown that in the case of all three molecular modifications there was a very similar distribution, which was characterized by the value of the polydispersion index $M_w/M_n = 2$. The applied esterification conditions referring to particular molecular variants of butyrylchitin are presented in Table I.

The sample membranes were obtained by casting from butyrylchitin solutions in methylene chloride on glass surfaces and by successive evaporation of the solvent by heating with an infrared radiator. The evaporation took place as the result of heating at 60°C for 15 min. The removal of solvent was total. The tracing of solvent by means of IR examination of membranes did not give any evidence of the presence of solvent remnants.

The concentrations of butyrylchitin solutions due to particular molecular variants were (η) = 1.3, 2.4; (η) = 1.04, 3.0; and (η) = 0.54, 4.5 g/100 mL.

Testing Procedures

The recognition of the kind of *crystalline structure*, the evaluation of the crystallinity degree, and the assessment of the average lateral crystallite size was founded on WAXS investigations carried out on a DRON-2 diffractometer at the following operating parameters: CuK α , 15 mA and 40 kV and slit 0.5 \times 0.5 mm. The X-ray evaluation of the crystallinity degree was performed on the basis of measured integral diffracted intensities of the butyrylchitin sample and the standard reference sample (cellulose I) of known crystallinity degree, by regarding the differences in X-ray scattering ability of both kinds of specimens, according to the procedure of Hermans and Weidinger.⁵

The degree of crystallinity has been additionally determined by means of the densitometric and thermoanalytical DSC method. In the case of the den-

sitometric method, the degree of crystallinity was calculated from the formula

$$X_{\text{dens}} = (d_{\text{cr}}/d_s) \cdot [(d_s - d_{\text{amph}})/(d_{\text{cr}} - d_{\text{amph}})]$$

on the basis of the measured sample density d_s and the theoretical values of the crystalline, d_{cr} , and amorphous, d_{amph} , densities of butyrylchitin established by the authors. The sample density was measured using the gradient column technique in the mixture of toluene and CCl₄ at 20°C. The value of d_{cr} was calculated on the basis of the assumed lattice unit cell described below. The theoretical amorphous density d_{amph} was computed from the formula

$$d_{\text{amph}} = K \cdot M/N \cdot \sum \Delta V_i$$

where K is the coefficient of molecular packing of the amorphous phase; N , the Avogadro constant; M , molecular weight of the chain repeat unit $M = 343$; $\sum \Delta V_i$, the van der Waals volume of the repeat unit; the sum of the van der Waals increments of the constituent groups $\sum \Delta V_i = 292.85$ (Å³). In the case of a lack of information about the packing coefficient K for amorphous butyrylchitin, an attempt was made to estimate it in an indirect way.

Taking into consideration the chemical resemblance between butyrylchitin and triacetatecellulose, the K value sought was calculated as the corrected K value for triacetatecellulose. The correction consisted of regarding the differences in the size of the side groups of both polymers. The approximate value of K thus calculated is $K = 0.534$.

The value of the theoretical amorphous density of butyrylchitin computed from the above formula is equal to $d_{\text{amorp}} = 1.0309$ (g/cm³). Data referring to the amorphous density of butyrylchitin and supplementary to chitin, chitosan, and cellulose are compiled in Table II.

Table I Esterification Process Parameters Applied at Obtaining Butyrylchitin with Different Molecular Weight

Intrinsic Viscosity Aceton 20°C (η)	Reaction Temperature (°C)	Time of Reaction (h)	Relation of Mass in Respect to Chitin	
			Butyric Anhydrate	Perchloric Acid
1.30	20	4	12.1	0.271
1.04	20	48	18.7	0.506
0.54	40	24	19.06	0.470

Table II Van der Waals Chain Unit Volume, Coefficient of Molecular Packing, and Amorphous and Sample Densities of Chitin, Butyrylchitin, Chitosan, and Cellulose

Polymer	Molecular Weight of Chain Unit	$\sum \Delta V_i$ (Å ³)	$\sum \Delta V_i$ (cm ³ /mol)	K	d_{amph} (g/cm ³)	d_{sample} (g/cm ³)
Chitin	203	169.5	102.1	0.672	1.3364	1.3870
Butyrylchitin	343	292.85	176.3	0.534	1.0390	1.2240
						1,2260
Chitosan						
100% deacetyl	161	133.6	80.4	0.713	1.42268	1.4750
Cellulose	162	131.9	79.5	0.713	1.4550	—

In the case of the thermoanalytical method, the evaluation of the crystallinity degree was based on the appraisal of the high-temperature endothermic peaks of the DSC thermograms. The values of the crystallinity degree X_{DSC} were calculated by the formula

$$X_{\text{DSC}} = (a_{\text{BCH}}/a_0)/X_0$$

where a_{BCH} and a_0 are the areas of the high-temperature peaks, respectively, for butyrylchitin membranes and the reference chitin specimen membrane for which $a_0 = 4.52 \text{ cm}^2/\text{mg}$; X_0 is the degree of crystallinity of the reference chitin membrane $X_0 = 0.41$.

The average lateral crystallite sizes D_{010} and D_{100} were calculated on the basis of the measured half-width of the diffraction peaks 010 and 100 of the WAXS diagrams from the fundamental Scherrer expression.

The *morphological structure* of the membranes was examined qualitatively. This was in order to recognize the possible presence of spherulites and to assess the homogeneity of the morphological building. The appraisal was based on polarization-interference microscopical observations by the application of the differential homogeneous interference field of 0 and 1 order. The observations were carried out on the BIOLAR-PI microscope in monochromatic light, $\lambda = 0.589 \mu\text{m}$, at magnification 12.5×20 .

The investigations of the *molecular structure* were based on FTIR spectroscopy studies and performed on SHIMADZU FT-IR 8101M at operating parameters: measuring mode A, resolution $4.0\text{--}8.0 \text{ cm}^{-1}$, accumulation 40 and 200, detector 2.8 mm/s , and apodization Happ-Genzel.

The appraisal of thermal properties was based on thermograms received from the DSC technique.

They were obtained on a DuPont 990 thermoanalyzer at the following operating parameters: nitrogen atmosphere, heating rate 10 degrees/min, and calorimetric sensitivity 1 mcal/s.

The electrical properties of membranes were evaluated on the basis of assigned values of volume resistivity: ρ . The volume resistivity, ρ , was calculated from the formula

$$\rho = U \cdot F / I_{\text{corr}} \cdot g [\Omega\text{m}]$$

where U is the applied electrical tension (10 V); F , the surface area of the attached electrodes (cm²); g , the membrane thickness (cm); and I_{corr} , the corrected intensity of the stabilized conductivity current (10^{-9} A).

The I_{corr} is defined by the equation

$$I_{\text{corr}} = I_{\text{meas}} - I_{\text{depol}}$$

where I_{meas} is the intensity of conductivity current measured 30 s after attaching the electrodes; and I_{depol} , the depolarization current intensity measured 30 s after switching off the applied 10 V voltage.

The current intensities were measured by a UNITRA 219 electrometer, applying metallic electrode clamps with the surface area of 4.9 and 5.1 cm². The values of I_{meas} and I_{depol} were assigned in a conditioning chamber at 25°C and 65% air humidity. It was stated in the preliminary examination that the volume conductivity of the membranes considered depends on the direction of the electrical current flowing through the membrane. Taking into consideration this effect, the measurements were conducted twofold by changing the arrangement of the electrometer clamps with respect to the membrane surfaces. The arrangement of the clamps at which the measured current intensities I_{meas} and I_{depol} were

bigger was designated the A-type; the arrangement of clamps at which these values were lower was designated the B-type.

The investigation into the *mechanical properties* comprised measurements of tensile strength and elongation at break. To assess the type of deformation at stretching, the course of the stress-strain curve was analyzed. The appraisal was conducted on the 1111 INSTRON table universal testing instrument at operating parameters of temperature, 20°C; rate of extension, 50 mm/min; and extended length and breadth of the sample, 10 × 5 mm.

Within the appraisal of the *optical properties*, the optical anisotropy and the refraction indices were assessed. These examinations were conducted on a BIOLAR-PI polarization-interference microscope utilizing a monochromatic light $\lambda = 0.580 \mu\text{m}$ at 20°C.

The assessment of *solubility* and *swelling ability* was performed as follows: The immediate dissolving of butyrylchitin in pure solvents like acetone or dimethylformamide (DMF) excluded the possibility

of performing a quantitative appraisal of the solubility. As the relevant solvent for such an appraisal, water-diluted DMF was chosen. Mixtures of DMF and water in the proportions 5 : 1, 4 : 1, 3 : 1, 2 : 1, and 1 : 1 were checked. From the point of view of ensuring a good resolution of the measured dissolving times, the mixtures 3 : 1 and 4 : 1 were most convenient. The dissolving times were measured at the temperature of 22°C. The swelling ability of the membranes in the physiological salt solution after the time of 15 min at 22°C was tested. To measure the swelling ability, the relative increments of linear sample dimensions were taken.

RESULTS AND DISCUSSION

Crystalline Structure

The X-ray diffraction intensity distribution curves obtained in the case of all three molecular variants

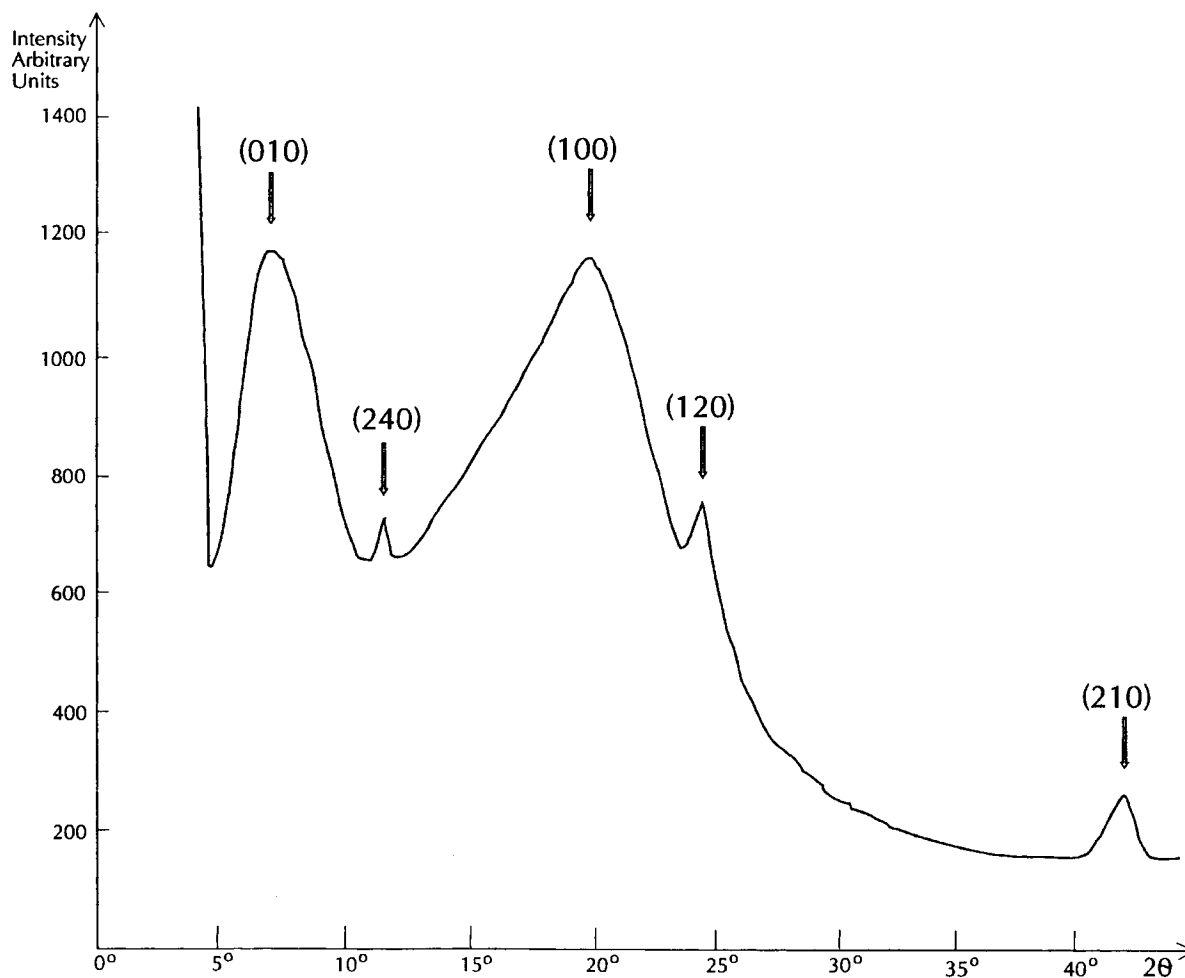


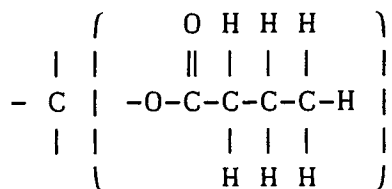
Figure 1 WAXS intensity distribution curve of butyrylchitin membrane.

Table III X-ray Diffraction Data of Butyrylchitin Membranes

Reflection Intensity	Bragg Angle $2(Q)^\circ$	Interplanar Spacing d_{hkl} (Å)	Miller Indices (hkl)
Strong	6.6–7.0	13.4	(010)
Very weak	12.3	7.2	(240)
Strong	19.8–20.2	4.4	(100)
Weak	24.6	3.7	(120)
Medium	42.0	2.1	(210)

exhibit the appearance of analogous diffraction peaks (Fig. 1). The reflections ascertained are depicted in Table III.

The diffraction peaks stated to give rise to the assumption of an orthorhombic unit cell with the parameters of $a = 4.4 \text{ \AA}$, $b = 13.4 \text{ \AA}$ and $c = 10.3 \text{ \AA}$ as a very probable unit cell of the butyrylchitin lattice. It is worth noticing that the cell dimension b is very consistent with the theoretical length of chain side groups;



which is equal to 13.8 \AA . Comparison of this value with the b dimension of the unit cell leads to a supposition that the butyrylchitin lattice is characterized by a parallel arrangement of molecules adjacent to the direction of the b edge of the unit cell (Fig. 2). The volume of the assumed unit cell is 571.03 \AA^3 . Assuming the described constitution of the unit cell and assuming the contribution of two chain repeat units along the c edges, one obtains the theoretical crystalline density 1.8758 g/cm^3 .

As compared to chitin,⁶⁻¹⁰ the diffraction pattern of butyrylchitin reveals a minor number of reflections, which are additionally weakly pronounced. This proves univocally that the butyrylchitin lattice is more defective, i.e., less perfect in geometrical regularity, than is the chitin lattice. This fact seems to correspond well with the greater length of side groups in butyrylchitin than in chitin. The long side groups of butyrylchitin play, as can be expected, an inhibiting role in the crystallization process.

The established values of the degree of crystallinity and average lateral crystallite size pertaining

to the examined membranes and referring additionally to membranes made of chitin and chitosan are collected in Table IV. The results obtained lead to the following conclusions:

1. The values of the degree of crystallinity of butyrylchitin depend on the measuring technique applied. The highest values refer to the densitometric technique (0.34–0.35), and the lowest, to the X-ray diffraction technique (0.22–0.26). It seems that the densitometric technique overestimates the crystallinity. The comparatively bigger values in the case of the densitometric appraisal seem to be due to the inadequateness of the assumed theoretical values of the crystalline and amorphous densities. The first one is overestimated; the second one is underestimated as compared to real values.
2. The crystallinity of butyrylchitin membranes is markedly smaller than for membranes made of the initial polymer, i.e., chitin. That proves the lower crystallization ability of butyrylchitin as compared to that of chitin. The great length of the chain side groups of butyrylchitin, which plays the role of spatial hindrance opposing the ordering of molecules into the lattice, should be regarded as the decisive reason for such a relationship.
3. The crystallinity of membranes is contingent on the molecular weight. With increasing intrinsic viscosity, the degree of crystallinity diminishes from 0.26 to 0.22 due to the X-ray method and from 0.30 to 0.25 due to the DSC technique.
4. The average lateral crystallite size in the membranes does not depend on the molecular weight of the butyrylchitin. It is worth noting that the average lateral crystallite sizes of butyrylchitin membranes are comparatively smaller than in chitin and chitosan membranes.

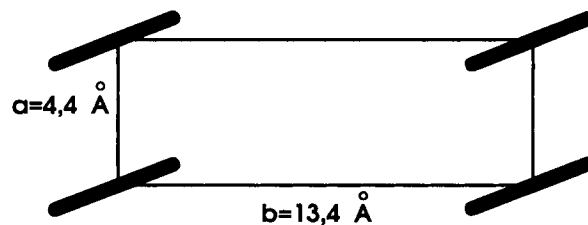


Figure 2 Lattice unit cell of butyrylchitin; projection on the ab plane.

Table IV Crystalline Structure Parameters of Chitin, Butyrylchitin, and Chitosan Membranes

Polymer	Degree of Crystallinity						Average Crystallite Size Perpendicular to Lattice Plane	
	Density Values			X_{dens}	X_{difrac}	X_{DSC}	D_{010} (Å)	D_{100} (Å)
	d_{sample} (g/cm ³)	d_{amrph} (g/cm ³)	d_{cr} (g/cm ³)					
Chitin	1.3870	1.3364	1.4574	0.44	0.53	0.32–0.41	149	108
Butyrylchitin								
(η) = 0.54	1.2362	1.0390	1.8758	0.36	0.26	0.30	53	23
(η) = 1.04	1.2380	1.0390	1.8758	0.36	0.23	0.29	50	23
(η) = 1.3	1.2340	1.0390	1.8758	0.35	0.22	0.25	50	22
Chitosan I type								
90% deacetylation	1.4750	1.4268	1.8395	0.15	0.15–0.18	—	94–114	—
Chitosan II type								
60% deacetylation	1.4780	1.4268	1.7698	0.17	0.29–0.40	—	66–79	99–114

Morphological Structure

All membranes examined did not exhibit in the microscopical picture the characteristic Maltese cross brightenings, which are evidence for the presence of spherulites. The pictures of the membrane surfaces revealed a homogeneous interference coloring, which testifies to homogeneity of the crystalline–amorphous structure with a fringed micelle structure of the crystalline regions.

Molecular Structure

The main aims of the investigations concerned two items: to appraise the differences in the esterification degree of chitin and to evaluate the influence of esterification degree on the crystallization ability of butyrylchitin.

The following absorption bands were considered, which are correlated with the characteristic groups of butyrylchitin: C=O (1740 and 1670 cm⁻¹), —CH₃ (1170 cm⁻¹), —NH— (1530 cm⁻¹), CH ring (1255 cm⁻¹), and the intermolecular bond —NH···OC— (3300 cm⁻¹). To receive a quantitative appraisal, independent of the influence of differentiated thickness of the samples, values of relative absorbance were established, i.e., values of the quotient of absorbance of the regarded band and the absorbance of a relevant reference band. As reference absorption bands, the following were chosen:

- 1255 cm⁻¹ (CH wagging ring) for the analyzed 1740, 1170, and 3300 cm⁻¹ bands.

- 1670 cm⁻¹ [amid I(CO)] for the analyzed 1740 and 3300 cm⁻¹ bands.
- 1530 cm⁻¹ (intermolecular NH···OC/—NH) for the analyzed 3300 cm⁻¹ band.

The established values of the relative absorbances for bands taken into consideration are presented in Table V. The analysis of the results obtained leads to the following conclusions:

- The relative absorbance of the 1740 cm⁻¹ band correlated with the C=O groups increases with enhancing intrinsic viscosity. This peculiarity shows that the increase of molecular weight is in line with progressing esterification.
- The relative absorbances of the band 1170 cm⁻¹ correlated with the CH₃ groups is growing with increasing (η) value. This relationship confirms the increasing number of CH₃ groups as a result of the progress of esterification.
- The relative absorbances of the 3300 cm⁻¹ absorption band that are characteristic for the NH···OC bonds diminish with increasing (η) value. The intermolecular bond NH···OC is, as can be assumed, connected with regions of highly ordered molecules (crystalline regions). The diminution of relative absorbances of this band should be interpreted as evidence for a reducing of the content of ordered regions that occurs as a result of the enhancement of molecular weight. Taking into consideration that the increase of the molecular weight is caused by the progress of esterification, it can be fur-

Table V Relative Absorbances of Absorption Bands in Butyrylchitin and Chitin Membranes

Order Number	Absorption Band and Correlated Chemical Group	Butyrylchitin Sample			Chitin
		(η) = 0.54	(η) = 1.04	(η) = 1.3	
1	1740 cm ⁻¹ /1255 cm ⁻¹ C=O, CH-wagging ring	2.04	2.24	5.00	—
2	1740 cm ⁻¹ /1670 cm ⁻¹ C=O, amide I (CO)	1.02	1.15	2.80	—
3	1170 cm ⁻¹ /1255 cm ⁻¹ —CH ₃ , CH-wagging ring	1.13	1.53	3.38	—
4	3300 cm ⁻¹ /1255 cm ⁻¹ intermolecular, NH···OC/CH—wagging ring	4.78	2.41	1.03	22.5
5	3300 cm ⁻¹ /1530 cm ⁻¹ intermolecular NH···OC/—NH—	0.87	0.67	0.63	1.71
6	3300 cm ⁻¹ /1670 cm ⁻¹ intermolecular, NH···OC/amide I (CO)	2.39	1.24	0.58	1.84

ther concluded that the increase of the degree of esterification leads to a diminished crystallization ability of the butyrylchitin.

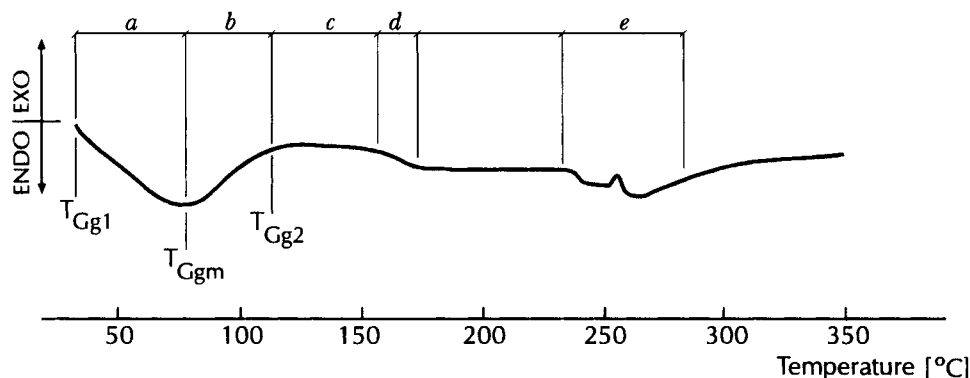
The pertinence of such a conclusion is simultaneously corroborated by the high values of the relative absorbances of the 3300 cm⁻¹ band in the case of the chitin membranes.

Thermal Properties

The thermograms obtained testify to the fact that the trajectory of the curves is the same, independent

on the molecular weight of butyrylchitin. The thermogram curve (Fig. 3) always exhibits four specific temperature intervals:

- The endothermic minimum partition in the vicinity of 75°C.
- The endothermic slope of the base line in the range 110–160°C.
- The inflection of the base line in the vicinity of 170°C.
- The endothermic concavity revealing small peaks in the thermal partition 250–280°C.


Figure 3 DSC thermogram of butyrylchitin membrane.

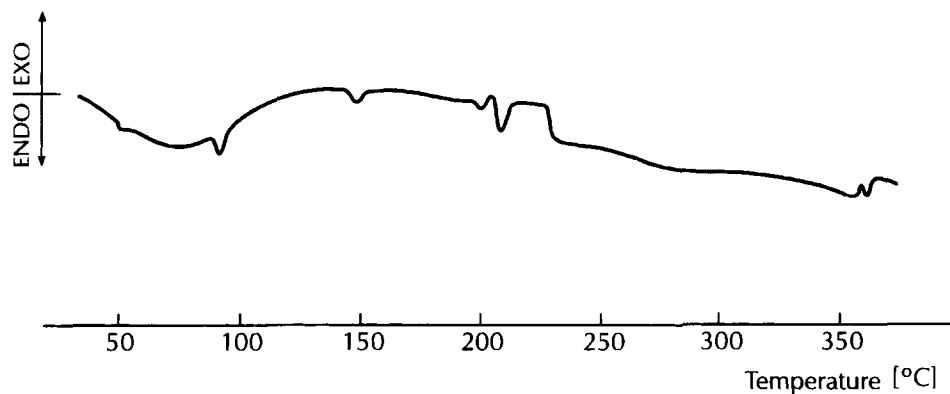


Figure 4 DSC thermogram of chitin membrane.

The sections of the thermograms described above reflect the procedure of the following thermal transitions at heating of membranes in an inert gas atmosphere:

The endothermic minimum at 75°C seems to reflect the initial stage of the glassy transition referring to less straightened molecules in the amorphous phase that are likely not connected with crystalline regions. The endothermic slope of the base line within the range 110–160°C may visualize the advance of glassy transition in a more ordered amorphous phase. The inflection of the base line in the vicinity of 170°C should be, perhaps, interpreted as the termination of the glassy transition proceeding in amorphous regions composed of stretched molecules joined with crystalline regions.

The endothermic concavity in the range of 250–280°C seems to be due to the thermal decomposition of crystalline regions, which is, in general, similar

to the melting process of crystallites in thermotropic polymers. The relatively weakly pronounced concavity, the broad temperature range, and the incoherent path of the curve prove a relatively small content of crystalline regions, revealing simultaneously a high imperfection in their lattices.

It can be assumed that the thermal decomposition of the crystalline regions is a result of two overlapping partial processes: the thermal disintegration into tiny fractions and a successive pyrolytical destruction of these fragments. It can be supposed that these procedures are illustrated by small peaks within the range of the concavity.

It should be noted that the thermal decomposition of crystalline regions inferred from the thermograms corresponds well with the effect of thermoplasticity of butyrylchitin membranes observed by microscopical examination. By applying a heating Boetius table, one can observe that after exceeding the tem-

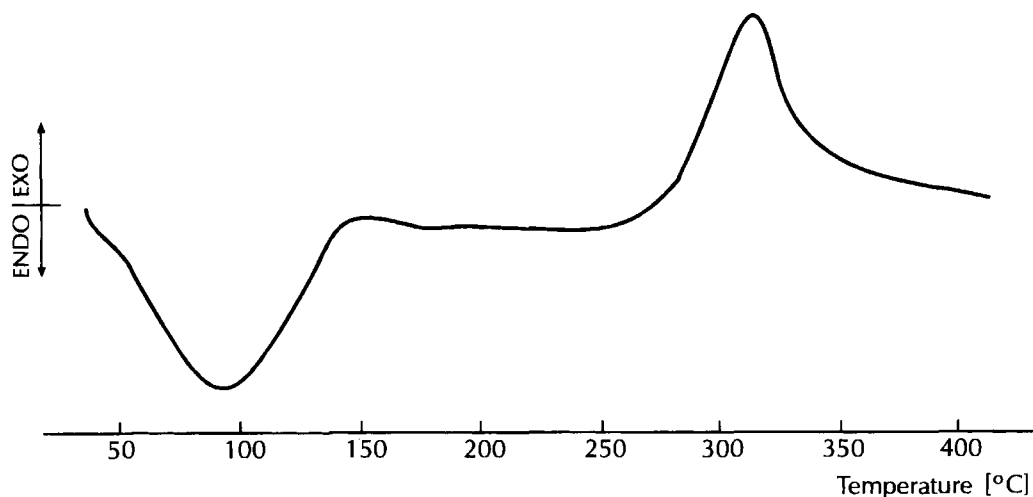


Figure 5 DSC thermogram of chitosan membrane.

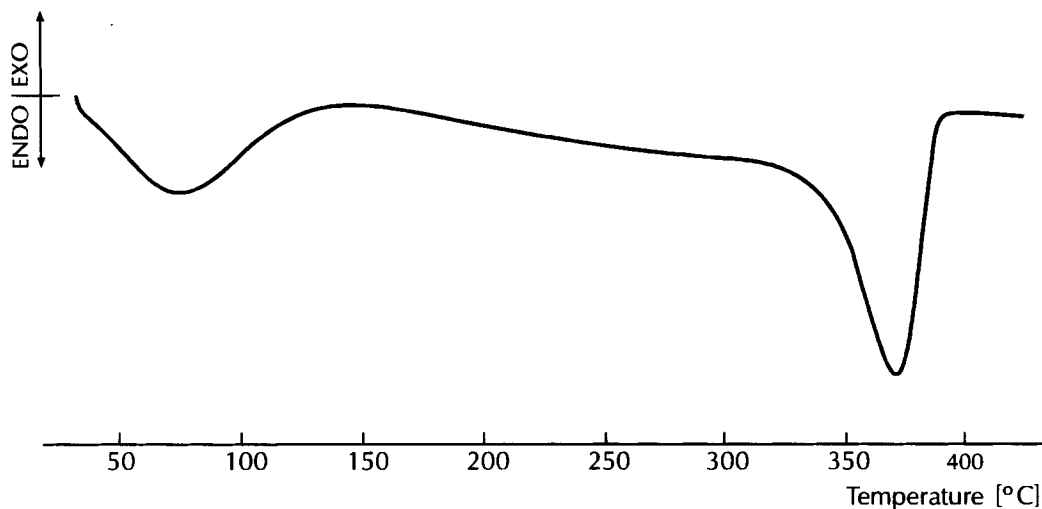


Figure 6 DSC thermogram of native cellulose sample.

perature of 220°C the coherent morphological membrane structure disappears and a plastic deformation takes place.

To extend the thermal appraisal, additionally, investigations of chitin and chitosan membranes were carried out. The thermograms of these samples are presented in Figures 4–6. As one can see, the thermograms of butyrylchitin membranes differ essentially from thermograms of chitin and chitosan membranes. The main difference consists of the lack of an endothermic concavity in the range of 250–280°C in the case of chitin and chitosan. It allows the conclusion that, in the case of the last two polymers, a thermal decomposition of the crystalline regions does not occur. In the case of chitosan, there

appears at 315°C a strong exothermic peak whose existence is difficult to explain.

Within the range of the quantitative appraisal of the thermal properties, there were ascertained the following specific transition temperatures:

- The initial, the maximum intensity, and the final temperature of the commenced stage of the glassy transition: T_{Gg1} , T_{Ggm} , and T_{Gg2} .
- The initial, the average, and the final temperature of the terminal stage of the glassy transition: T_{Gd1} , T_{Gds} , and T_{Gd2} .
- The initial temperature of the thermal decomposition of the crystalline regions: T_{Tp} .

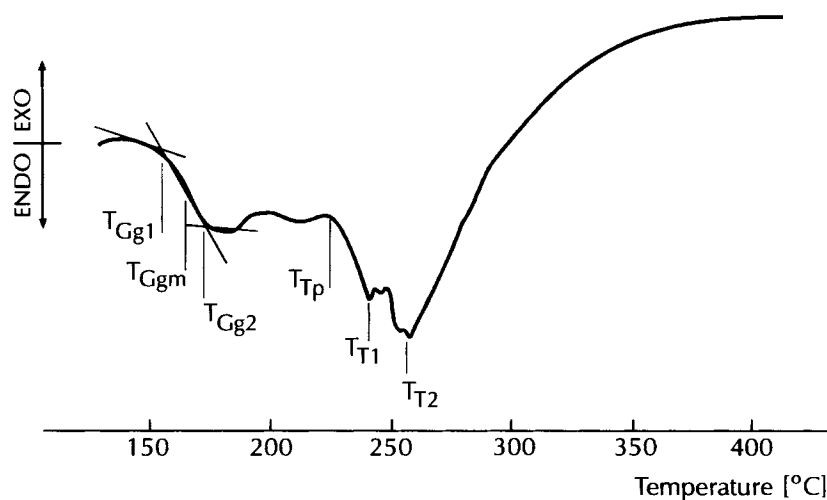


Figure 7 DSC thermogram of butyrylchitin membrane; characteristic transition temperatures.

Table VI Temperatures of the Glassy Transition and Thermal Decomposition of Crystalline Regions

Sample	Initial Stage of the Glassy Transition			Advanced Stage of the Glassy Transition			Thermal Decomposition of Crystalline Regions		
	T_{Gd1} (°C)	T_{Gdm} (°C)	T_{Gd2} (°C)	T_{Gg1} (°C)	T_{GgS} (°C)	T_{Gg2} (°C)	T_{Tp} (°C)	T_{T1} (°C)	T_{T2} (°C)
Butyrylchitin									
(η) = 0.54	35	75	110	155	163	170	227	240–245	257–270
(η) = 1.04	35	85	120	155	163	170	275	285–290	295–305
(η) = 1.3	35	75	115	160	168	175	277	290	305–315
Chitin	35	75	120	260	278	295	325	—	410

- The temperature of the thermal melting of crystalline regions: T_{T1} .
- The temperature of the pyrolytical destruction of fragmented crystalline regions: T_{T2} .

The assigned temperature values are compiled in Table VI. The results achieved allow us to draw the following conclusions:

- The course of the initial stage of the glassy transition seems to be almost independent of the molecular weight of butyrylchitin. At the same initial temperature with increasing molecular weight, only a slight increase in the final temperature occurs.
- The course of the terminal stage of the glassy transition depends on the molecular weight of butyrylchitin. A slight tendency to increase the temperatures with an enhancing (η) value is conspicuous. In comparing the values of the transition temperatures of butyrylchitin and chitin samples, one can see that in the case of chitin the transition takes place at markedly higher temperatures. This could mean that in case of chitin the so-called taut tie molecules (TTM) are more strongly connected with the crystalline regions than they are for butyrylchitin.
- The course of the thermal decomposition of crystalline regions is evidently dependent on the molecular weight. With increasing molecular weight, the values of relevant temperature increase. Taking into account that with increasing molecular weight the degree of crystallinity diminishes, it can mean that in the case of lower crystallinity the thermal stability of crystalline butyrylchitin regions is better. Furthermore, it would also suggest that in the case of lower crystallinity the lattice perfection is better than for higher crystalline samples.

- The comparison of relevant thermal decomposition temperatures of butyrylchitin and chitin samples indicates a higher resistance of crystalline regions against heat for chitin than for butyrylchitin.

Electrical Properties

The assigned results, which are mean values of three independent measurements for each sample, are presented in Table VII. These results allow us to draw the following conclusions:

- The electrical volume conductivity depends on the manner in which the electrometer clamps are jamming the membrane sample. This may occur for two reasons: the difference in the smoothness of both membrane surfaces, which can be due to differences arising at the solidification of the membrane. One surface is in contact with the glass surface of the sample carrier; the second one is accessible for free evaporation of the solvent. The second reason may be connected to a different concentration of dipol groups in both surface layers of the membrane. It is worth mentioning that the differences in the I_{depol} values for the A and B types of clamp arrangements are of a lesser magnitude than for the I_{meas} values. It enables us to suppose that the difference of dipol group concentration in both surface layers is less probable than is the differences in the smoothness of the surfaces.
- The volume electrical conductivity depends on the molecular weight of butyrylchitin. The highest conductivity refers to samples with (η) = 1.3, and the lowest, to samples with (η) = 1.04.
- The intensity of the depolarization current depends on the molecular weight. The lowest values have been established for samples with the

lowest molecular weight: $(\eta) = 0.54$, and the highest, for the high molecular variant: $(\eta) = 1.3$.

To extend the appraisal, membranes cast from solutions of butyrylchitin in acetone and methanol were taken into consideration. The relevant results are compiled in Table VIII. The comparison of the values for membranes manufactured from solutions in methylene chloride, acetone, and methanol lead to the following statements: The membranes made of low molecular butyrylchitin cast from acetone and methanol solutions reveal a higher electrical conductivity than that of those cast from the methylene chloride solution. In the case of high molecular butyrylchitin, the relationship is the opposite.

Aiming to enrich the appraisal, complementary conductivity measurements on chitin and chitisan membranes were carried out. The assigned values are presented in Table VIII. Comparing these values with data pertaining to butyrylchitin membranes, the following conclusions can be drawn:

- The chitin membranes reveal a 10^4 times better volume conductivity than that of the butyrylchitin samples.
- The chitosan membranes irrespective of the degree of deacetylation and the kind of solvent utilized exhibit 10^4 times better conductivity than that of butyrylchitin membranes.

Mechanical Properties

Complementary to the basic membranes of butyrylchitin dissolved in methylene chloroide, membranes cast from acetone and methanol solutions were taken into consideration. The results achieved, which are mean values of 20 independent measurements with the statistical error of the mean value $\pm 3\%$, are collected in Table IX. The typical stress-strain curves are presented in Figure 8. The analysis of results leads to the following conclusions:

- The tensile stress of membranes cast from solutions of methylene chloride increases strongly with growing molecular weight of butyrylchitin. Such a dependence does not appear in the case of membranes cast from solutions of acetone and methanol. For samples of the last type, an opposite tendency becomes evident, i.e., a diminution of the tensile stress with increasing (η) value.
- The kind of utilized solvent influences the tensile stress of membranes. In the case of low molecular weight, the tensile strength is smaller

Table VII Electrical Conductivity Dates of Butyrylchitin Membranes Casted from CH_2Cl_2 Solutions

Sample	A-type Clamp Arrangement				B-type Clamp Arrangement				$\frac{(\rho_A + \rho_B)}{2}$ $\rho \times 10^{11}$ (Ωm)
	$I_{\text{meas}} \times 10^{-9}$ (A)	$I_{\text{depol}} \times 10^{-9}$ (A)	$I_{\text{com}} \times 10^{-9}$ (A)	$\rho \times 10^{11}$ (Ωm)	$I_{\text{meas}} \times 10^{-9}$ (A)	$I_{\text{depol}} \times 10^{-9}$ (A)	$I_{\text{com}} \times 10^{-9}$ (A)	$\rho \times 10^{11}$ (Ωm)	
$(\eta) = 0.54$	0.25	0.005	0.25	25.2	0.155	0.01	0.15	34.2	29.7
$(\eta) = 1.04$	0.06	0.014	0.048	99.8	0.076	0.080	0.085	372.5	236.1
$(\eta) = 1.3$	4.02	0.34	3.83	3.32	1.02	0.020	1.000	7.01	5.17

Table VIII Electrical Conductivity Dates of Burylychitin, Chitosan, and Chitin Membranes Differently Casted

Sample	A-type Clamp Arrangement				B-type Clamp Arrangement				$(\rho_A \rho_B)/2$ $\rho \times (\Omega m)$
	I_{meas} (A)	I_{depol} (A)	I_{corr} (A)	ρ (Ωm)	I_{meas} (A)	I_{depol} (A)	I_{corr} (A)	ρ (Ωm)	
B-chitin (η) = 0.54 acetone	0.64×10^{-9}	0.05×10^{-9}	0.59×10^{-9}	4.16×10^{11}	0.1×10^{-9}	0.0	0.1×10^{-9}	24.5×10^{11}	14.4×10^{11}
B-chitin (η) = 0.54 methanol	0.20×10^{-9}	0.0	0.20×10^{-9}	12.3×10^{11}	0.1×10^{-9}	0.0	0.1×10^{-9}	24.5×10^{11}	18.42×10^{11}
B-chitin (η) = 1.3 acetone	0.35×10^{-9}	0.05×10^{-9}	0.30×10^{-9}	8.18×10^{11}	0.55×10^{-9}	0.05×10^{-9}	0.5×10^{-9}	4.91×10^{11}	6.55×10^{11}
B-chitin (η) = 1.3 methanol	0.15×10^{-9}	0.0	0.15×10^{-9}	16.4×10^{11}	0.35×10^{-9}	0.0	0.35×10^{-9}	7.01×10^{11}	11.7×10^{11}
Chitosan, 60% deacetylated HCOOH; NaOH	0.45×10^{-5}	—	0.45×10^{-5}	6.40×10^7	0.80×10^{-5}	—	0.80×10^{-5}	3.60×10^7	5.0×10^7
Chitosan, 60% deacetylated CH ₃ COOH; NH ₄ OH	0.065×10^{-5}	—	0.065×10^{-5}	44.31×10^7	0.085×10^{-5}	—	0.085×10^{-5}	33.9×10^7	39.1×10^7
Chitosan, 90% deacetylated HCOH; NaOH	0.35×10^{-5}	—	0.35×10^{-5}	8.23×10^7	0.40×10^{-5}	—	0.40×10^{-5}	7.20×10^7	7.7×10^7
Chitosan, 90% deacetylated CH ₃ COOH; NH ₄ OH	0.035×10^{-5}	—	0.035×10^{-5}	8.23×10^7	0.045×10^{-5}	—	0.045×10^{-5}	6.4×10^7	7.3×10^7
Chitin	0.39×10^{-5}	—	0.37×10^{-5}	6.63×10^7	0.24×10^{-5}	—	0.24×10^{-5}	10.2×10^7	8.4×10^7

when applying methylene chloride as a solvent than by utilizing acetone or methanol. In the case of higher molecular weight, the relationship is the opposite. The tensile stress of membranes cast from methylene chloride is 5.5–8.8 times greater than for membranes cast from acetone and methanol solutions.

- The total extensibility appraised on the basis of elongation at rupture shows in the case of samples cast from methylene chloride a tendency to enhance with increasing molecular weight. Exactly the opposite effect occurs for membranes cast from acetone and methanol solutions.
- The ascertained values of elongation at rupture prove indirectly the differences of cohesion energy of membranes examined. The elongation values obtained indicate that the application of acetone or methanol as solvents causes an increase of cohesion energy in the case of low molecular butyrylchitin, as compared to the application of methylene chloride as the solvent. In the case of high molecular butyrylchitin, the application of the solvents described leads to opposite effects.
- The differentiation in the shape of the stress-strain curves proves that there proceeds a different kind of extensibility, in particular, molecular variants of membranes. Membranes made of butyrylchitin with the lowest molecular weight, $(\eta) = 0.54$, reveal a stress-strain curve of an almost straight-line course. This indicates an explicit elastic deformability: The total deformation consists almost entirely of elastic deformation. The steep slope of the stress-strain curve proves simultaneously the high value of the initial extensibility modulus. The increasing molecular weight alters the course of the stress-strain curve. The curves reveal a nonlinear character. This demonstrates that

Table IX Mechanical Properties of Butyrylchitin Membranes

Sample Variant	Tensile Strength (MPa)	Elongation at Break (%)
$(\eta) = 0.54$	32.8	1.9
$(\eta) = 1.04$	46.4	9.7
$(\eta) = 1.3$	171.6	5.9
$(\eta) = 0.54$ methanol	53.3	8.1
$(\eta) = 1.3$ methanol	19.3	1.9
$(\eta) = 0.54$ acetone	51.1	5.7
$(\eta) = 1.3$ acetone	30.8	1.5

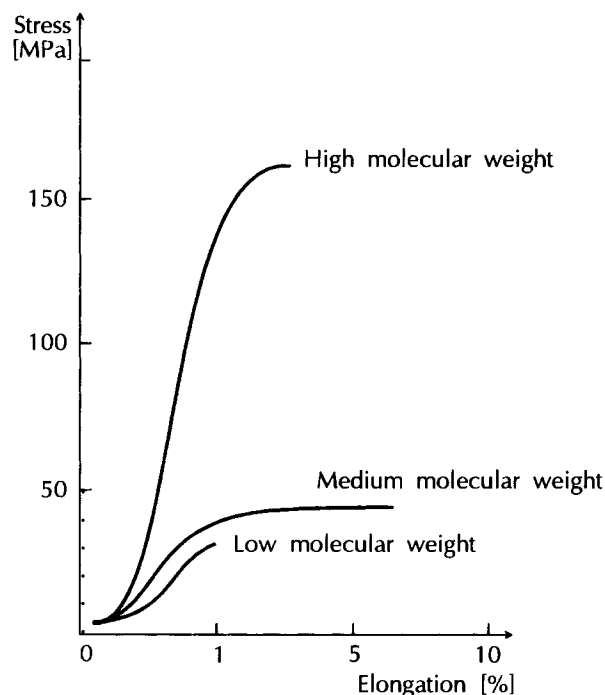


Figure 8 Stress-strain curve of butyrylchitin membrane, $(\eta) = 0.54$.

the total deformations comprise, additionally, viscoelastic and plastic deformation components.

Optical Properties

The lack of interference lines in the interference-polarization microscopical pictures of all variants of the examined membranes prove that all samples were optically isotropic. That enables us to conclude that in the case of all kinds of samples internal orientation does not occur as much as in respect to the amorphous as to the crystalline components of the membranes. The values of the refractive indices, as averages of 20 values gained in independent measurements established for monochromatic light, $\lambda = 0.580 \mu\text{m}$, are as follows:

$$n_{\eta=0.54} = 1,4915; n_{\eta=1.04} = 1,4903;$$

$$\text{and } n_{\eta=1.3} = 1,4899.$$

Solubility

The assigned dissolving times as averages of 10 independent measurements are presented in Table X. The results show that with increasing molecular weight the time of dissolving decreases. By knowing that the solubility of a polymer diminishes with increasing crystallinity, the results of solubility tests

prove indirectly the before-stated relationship between the molecular weight and crystallinity of butyrylchitin membranes.

Swelling Ability

It could be stated that an isotropic kind of swelling took place in all kinds of samples tested. This proves the previously reported results of optical measurements about the isotropic building of the samples. The relevant results of the measured increments of linear sample dimensions, which are mean values of 10 independent measurements for each sample, are presented in Table XI.

The results deliver evidence that with the diminishing (η) values the swelling ability decreases, because, as is well known, the swelling ability of a polymer decreases with increasing crystallinity. The ascertained relationship by itself confirms that the increase in molecular weight causes a decrease in crystallinity.

CONCLUSIONS

1. Membranes cast from methylene chloride solutions of butyrylchitin with differentiated average molecular weight show a partially crystalline structure. The established crystalline regions irrespective of the molecular weight are of the fringed micelle type with an orthorhombic lattice arrangement with a unit cell of $a = 4.4 \text{ \AA}$, $b = 13.4 \text{ \AA}$; and $c = 10.3 \text{ \AA}$ and density $d_{cr} = 1.8758 \text{ g/cm}^3$. The degree of crystallinity appraised using the X-ray technique is 0.22–0.26; using the densitometric technique, 0.35–0.36; and using the DSC method, 0.25–0.30. These values are markedly lower than for chitin membranes (0.44–0.53). It was stated that the growth of the esterification degree leads to a reduction of crystallization ability of the butyrylchitin membranes. The geometrical perfection of the lattice is very low, worse than for chitin

Table X Solubility of Butyrylchitin Membranes

Sample	Dissolving Time (s)	
	Mixture 4 : 1	Mixture 3 : 1
$(\eta) = 1.30$	125	140
$(\eta) = 1.04$	138	240
$(\eta) = 0.54$	273	300

Table XI Swelling Ability of Butyrylchitin Membranes

Sample	Increment of Dimension (%)
$(\eta) = 1.30$	4.0
$(\eta) = 1.04$	2.6
$(\eta) = 0.54$	1.6

membranes. The average lateral crystallite sizes are of the order $D(100) = 22\text{--}23 \text{ \AA}$ and $D(010) = 50\text{--}53 \text{ \AA}$, much lower as compared to chitin.

2. The thermal and electrical properties of butyrylchitin membranes differ essentially from those of chitin and chitosan membranes.
3. The membranes exhibit a differentiated extensibility depending on the molecular weight of butyrylchitin. For the lowest molecular weight considered, the deformability is nearly strictly elastic, and for the larger molecular weight, is of the viscoelastic type.
4. The solubility and swelling ability in the physiological salt solution depend on the molecular weight of butyrylchitin.

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Received September 24, 1993

Accepted April 14, 1994