Sorption of Water Vapour by *N*-Vinyl Caprolactam Oligomers

[a]I. N. RUBAN*, [a]O. E. SIDORENKO, [a]V. O. KUDYSHKIN, [a]N. I. BOZOROV, [a]M. YU. YUNUSOV,
[a]N. L. VOROPAEVA, [b]G. KOGAN, and [a]S. SH. RASHIDOVA

[a]*Institute of Polymer Chemistry and Physics, Academy of Sciences of the Uzbekistan Republic,*
700128 Tashkent, Uzbekistan
e-mail: polymer@rol.uz

[b]*Institute of Chemistry, Slovak Academy of Sciences, SK-845 38 Bratislava*

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Water vapour sorption by vinyl caprolactam polymer samples with the molar masses in the range of 2.6—25 × 10^3 g mol^{-1} was investigated. Influence of the degree of polymerization on sorption was discovered for the oligomers. This dependence was not observed for the high-molar-mass polymers. The possible causes of this phenomenon are discussed.

Investigation of the physicochemical properties of polyvinyl caprolactam (PVCL) has attracted attention of many researchers. Such interest is explained mainly by specific hydration properties of this polymer, which are affected by the size of the macromolecule. A possibility to design a polymer with specific pre-determined hydration properties makes PVCL an attractive target for application in various areas of biotechnology and medicine [1]. The majority of the publications regarding the interactions of PVCL with water dealt with the diluted solutions of the polymer. *Yanul et al.* [2] studied water vapour sorption by films of high-molar-mass PVCL and observed that even a small amount of absorbed water caused a substantial decrease of the glass transition temperature of the polymer. In the present paper the investigation of water vapour sorption by PVCL samples with relatively low molar masses (MM) is reported.

EXPERIMENTAL

Radical polymerization of vinyl caprolactam (VCL) into PVCL was carried out at 60 ℃ in the presence of the azobis(isobutyronitrile) initiator changing the VCL—IPA ratio at the constant concentration of AIBN in the reaction mixture [3]. At these conditions, polymers with relatively low molar masses possessing terminal hydroxyl groups, which are formed as the result of chain transfer reaction on IPA, were obtained. For quantitative determination of the terminal hydroxyl groups, an acetylation method was used. Number-average molar masses (M_n) of PVCL were calculated under assumption that every macromolecule contained only one hydroxyl group. The conditions of VCL oligomers synthesis in IPA solution have been previously established and reported [3]. The content of terminal hydroxyl groups $w(\text{OH})$ and M_n values of PVCL have been established as follows [3]

$w(\text{OH})/\%$	0.65	0.47	0.31	0.25	0.18	–
$M_n/(\text{g mol}^{-1})$	2600	3600	5500	6800	9500	25000

Water vapour sorption by PVCL powder was studied by using a high-vacuum sorption device equipped with a mercury seal and quartz Mack—Bain balances. The sorption was measured in the interval of relative humidity from 0 to 100 %, at (25 ± 0.5) ℃. Prior to the experiments, the studied PVCL powder samples and water were degassed in vacuum at a residual pressure of 0.013 Pa until constant mass was reached. The solvent was applied to a sample in gradually increasing portions. Elongation of the spring was measured using a catetometer KM-8. Total relative error of the measured value of absorbed water per 1 g of the polymer did not exceed 3 %, while the systematic relative error of measuring of vapour pressure did not exceed 0.1 %.

RESULTS AND DISCUSSION

Isotherms of water vapour sorption for the synthesized vinyl caprolactam oligomers have been obtained. The observed features of the sorption isotherms were characteristic of the crumbly packed glass-like polymers. Basing on the dependence of the extent of water vapour sorption on the relative humidity, the number of water molecules (n) associated with one monomer unit of the polymer has been calculated. The depen-

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*The author to whom the correspondence should be addressed.

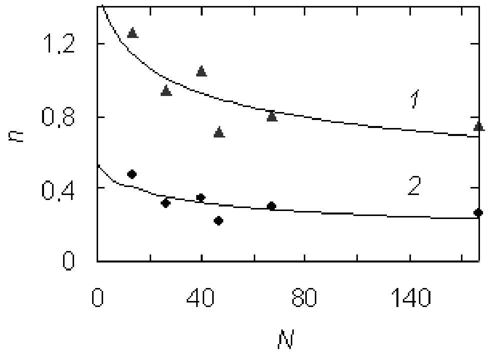

Fig. 1. Dependence of the number of water molecules per one monomer unit (n) on the degree of polymerization (N). Relative humidity: 100 % (*1*), 80 % (*2*).

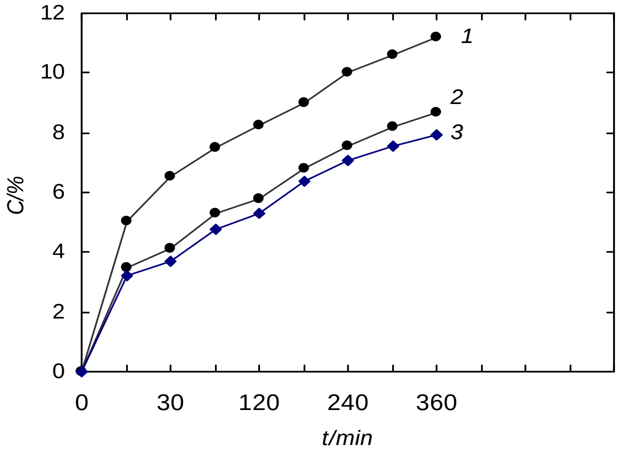

Fig. 2. Dependence of the degree of sorption of water vapour (C) by the PVCL samples with $M_n = 2600$ g mol^{-1} (*1*), 25000 g mol^{-1} (*2*), and 9500 g mol^{-1} (*3*) on time. Relative humidity: 100 %.

dence of n value on the degree of polymerization (N) is shown in Fig. 1.

The results obtained demonstrate that at the equal magnitude of relative humidity, the highest water sorption is observed for PVCL samples with low MM. The effect of molar mass on sorption is exhibited for the PVCL samples with low M_n at high values of the relative humidity. Such dependence disappears with increasing degree of polymerization to $N = 40$—50.

The kinetics of water vapour sorption by PVCL powder was investigated as well (Fig. 2). The experiments have been carried out with the samples of the lowest and of the highest molar masses. The obtained results demonstrate that the moisture sorption rate by sample with $M_n = 2600$ g mol^{-1} is much higher than that of the samples with $M_n = 9500$ g mol^{-1} and $M_n = 25000$ g mol^{-1}, which have almost coinciding curves of sorption kinetics. The rate of water vapour sorption is dramatically decreased on reaching a certain value of n. Moreover, while for the PVCL sample with $M_n = 2600$ g mol^{-1} such retardation is observed at $n = 0.45$, the similar retardation effect for the samples with $M_n = 9500$ g mol^{-1} and 25000 g mol^{-1} occurs already at $n = 0.28$. Apparently, a sharp drop of sorption rate is associated with the filling all active sites of the sorption (C═O groups). The fact that in the case of lower-molar-mass PVCL oligomers the decrease of sorption rate is observed at higher n values may imply better accessibility of the carbonyl groups of the smaller oligomers for water vapour. Subsequently, PVCL samples with low M_n values reveal more pronounced hydrophilic properties.

It is known that certain physicochemical properties of the polymers reveal dependence on the molar mass, which disappears at sufficiently high values of the degree of polymerization. This phenomenon can be explained by the fact that at low MM the terminal groups of the oligomers may influence their properties. Such influence disappears at high N values, when concentration of terminal groups becomes negligible. In this respect, it should be noted that every monomer unit of PVCL contains one hydrophilic carbonyl group, which forms hydrogen bonds with water molecules. Thus, the increase of the number of terminal hydroxyl groups in the polymer should not substantially affect its hydrophilicity. This conclusion has been confirmed by investigation of water vapour sorption by polyvinyl alcohol (PVA) with molar mass 28000 g mol^{-1}. The experiments were carried out at the same conditions as at the study of water sorption by VCL oligomers (Table 1).

At 100 % relative humidity, water vapour sorption by PVA is equal to 21 %. This value approximately corresponds to 0.65 water molecules per one monomer unit. Under the experimental conditions used (100 % relative humidity), the samples contain 0.76—1.26 water molecules per monomer unit (depending on M_n).

Table 1. Dependence of Water Vapour Sorption (Degree of Sorption α) by PVA and of the Number of H_2O Molecules (n) per One PVA Monomer Unit on Relative Moisture

Parameter	Relative moisture/%						
	10	30	50	65	80	90	100
α/%	0.1	0.3	0.8	2.0	6.0	17.0	21.0
n/PVA unit	–	–	–	0.05	0.16	0.50	0.65

Thus, PVCL is even more hydrophilic than polyvinyl alcohol. Hence, a conclusion can be made that increased number of hydroxyl groups in a polymer cannot explain the fact of a significant raise of water vapour sorption with decreasing M_n value. The results obtained cannot be explained by the change of macromolecule chain rigidity. It is known that the increase of polymer molar mass leads to the growth of kinetic flexibility of the chains and results in the increase of vapour permeability [4]. In our experiments, the rise of the water vapour sorption was observed with the decreasing molar mass.

The obtained results are in agreement with the published experimental data regarding the interaction of water and PVCL in solution. It is known that the gradual partial dehydration of monomer units and formation of hydrated layers occur at the increasing degree of polymerization. In particular, this is typical for formation of the first layer that interacts with C=O groups in the areas of low polarity. With the increase of MM, monomer units tend to shield C=O groups thus impeding their interaction with the molecules of solvent [1]. This can be illustrated by the increasing phase separation temperature of PVCL in water (T_{fr}) with the decreasing M_n value of the polymer fractions. A marked rise of T_{fr} is observed for polymer fractions with $M_n < 5 \times 10^3$ g mol^{-1} isolated by means of gel-permeation chromatography. The lower MM, the higher is T_{fr} and consequently more water molecules become associated on average with a monomer unit within a hydrated shell of the macromolecule [1].

We would like also to discuss another possible explanation of the observed phenomenon (disappearing of the dependence of sorption characteristics of the polymer on its molar mass). Let us consider adsorption of a solvent molecule by a macromolecule isolated from gas phase. At a temperature below glass-transition temperature, the macromolecule exists in globular state and can be considered as a "compact drop" [5]. In such a case, solvent molecules can be adsorbed only on a surface of such "drop". According to *Gubin* [6], it can be shown that the ratio (X) of the number of sub-particles located on the surface of a spherical particle (N_{S}) to the number of sub-particles being inside the "drop" (N) can be described by a formula

$$X = \frac{N_{\mathrm{S}}}{N} \propto N^{-\frac{1}{3}}$$

In our case N represents degree of polymerization. It is obvious that X is directly proportional to adsorption value, since the number of sub-particles on the spherical particle surface is proportional to the number of adsorbed solvent molecules, and total number of sub-particles inside the particle corresponds to the mass of a sorbent.

As the macromolecule sorbs molecules of an appropriate solvent, it becomes a fractal object having a fractal dimension $D_{\mathrm{F}} = 5/3$ [7]. Since a macromolecule is a mass fractal, its surface is fractal too, with the same fractal surface dimension [8—10].

$$D_{\mathrm{F}} = D_{\mathrm{S}} = \frac{5}{3}$$

In accordance with this consideration, one can formulate the following formulae for the total number of sub-particles inside the fractal particle N, for the number of sub-particles on the fractal particle surface N_{S}, and for the surface area of mass fractal particle S

$$N \propto R_{\mathrm{G}}^{D_{\mathrm{F}}}$$

$$N_{\mathrm{S}} \propto S \propto R_{\mathrm{G}}^{D_{\mathrm{S}}}$$

where R_{G} is the radius of gyration of the fractal object. Thus, in agreement with the above considerations, one can obtain

$$X = \frac{N_{\mathrm{S}}}{N} \propto R_{\mathrm{G}}^{D_{\mathrm{S}} - D_{\mathrm{F}}} \propto 1$$

So, contrary to the solid object, where the ratio of the number of sub-particles on the spherical particle surface to the total number of sub-particles inside the particle X decreases with increasing mass of the particle, for the fractal object X this value is independent of the mass of the particle. This property of mass fractal object can be explained in the following way: the fractal dimension D characterizes the degree of "openness" of the fractal. The lower is the value of D, the more intensively particles penetrate into the fractal cluster [11]. According to *Bartenev* and *Frenkel* [7], fractal properties of the real fractals are exhibited within a particular space interval. Therefore, dependence of X upon N occurs for oligomers at relatively small N, when the molecule does not exhibit fractal properties. However, this dependence disappears at sufficiently high N values, when the macromolecule exhibits fractal properties.

It should be also mentioned that our considerations are not restricted to the described case, in which we have taken into account an isolated macromolecule rather than a polymer sample consisting of interpenetrating coils. According to *Khokhlov* [5], for sufficiently high N values the polymeric macromolecule reveals the properties of a real mass fractal both in the surrounding of the similar chains and in a dilute solution in a good solvent [7].

Thus, the above considerations may explain the reason of the decrease of water vapour sorption at the increasing N for the oligomers of VCL.

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