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Synthesis and structure of new composite hydrogels based on poly(*N*-vinyl caprolactam) with nanosized anatase

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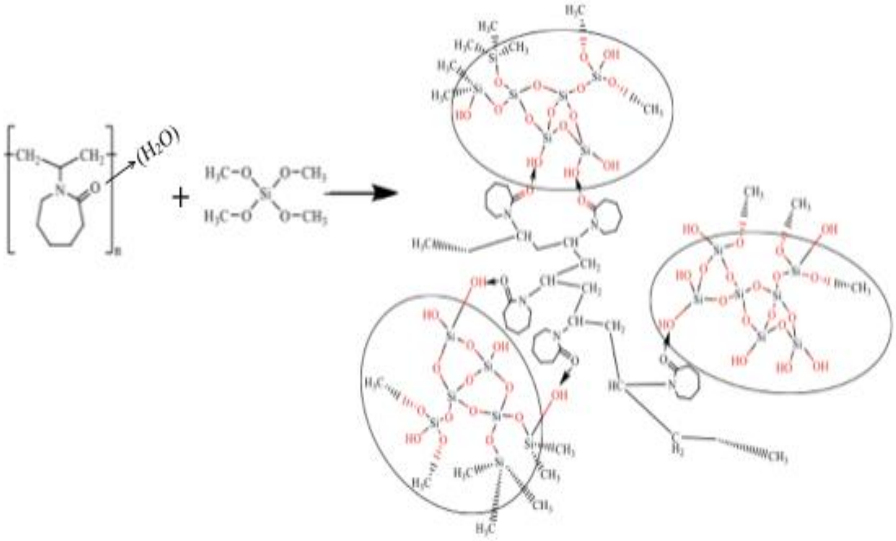

Figure S1 Scheme of PVCL hydrogel formation.

Powder X-ray diffraction (XRD) patterns of all hydrogels both in the initial (**1**) and powdered (**2**) states were measured on a HZG-4 diffractometer (graphite monochromator); CuK_α radiation, in a step-scan mode (the count time was 10 s per step, the step size was 0.02°, the 2θ angle range was 2° to 50°). The diffraction patterns were processed and the parameters of the substructure were calculated using the "Program for processing diffraction patterns of nanoscale and amorphous substances and calculations of substructure characteristics".[S1] The average sizes of crystallites of nanosized A and the average sizes of ordered domain regions for supramolecular PVCL structures in the synthesized composite hydrogels were calculated by the following equation $D = K\lambda/\beta\cos\theta$ (*eq. 1*), where $\lambda(\mathrm{Cu}_{K\alpha})$=1.54051 Å is the wavelength, β is the integral peak width, and K=0.9 is the empirical coefficient, 2θ~25° for A, ~9 and 18° for PVCL). The standard deviation was ±5%.

Table S1 Powder X-ray diffraction data for PVCL in PVCL and A/PVCL hydrogels.

Sample	Initial sample (**1**)			Dried and ground sample (**3**)		
	I, %	2θ, °	d, Å	I, %	2θ, °	d, Å
PVCL	62	11.60	7.62	50	9.26	9.54
	-*			58	10.92	8.11
	-*			100	20.32	4.370
	100	26.56	3.353	-*		
	55	41.10	2.199	-*		
A/PVCL	78	11.56	7.64	100	11.95	7.40
	-*			53	20.10	4.414
	100	27.94	3.191	-*		

* - peaks were not observed

Scanning electron microscopy. The morphology of PVCL and A/PVCL hydrogels both in air-dried (**2**) and freeze-dried (**4**) states were studied by scanning electron microscopy (**SEM**). Images were obtained using a JSM 7500F ultra-high-vacuum high-resolution scanning electron microscope equipped with a cold autoemission cathode (JEOL, Japan). The elemental composition of the samples was determined by **energy-dispersive X-ray** (**EDX**) microanalysis in a region with lateral sizes from 2×2 to 100×100 μm using an INCA Penta FET-x3 energy-dispersive X-ray microanalysis system (OXFORD INSTRUMENTS, UK) coupled with a scanning electron microscope. The analyzer was equipped with a nitrogen-cooled silicon lithium detector; the resolution was 129 eV for carbon. The detector was calibrated based on CoK_α radiation from the cobalt metal standard. The elemental composition was measured at electron beam energy of 15 keV. The information depth λ (λ~3.1 μm) was evaluated using the “Depth of X-ray Production” program.

The measurements were performed under ultra-high vacuum (about 10^{-8} Pa), which required a special sample preparation of initial native gels (drying). Also, we prepared samples by freeze-drying (**4**), which is the mildest form of drying used to remove moisture from the product, during which the properties and, what is most important, the structure of the sample remain almost unchanged.[S2] The freeze-drying involves the freezing of the sample to very low temperatures followed by drying under vacuum. During this process, the liquid is completely removed from the frozen sample by sublimation of ice, *i.e.*, the liquid is transformed directly from the gaseous to solid state. This technique allows the preparation of dry tissues, medications, products, and so on without loss of structural integrity and biological activity. This technique was applied to prepare hydrogels in studies.[S3] The freeze-drying has long been successfully used, along with other techniques (*e.g.*, critical point drying), for the preparation of biological specimens for SEM studies.[S4] Samples of PVCL hydrogel and A/PVCL composite hydrogel were frozen under atmospheric pressure using liquid nitrogen, in which the samples were kept for 30 min. Then the samples were cut into chips under nitrogen and placed in a JEE-420D vacuum evaporator, where they were kept for 24 h under a pressure of 3×10^{-3} Pa. After drying, 10-nm-thick platinum thin films were deposited onto the samples using a JFC-1600 vacuum magnetron sputtering system. This procedure was employed in order to avoid the degradation of polymer samples upon exposure to an electron beam probe and also to prevent charging of the dielectric layer by an incident electron beam. Then the samples were placed in a scanning electron microscope chamber. The operating modes were chosen with regard to the possible degradation of samples by an electron beam probe: the accelerating voltage was 5 kV; the electron probe current was low (5×10^{-12} A), which was provided by a cold autoemission cathode. Images were obtained using low-energy secondary electrons because this mode ensures the highest resolution (at an incident beam energy of 5 keV, the resolution was 1.5 nm).

According to the EDX data, the surface and cross-section of both the air-dried and freeze-dried samples conclude:

1) The surface and cross-section of freeze-dried A/PVCL samples (**4**) contain a smaller amount of carbon (<60 at.%) and more titanium (>5 at.%) compared to samples dried by air-drying (**2**) (~80 at.% for C, ~<5 at.% for Ti);

2) The surface and cross-section of air-dried A/PVCL (**2**) samples contain approximately the same amount of oxygen (~16.1 at.%), nitrogen (~6.4 at.%) and titanium (~20 at.%). The same trend is observed for samples after freeze-drying;

3) Drying in the air (**2**) leads to an increase in the oxygen content (mainly in the form of water) in the cross-sections of PVCL and A/PVCL samples compared to the surface. The removal of water molecules first occurs from the surface of the samples, and with this type of drying the water remains in the bulk of the sample;

4) The surface and cross-section of the freeze-dried hydrogel A/PVCL hydrogel contain less than 3 at.% Si from the starting components, which is not observed for PVCL hydrogel.

Swelling degree. Hydrogels were air-dried at 20ºC to constant weight (**2**) and placed in a vessel filled with water (25-fold excess with respect to the weight of the dried hydrogel sample) for achieving swelling to constant weight at 20ºC. Swollen hydrogel samples were weighed at regular time intervals during 200 hours. The degree of swelling was calculated by the formula $W=(m-m_0)/m_0\times100\%$ (*eq. 2*), where W is the swelling degree, %; m is the weight of PVCL or A/PVCL hydrogel at a certain time after swelling, g; m_0 is the weight of the hydrogel sample dried to constant weight (irregularly shaped pieces, ~0.1 g).

The swelling process of PVCL and A/PVCL obeys the second-order kinetics: $\frac{dW}{dt} = K(W_\infty - W)^2$ (*eq. 3*), where W_∞ is the equilibrium degree of swelling (%), W is the swelling degree (%) at a given time t. The experimental data plotted on the t/W-t coordinates are described by the linear function $\frac{t}{W} = \frac{1}{KW_{\infty}^{2}} + \frac{t}{W_{\infty}}$ (*eq. 4*). The latter was used to determine the swelling rate constant (K, %×min^{-1}) (Table S2).

Table S2 Swelling rate constants (K) and swelling degrees (W, %) for dried PVCL and A/PVCL hydrogels (**1**) in water.

	PVCL	A/PVCL
Swelling rate constant, K, %×min^{-1}	4.44×10^{-6}	3.52×10^{-6}
Swelling degree, W, %	540	1007

Diffusion of water into any hydrogel involves the transfer (migration) of water into pre-existing spaces (pores) between hydrogel chains, while the swelling of hydrogel involves the motion of its segments (walls).[S5] Kinetics of hydrogel swelling is most frequently mathematically described by power-law equation (*eq. 5*): $\frac{M_t}{M_{\infty}} = k \cdot t^{n}$, where M_t and M_{∞} - the amounts of absorbed solvent (in our case, it is water) in time t and in equilibrium state (g×g^{-1}), k – swelling constant rate (g×g^{-1}×min^{-1}), t – время набухания (min), n – diffusion constant (-). Based on the relative rates of diffusion and polymer relaxation (structural rearrangement of hydrogel through a motion of polymer chains and transition of the system to the equilibrium state), three diffusion mechanisms can be distinguished[S6]:

1. Fickian diffusion, in which the rate of diffusion is much less than that of polymer relaxation (n=0.45 is the diffusion constant);

2. The mechanism, in which the rate of diffusion is much faster than that of relaxation processes ($n \geq 0.89$);

3. Mechanisms (systems) characterized by non-Fickian or anomalous diffusion, which occurs when the rates of diffusion and relaxation are comparable ($0.45<n<0.89$).

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