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Синтез полімерів

Polymer blends based on polyurethane ionomer and chitosan

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Polymer composites based on binary blends of a synthetic polyurethane cationomer (CPU) and the natural polymer - chitosan, with content ranges from 1 up to 75 wt % have been prepared. The structural morphology of binary blends of ion-containing polymers – polyurethane cationomer (CPU) and chitosan having protonated amino groups – have been studied using WAXS (wide angle X-rays scattering), SAXS (small angle X-rays scattering) methods and DSC (differential scanning calorimetry). The structural formation processes in the blends of two ion-containing polymers are shown to be controlled by the compatibility of their components. It has been established that the synthesized polyurethane cationomer (CPU) is an amorphous polymer and has pronounced microphase structure with spatial periodicity in the arrangement of its hard and soft domains. The Bragg distance (interdomain space distance) between similar (concerning their electronic density) domains (D) was determined to be 4,7 nm. Neat chitosan, having ionic (protonated) amino groups in its chain is shown to be an amorphous-crystalline polymer and there is no periodicity in spatial location of heterogeneous micro-areas (crystallites and amorphous micro-areas) in its structure.

Keywords: polymer composite, blends, morphology, polyurethane ionomer, chitosan, X-ray diffraction.

1. Introduction

Chitosan is a naturally occurring polysaccharide and its derivatives are known to have a great potential with regard to their application for industrial needs as well for scientific investigations connected with the development of novel functionalized materials [1]. Chitosan – product of chitin deacetylation (the second abundant natural polymer after cellulose) – possesses free amino groups in its anhydroglucose units which are able to be chemically modified by different functionalities [2].

Chitosan is also biodegradable and biocompatible polymer and, thus, it has a wide range of applications in medicine, e.g. as supporting and treating material for bandages, component of gels, coatings for wound healing and burns recovery, in drug-release polymer systems and as a sorbent for removing heavy metals from waste waters [3]. On the other hand, it has some disadvantages concerning practical aspects of its applications such as poor mechanical strength, insufficient elasticity and hydrophility of films obtained on its base. In order to overcome the above drawbacks we have developed binary compositions based on a polyurethane cationomer (CPU) and chitosan.

Development of a novel composites by preparing mixtures based on chitosan and other polymers allows the development of materials with advanced physico-mechanical parameters to be obtained and, even so, preserving and enhancing valuable properties inherent to that of neat chitosan.

Several studies deal with polymer blends based on chitosan and other polymers, investigating their properties, e.g. chitosan-polyethylene oxide based membranes [4], poly(ε-caprolactone) with chitosan and whey-protein-isolate [5, 6], chitosan-polyvinyl alcohol [7-9], but in all cases the structure and characteristics of polyurethane-chitosan compositions are studied to a lesser extent [10–11].

Thus, this research focuses on developing composites of chitosan as a natural polymer with CPU synthesized via a base of N-aminoethylpiperazine. The morphology and thermal behavior of the obtained CPU-chitosan films and starting components have been investigated by IR, WAXS and SAXS, DSC methods with potential application in biomedical sciences.

2. Experimental

2.1. Materials

For synthesis polyoxypropylene glycol (trade mark "Jeffox" PPG -1000) being kindly supplied by Huntsman Corporation, molecular weight (M_n) 1000 g/mol. PPG-1000 was vacuum dried (5 mm Hg) at 70 °C prior to use. 2,4-tolulenediisocyanate (2,4-TDI) was purchased from "Merck" (Germany) n_D= 1,5689(20 °C). N-aminoethylpiperazine, molecular weight 129,21, boiling point = 222 °C (760 mm Hg) was kindly supplied by the Huntsman Corporation. Chitosan, [2-Amino-2-deoxy- 1,4)-β-D-glucopyranan] molecular weight 400 000, was purchased from "Fluka" (Switzerland). Solvents – dimethylformamide (DMF) and acetone was dried over CaH_2 and distilled before use.

2.2. Synthesis of polyurethane cationomer (CPU)

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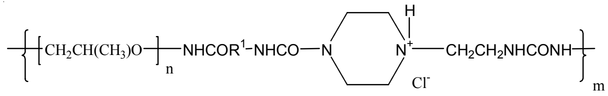
CPU synthesis was fulfilled in two steps. In the first step, isocyanate prepolymer (IP) based on PPG-1000 and 2,4-TDI (molar ratio of 1:2) was synthesized. In the second step, N-aminoethylpiperazine as a chain extender was added to the IP dissolved in the DMF-acetone mixture under intense stirring. After the exothermic reaction took place within 30 min, to the resulting product a calculated amount of hydrochloric acid was added to give the cationomer (CPU). The isolated product is soluble in water and has the following chemical structure:



where: n=17, m=25 , R^1= 2,4-$CH_3C_6H_3$.

Molecular weight of the polymer obtained was determined using HPLC and being equal to 35000 g/mol.

2.3. Preparing of composites based on CPU and Chitosan

A calculated amount of neat chitosan (wt) was dissolved in 2 % of hydrochloric (or acetic) acid to give 3% chitosan solution. Then, 10 % solution of ionomer was prepared by dissolving the CPU (10 g) in 2 % of hydrochloric acid (80 g) with a small amount of DMF (10 g). The resulting solutions of chitosan and CPU were mixed in proportional shares to yield composites, having chitosan contents ranging from 1 % up to 75 wt %.

After drying at T= 65 °C to a constant mass, the flexible films (these partially swell in DMF) with a chitosan content of 1, 5, 25, 50, 75 wt %, respectively, were obtained.

CPU, chitosan, and their composites were investigated by FTIR spectroscopy (Tensor-37, Bruker (Germany) in the frequency range of 400–4000 cm^{-1}.

The thermal behavior of the blends and the related polymers was examined using the DSC technique (temperature interval from -90 to +200 °C) with a calorimeter Q 100, modulated DSC, TA Instruments (UK). The measurements were made in a nitrogen purge gas (50 ml/min) with temperature variations of +/-0,01 °C.

The molecular weight of the synthesized CPU was determined using HPLC (size exclusion technique), Du Pont 8800 LC with sensor adjusted to the wave-length at 280 nm. Chloroform was used as eluent with 5% of methanol for blocking of active adsorption particles located on the silica gel surface [12]. Calibration was carried out with standard polystyrene (mol. weight 30000 g/mol, M_w/M_n=2).

The structural parameters of CPU-chitosan composites on the molecular level were monitored by the WAXS method. The WAXS measurements were performed according to the Scherrer technique in the transmission mode on a DRON-4-07 diffractometer.

The microheterogeneous structure of CPU-chitosan was investigated by the SAXS method with a KRM-1 camera. CuK_6-radiation monochromatized with a Ni-foil was employed, using a slit collimation of the incident beam according to the Kratky method complying with the conditions of an infinite height of the incident X-ray beam [13,14]. Scattered X-rays were detected with a scintillation counter in an automated stepwise scanning mode. The measured values of scattering intensity were corrected for attenuation of the incident X-ray beam by the tested samples and subsequent abstraction of the intensity of background X-ray scattering by the collimator system. The values of scattered intensity were normalized to the scattering volume. The obtained X-ray scattering profiles smeared by slit collimation were corrected following the Schmidt method [15] using an original program based on the algorithm Delphi-6.0.

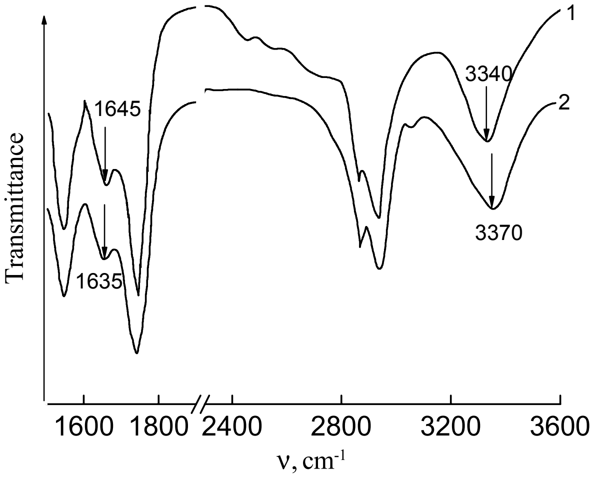


Fig.1. FTIR spectra of CPU (*1*) and PU in non-ionic form (*2*)

3. Results and Discussions.

In order to characterize the compounds applied in this work, we compared their IR spectra. Spectral data in the area of $\nu_{C=O}$ and ν_{NH} for polyurethane both in ionic (CPU) and non-ionic (PU) forms are shown in fig.1.

Comparative analysis showed that, after quaternization of the nitrogen atoms in the chain of the PU, the range of absorption bands emerged at 2350–2700 cm^{-1}, relating to the $\nu_{NH}{}^{+}$, while in the absorption region which is sensitive to hydrogen bonding, one can see that, the stretching bands ($\nu_{C=O}$) of urea fragments are shifted to the high frequency end ($\nu_{C=O}$ for PU =1635 cm^{-1} and 1645 cm^{-1} for CPU, respectively), and ν_{NH} is simultaneously shifted to the low-frequency field: 3370 cm^{-1} for PU, and 3340 cm^{-1} for CPU. Such variations could be assigned to the appearance of additional electrons donated in the cationomer, in particular, halide-ions taking part in the formation of ion-molecular hydrogen bonds like $NH^+ \ldots Cl^-$, as described elsewhere [16]. It should be noted that, urethane groups located at the periphery of hard domains and being unbounded by hydrogen bonds normally exhibit a higher intensity of carbonyl group stretching vibrations ($\nu_{C=O}$ at 1740 cm^{-1}).

Chitosan is a polar polymer, characterized by a strong, wide absorption band at n=3470 cm^{-1} (these are stretching

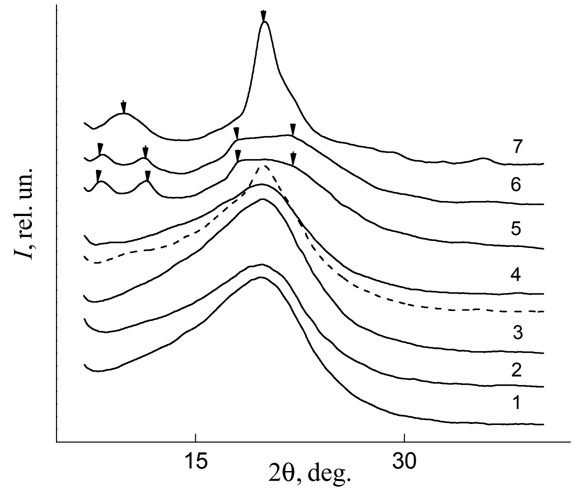


Fig. 2. WAXS profiles for CPU-chitosan binar blends having 0 (*1*), 1 (*2*), 5 (*3*), 25 (*4*), 50 (*5*), 75 (*6*) and 100 % wt. of chitosan (*7*): experimental (firm lines) and additives (dotted lines) values

vibrations of OH, NH and NH_2 groups). Undoubtedly, the mixture of two polar polymers having ionic groups in their chains may lead to the re-arrangement of intermolecular hydrogen bonds, ion-molecular ones in both systems. It is evident, starting from a 25 wt % of chitosan in the composites, that the stretching band of C=O for the urethane groups is shifted from 1740 cm^{-1} (for neat CPU) to the high-frequency region ν=1760 cm^{-1} (for the composite), and the hydroxyl groups of chitosan forms stronger bonds, e.g., in the compositions CPU + 75 wt % chitosan ν_{OH} is located at 3440 cm^{-1}, while for neat chitosan it occurs at 3470 cm^{-1} (spectra for blends are not included here).

According to the WAXS data obtained for the starting polymers and their blends (see fig. 2), it was shown that neat CPU is an amorphous polymer, while chitosan has an amorphous-crystalline structure (degree of crystallinity is around 60%). The effective crystallite size was determined by the Scherrer method to be 4,5 nm. Successive increments of chitosan content in the blends (from 1 to 25 wt %) does not lead in noticeable changing of the structure of the polymer blends. Their macrochain fragments display a short range order in spatial location, indicating that the CPU structure plays a dominant role in the structure formation process of the blends.

However, comparison of the experimental WAXS curve (fig. 2, solid line) of a blend, having 25 wt % chitosan (curve 4) with the calculated curve (dotted line), taking into account the additivity of the contributions of blend components to the total X-ray diffraction intensity, according to the equation below:

$$I_{add} = w_1 I_1 + w_2 I_2 ,$$

(where I_1, I_2 are the intensities of CPU and chitosan, and w_1, w_2 – are the corresponding component weight fractions in the blend) showed that they are strongly differed. This confirms the non-additive processes of structural formation in these blends.

Inserting 50 wt % of chitosan into the composite leads to a phase inversion, whereas modified chitosan (in ionic form) starts to dominate in the structure formation, but at the same time, mixtures holding an amorphous-crystalline character, essentially differing from neat chitosan. At a content of 50 wt % chitosan, the microregions possessing a long range order are arranged in a spatial arrangement of macrochain fragments (crystallites) with a structure, essentially different to that of neat chitosan (curves 5, 7).

This proves, above all, that the “unallowable” multiplet at 2θ=9,7° existing in the diffractogram of neat chitosan is divided into two diffraction maximums (2θ=8,2 and 11,2°) for its blend with CPU, and in the area of the main diffraction maximum for neat chitosan (19,9°) an “unallowable” multiplet is realized at angles 2θ=14,4–28,1°.

The mixture having 75 wt % of chitosan holds the analogue crystalline structure. Such alteration in the crystalline structure of ionic chitosan, forming blends with the urethane-containing polymer, also have ionic groups in its hard blocks is likely to be due to the existence of interpolymer complexes in the obtained composites.

To confirm the above assumption, a SAXS study has been carried out in order to evaluate the character of the microheterogeneous structure of the blends. As one can see from the SAXS patterns presented in fig. 3, the microheterogeneous structure of the blends is strongly determined by the content of the components and has an extreme character.

The display of a crisp interference maximum on the scattering pattern of the neat CPU (curve 1) indicates the existence of a well-ordered microphase structure in its bulk – hard domains and microregions, enriched with soft blocks (“soft domains”), which have periodicity in their spatial arrangement. Interchange period for similar microregions of heterogeneity (*D*), according to the Bragg equation ($D=2\pi/q_m$, where q_m is position of interference maxi-

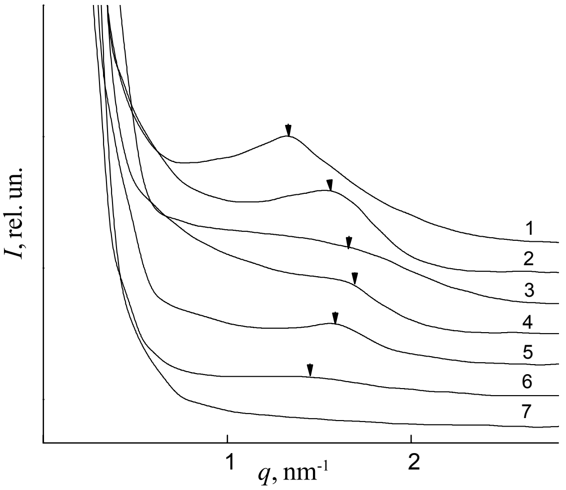


Fig. 3. SAXS profiles for CPU-chitosan binar blends having 0 (*1*), 1 (*2*), 5 (*3*), 25 (*4*), 50 (*5*), 75 (*6*) and 100 % wt. of chitosan (*7*)

Table 1. Parameters characterizing the microheterogeneous structure of CPU – chitosan blends (SAXS)

Chitosan content, wt %	q_m , nm	D, nm	l_p, nm	Q , rel.units
0	1,32	4,7	2,1	10,5
1	1,54	4,1	1,6	9,8
5	1,63	3,8	1,5	10,1
25	1,64	3,8	1,8	9,1
50	1,57	4,0	2,9	8,1
75	1,43	4,4	6,4	6,8
100	-	-	66,0	6,2

mum on scattering pattern, depicted as function: $I - f(q)$, where q=(4π/л)sinи is value of dispersion vector in reverse lattice proves to be 4,7 nm.

Microheterogeneous structure of ionic chitosan is essentially varied from that for CPU, since on its profile substantial scattering intensity near the primary beam was revealed (curve 7), confirming existence of heterogeneous micro-areas in the polymer bulk (micro-hollows or particles), which size and distance between them exceeds the resolving capacity of small-angle roentgen camera (50 nm) for detecting of their character and spatial arrangement. As for the heterogeneity, it could be due to both crystallites and ionic clusters being formed due to the Coulombic forces in the polymers' bulk, having a high concentration of ionic groups [17]. However, judging from the WAXS data, the effective size of the chitosan crystallites is almost equal to 4,5 nm (as stated above). Moreover, the estimation of l_p (parameter for the heterogeneity range) correlates directly with average size of the heterogeneous micro-areas in the pseudo-two-phase system ($l_p = \varphi_2 \langle l_1 \rangle = \varphi_1 \langle l_2 \rangle$, where l_1, l_2 and φ_1, φ_2 – are the size and inclusion volume fraction for micro-areas of 1st and 2nd types, respectively). These were calculated according to the Ruland method, [18, 19] based on SAXS data without collimation correction, and showed that the l_p value for chitosan proved to be approximately 65 nm (table 1).

As is evidenced by the SAXS profiles (fig. 3), consecutive increasing of the chitosan content in the blends resulted in a gradual decrease in the X-ray scattering intensity in the area of interference maximum, while its position (q_m) on the scattering profiles attains an extreme value at 5–25 wt % chitosan. According to the above information, the interdomain spatial distance (D) of similar (with regards to the value of their local electronic density) heterogeneous micro-areas, at the above content of chitosan, reaches its minimum value (table 1). However, calculation of the l_p parameter revealed that a minimum value of heterogeneous micro-areas is found at 5 % wt of chitosan in the blend. At increasing chitosan content in the blends (starting from 25 wt %) a gradual enhancement of their size occurred.

Qualitative assessment of alteration for microheterogeneous structure of blends investigated could be obtained from the following equation, taking into account their values of scattering invariants Q:

$$Q = \int_0^{\infty} I(q) q^2 dq,$$

i.e., structural parameter directly connected with mean-square fluctuation' value of electron density in a two-phase system:

$$Q \propto \varphi_1 \varphi_2 (\rho_1 - \rho_2)^2,$$

where φ_1, φ_2 and ρ_1, ρ_2 – inclusion volume fractions and electron densities for 1st and 2nd phases, accordingly [20].

As follows from the data in table 1, increasing the chitosan's share in the blend up to 5 wt %, does not change the heterogeneity level and being equal to that for neat CPU, whereas at chitosan content ≥ 25 wt %, the blend's heterogeneity level is decreased due to the substantial contribution of natural polymer into the structure forming processes.

The extreme concentration dependence of size parameters revealed for micro-heterogeneous structure (D and l_p) is attributed to the emergence of Coulombic interactions in the blends.

According to the DSC data (fig.4 and table 2) an increase in the chitosan part in the blends from 1 to 50 wt % results in a gradual decrease in the glass transition temperature ($T_{g,s}$) of the medium-interval values of CPU soft segments as compared with its parent value. As is well known, $T_{g,s}$ of urethane-containing polymers is a macroscopic parameter characterizing the level of their degree of microphase separation of soft and hard blocks – the closer this parameter to the glass transition temperature of the neat polyester glycol incorporated into PU, the higher the degree of segregation of its hard and soft blocks [21].

On the other hand, while studying the interpolymer complex formation process in the binary mixture of polymers – carboxyl containing polyurethane and polyvi-

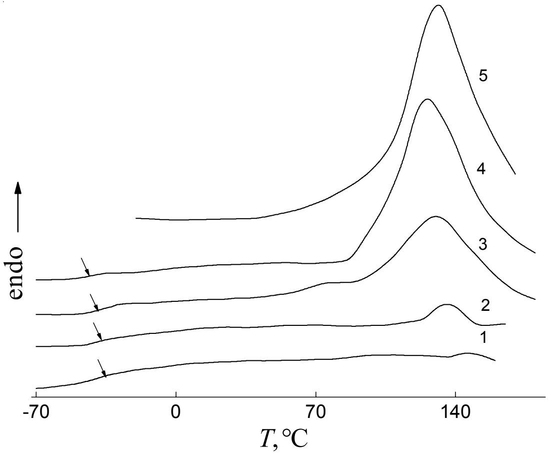


Fig. 4. Thermograms for CPU-chitosan binar blends having 0 (*1*), 5 (*2*), 25 (*3*), 50(*4*), and 100 % wt. of chitosan (*5*)

Table 2. Thermophysical properties of CPU-chitosan blends

Chitosan content, wt %	$T_{g,s}$, °C	ΔC_p, kJ/(kg·K)	T_m, °C
0	-32	0,56	-
1	-37	0,27	-
5	-37	0,25	135
25	-39	0,31	135
50	-43	0,23	126
75	-	-	130
100	-	-	132

nylpyrrolidone (PVP) – it was shown, that a positive deviation from additive values both for common glass transition temperature (T_g) of PU hard blocks and PVP chains, as well for $T_{g,s}$ of PU component itself, is realized in the whole concentration interval of components involved [22]. Furthermore, according to the work described in [16], a negative deviation from additive values of the common T_g of components of a binar polymer blend pin points their compatibility.

Therefore, based on the dependence of $T_{g,s}$ on the composition content for urethane-containing polymer and data presented in [22, 23], it is possible to conclude that for, at least, up to 50 wt % of chitosan in the blends, the components are compatible.

The melting temperature (T_m) of the crystalline phase of ionic chitosan is in an extreme dependence from blend compositions (table 2). The existence of lower values of T_m for 50 and 75 wt % chitosan content in the blends is in a good agreement with the results obtained earlier by a WAXS method and could be explained by another crystalline structure of chitosan. Such correlation leads us to conclude that, while chitosan content ranges between 50–75 wt % in the blends, the interpolymer complex formation process occurred due to the prevalence of polymer-polymer Coulombic interactions involving both ionic groups CPU and chitosan.

4. Conclusions.

Processes of structure formation in the blends of CPU with chitosan are realized in two areas of chitosan content: up to 25 wt % and more than 25 wt %. In the first area, the structure of CPU dominates in the blends and a *D* value (3,8 nm) is found to be less than that for neat CPU (4,7 nm) and chitosan's T_m (melting point) in the blends is higher (T_m = 135 °C), than for neat chitosan (T_m = 132 °C). In the second area, the chitosan crystalline structure (in fig. 1 it is marked by arrows) in the blends is changed, successively increasing *D* from 3,8 up to 4,4 nm with a corresponding T_m change for chitosan becoming lower (at 75 wt % of chitosan content in the blend its T_m is 126 °C), than for the parent chitosan.

In the blends of two ion-containing polymers structure formation processes are shown to be stipulated by the ability of their components to be compatible.

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Полімерні суміші на основі поліуретанового іономера та хітозану

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Розроблено полімерні композити на основі синтетичного катіонвмісного поліуретану й добавки природного полімеру хітозану з протонованими аміногрупами із вмістом від 1 до 75 мас.%. Морфологію таких бінарних сумішей досліджували методами ширококутового й малокутового розсіяння рентгенівських променів і диференціальної сканувальної калориметрії. Показано, що процеси структуроутворення в сумішах іонвмісних полімерів можна контролювати шляхом варіювання сумісності їх компонентів.

Встановлено, що синтезований у роботі поліуретановий катіономер є аморфним полімером і має яскраво виражену мікрофазову структуру з просторовою періодичністю в розташуванні жорстко- та гнучколанцюгових доменів, при цьому бреггівська відстань між однотипними за величиною електронної густини доменами становить 4,7 нм.

Вихідний хітозан з іонними (протонованими) групами в ланцюзі є аморфно-кристалічним полімером, в об'ємі якого відсутня періодичність у просторовому розташуванні мікрообластей гетерогенності (кристалітів і аморфних мікрообластей).

Ключові слова: полімерний композит, суміші полімерів, морфологія, поліуретановий іономер, хітозан, рентгеноструктурний аналіз.

Полимерные смеси на основе полиуретанового иономера и хитозана

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Разработаны полимерные композиты на основе синтетического катионсодержащего полиуретана и добавки природного полимера хитозана с протонированными аминогруппами с содержанием от 1 до 75 масс.%. Морфологию таких бинарных смесей исследовали методами широкоуглового и малоуглового рассеяния рентгеновских лучей и дифференциальной сканирующей калориметрии. Показано, что процессы структурообразования в смесях ионсодержащих полимеров можно контролировать путем варьирования совместимости их компонентов.

Установлено, что синтезированный в работе полиуретановый катиономер является аморфным полимером и имеет ярко выраженную микрофазовую структуру с пространственной периодичностью в расположении жестко- и гибкоцепных доменов, при этом брэгговское расстояние между однотипными по величине электронной плотности доменами составляет 4,7 нм.

Исходный хитозан с ионными (протонированными) группами в цепи является аморфно-кристаллическим полимером, в объеме которого отсутствует периодичность в пространственном расположении микрообластей гетероген-ности (кристаллитов и аморфных микрообластей).

Ключевые слова: полимерный композит, смеси полимеров, морфология, полиуретановый иономер, хитозан, рентгеноструктурный анализ.