Properties of Solutions of Poly-N-Vinylcaprolactam

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Synopsis

The properties of poly-N-vinylcaprolactam organic and aqueous solutions were studied. Toluene solutions present an increasing $[\eta]$ from 10 to 40°C. Aqueous solutions present a very accentuated diminishing of $[\eta]$ from 10 to 30°C. Above 30°C. the polymer precipitates from its aqueous solutions. The precipitation temperature does not depend on the concentration but on the molecular weight of the polymer. Some acid and basic agents have a marked influence on $[\eta]$ and the precipitation temperature of the aqueous solutions.

There are no studies about the behavior of poly-N-vinylcaprolactam solutions. It is only known that some poly-N-vinyllactams precipitate with heat from their aqueous solutions.

The temperature at which the precipitation phenomenon appears is dependent on the number of C atoms of the lactamic ring: for poly-N-vinylcaprolactam this temperature is about 35°C. and for poly-N-vinylpiperidone it is 64–65°C.[1]

In the case of poly-N-vinylpyrrolidone such a precipitation does not take place in the usual temperature range (0–100°C.). It was admitted that this abnormal phenomenon is due to the colloidal nature of aqueous solutions of poly-N-vinyllactams,[2] and it was supposed that the increasing temperature diminishes the polymer solvation.[3]

The object of the present work was the study of the behavior of poly-N-vinylcaprolactam solutions from the viewpoint of their viscosity and of the factors that influence the temperature at which the polymer precipitates from its aqueous solutions.

EXPERIMENTAL

Poly-N-vinylcaprolactam was obtained by radical polymerization of N-vinylcaprolactam in mass or in toluene solution.[4,5] The viscosities of the solutions of poly-N-vinylcaprolactam were determined with an Ubbelohde viscometer ($K = 0.004998$). The intrinsic viscosities were calculated from the formula[6]

$$[\eta] = [2(\eta_{sp} - 2.303 \log \eta_r)]^{1/2}/C$$

The temperature at which the polymer precipitates from its aqueous solution was determined with a precision of $\pm 0.1°C$. The phenomenon of precipitation by heating was studied for different concentrations (between 0.05 and 5%).

The solutions of poly-N-vinylcaprolactam were studied in twice-distilled water as well as in acid and basic aqueous solutions. For this purpose were used solutions of the same concentration as the neutral ones, to which were added measured amounts of acids (hydrochloric, sulfuric, perchloric, formic, acetic, propionic, lactic, trichloroacetic) and bases (ammonium hydroxide and natrium hydroxide).

RESULTS AND DISCUSSION

Poly-N-vinylcaprolactam has good solubility in several solvents, such as aromatic hydrocarbons, alcohols, ketones, dioxane, and chlorinated aromatic and aliphatic hydrocarbons. In such solvents the lower the molecular weight, the higher the solubility of the polymer. One of the best solvents for poly-N-vinylcaprolactam is water at 14–20°C. In water the solubility is very high (concentrations over 40% may be achieved), so that it is possible to affirm that cold water and this polymer are practically totally miscible. The solubility of the polymer in water has a dependence on its molecular weight the opposite of that in the case of organic solvents: the fractions of high molecular weight are more soluble than those of lower molecular weight. The polymers characterized by a low intrinsic viscosity ($[\eta] \leqslant 0.15$ dl./g., determined in toluene at 20°C.) are insoluble or hardly soluble in water.

One may say that the diminishing of the molecular weight of the polymer below a certain value causes a behavior that is similar to that of N-vinylcaprolactam (practically insoluble in water).

On heating of aqueous solutions of the polymer the phenomenon of precipitation, which was observed by Shostakovsky and Sydelkovskaya,[1] occurs. The appearance of the precipitate is very distinct, as is its disappearance on cooling.

The addition of some mineral salts, such as $CuCl_2$, $FeCl_2$, $CoCl_2$, $CoSO_4$, and $NiCl_2$, does not produce any visible change of the aqueous solutions and does not eliminate the reversible phenomenon of precipitation by heating and solubilization by cooling. $ZnCl_2$ and $HCOOH$ produce precipitation of the polymer from its aqueous solutions.

Effect of Concentration and Molecular Weight
on Temperature of Precipitation

The solubility of solid substances (including the polymers) in different solvents increases with temperature. There are very few exceptions to this behavior, and one of them is the solubility of poly-N-vinylcaprolactam in water.

In Table I are given the temperatures at which different fractions of poly-*N*-vinylcaprolactam precipitate from their aqueous solutions. The four polymeric fractions were obtained as follows. Three polymers were synthesized by radical bulk polymerization in the presence of air: (*1*) at 60°C., 580 min., with 0.13% azobisisobutyronitrile (AIBN); (*2*) at 70°C., 75 min., with 0.43% AIBN; (*3*) at 80°C., 75 min., with 0.85% AIBN. A 2.2 g. amount of polymer 1, 3.3 g. of polymer 2, and 4.0 g. of polymer 3 were dissolved in carbon tetrachloride, and from this solution were separated four fractions by fractional precipitation with *n*-heptane. The fractions were characterized by their intrinsic viscosities in toluene at 20°C.

TABLE I

Polymer fraction no.	$[\eta]$, dl./g. in toluene at 20°C.	Temperature at which precipitation begins, °C., at given concn.		
		0.05%	0.5%	5%
I	0.11–0.12	38.9	38.8	38.8
II	0.18	33.8	33.8	33.8
III	0.31	32.1	32.0	32.0
IV	0.45	30.5	30.6	30.5

As one may see from the data presented in Table I, in the range 0.05–5% the concentration of the solution does not influence the value of the temperature at which the polymer precipitates. This temperature depends on the dimensions of the macromolecules, diminishing when the molecular weight of the polymer increases.

Variation of Viscosity of Polymer Solutions with Temperature

We have studied the flow time of 0.3% poly-*N*-vinylcaprolactam solutions in toluene and in twice-distilled water versus the temperature. We observed that toluenic solutions show a normal, almost linear diminishing of the flow time when the temperature increases from 10 to 70°C., similar to the pure solvent; in the case of aqueous solutions, the flow time presents a marked diminishing in the temperature range from 10 to about 30°C., tending to the values of twice-distilled water by approaching the temperatures at which the polymer begins to precipitate; see Figure 1.

In Figure 2 are represented the results obtained for the dependence of intrinsic viscosities according to the temperature. As one may see, the toluene solutions present a relatively unimportant change of their viscosities in the studied temperature range, but the variation is interesting because of the increasing of $[\eta]$ between 10 and 40°C. The intrinsic viscosities of aqueous solutions diminish considerably with heating from 10 to 30°C. This fact is probably causally connected with the precipitation phenomenon that occurs between 30 and 40°C. As a result of this behavior the aqueous
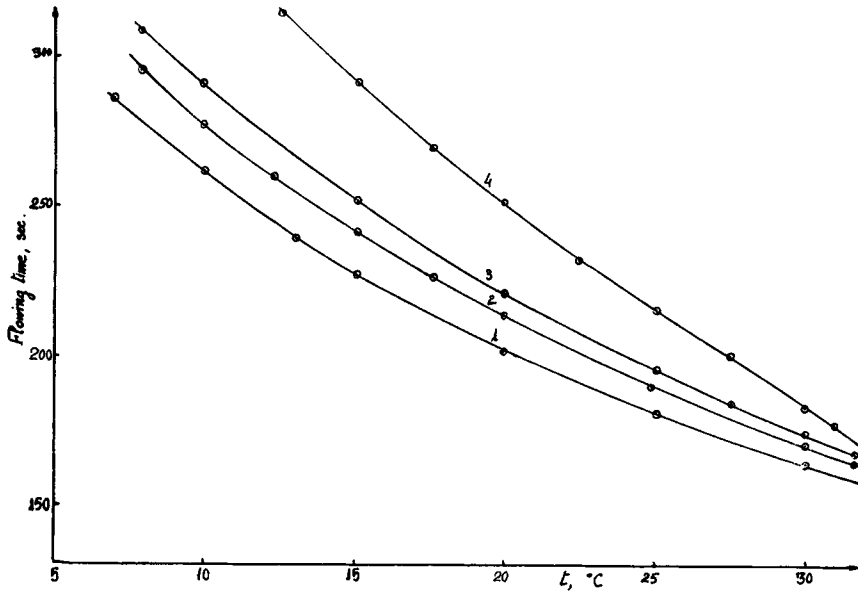
Fig. 1. Influence of temperature on flow time of poly-N-vinylcaprolactam aqueous solutions: (*1*) twice-distilled water, (*2*, *3*, *4*) 0.3% aqueous solutions of polymer fractions II, III, and IV indicated in Table I. Flow time determined with an Ubbelohde viscometer; $K = 0.004998$.
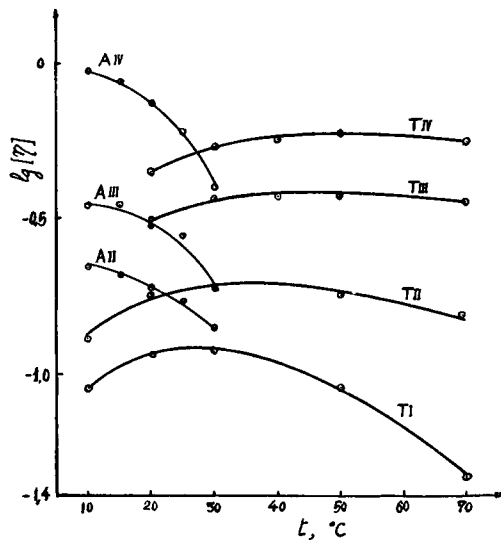

Fig. 2. Influence of temperature on intrinsic viscosity of poly-N-vinylcaprolactam solutions in (A) twice-distilled water and (*T*) in toluene. I, II, III, IV: different fractions of the polymer (see Table I).

solutions of poly-*N*-vinylcaprolactam are more viscous than the solutions of the same polymer in toluene up to 20°C. and less viscous at about 30°C.

The intrinsic viscosity of poly-*N*-vinylcaprolactam aqueous solutions varies greatly with the temperature, the higher the molecular weight of the polymer. The variation of the slopes indicates the existence of a discontinuity, of some critical phenomenon, near the temperature at which the polymer precipitates from its aqueous solutions.

Effect of Acids and Bases on Precipitation Temperature and Viscosity of Solutions

Sulfuric and hydrochloric acids do not produce visible qualitative changes of poly-*N*-vinylcaprolactam aqueous solutions, but they affect their precipi-
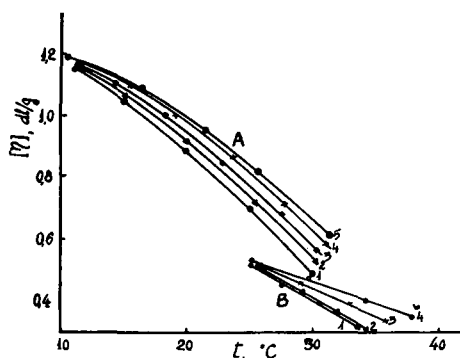

Fig. 3. Influence of hydrochloric acid on viscosity of poly-*N*-vinylcaprolactam aqueous solutions. (*A*) Polymer characterized by $[\eta] = 0.87$ dl./g. (determined in toluene at 25°C.), obtained by bulk polymerization of *N*-vinylcaprolactam at 75°C. with 0.15% AIBN in absence of air: (*1*) without acid; (*2, 3, 4, 5*) with 2×10^{-2}, 3.3×10^{-2}, 5.3×10^{-2}, and 7.3×10^{-2} mole/l. of HCl. (*B*) Polymer characterized by $[\eta] = 0.19$ dl./g. (determined in toluene at 25°C.), obtained by polymerization of *N*-vinylcaprolactam in solution of toluene (1 mole/l.) at 60°C. with 0.5% AIBN: (*1*) without acid, (*2, 3, 4*) with 1×10^{-2}, 2×10^{-2}, and 4×10^{-2} mole/l. of HCl.
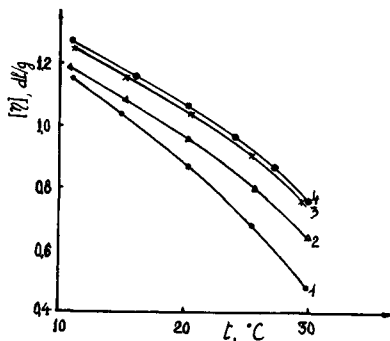

Fig. 4. Influence of sulfuric acid on viscosity of poly-*N*-vinylcaprolactame (polymer of Figure 3*A*) aqueous solutions: (*1*) without acid; (*2, 3, 4*) with 2×10^{-2}, 4×10^{-2}, and 6×10^{-2} mole/l. of H_2SO_4.
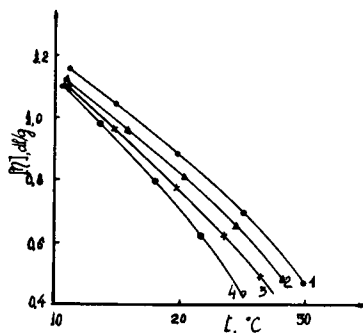
Fig. 5. Influence of trichloroacetic acid on viscosity of poly-N-vinylcaprolactam (polymer of Figure 3A) aqueous solutions: (*1*) without acid; (*2, 3, 4*) with 0.85×10^{-2}, 2×10^{-2}, and 3.1×10^{-2} mole/l. of Cl_3CCOOH.
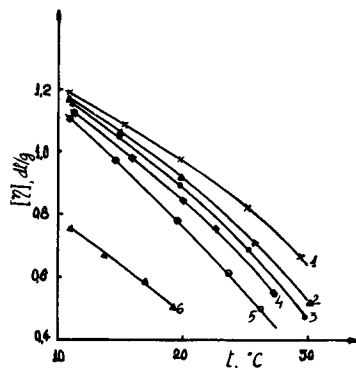

Fig. 6. Influence of different acids and bases on the viscosity of poly-N-vinylcaprolactam (polymer of Figure 3A) aqueous solutions: (*1*) 2×10^{-2} mole/l. of H_2SO_4; (*2*) 2×10^{-2} mole/l. of HCl; (*3*) without any agent; (*4*) 5.6×10^{-2} mole/l. of NaOH; (*5*) 2×10^{-2} mole/l. of Cl_3CCOOH; (*6*) 1.5×10^{-2} mole/l. of $HClO_4$.

tation temperature and viscosity. In Figures 3 and 4 are shown the variations in viscosity with temperature, of the polymer aqueous solutions with and without hydrochloric acid and sulfuric acid. One can observe that these acids produce an increase of the viscosity of the solutions.

Feeble organic acids (acetic, lactic, propionic) do not modify the viscosity of the solutions, in opposition to strong organic acids (trichloroacetic), which cause a diminishing of the viscosity; see Figure 5. The effect of strong organic acids is thus the opposite of that of hydrochloric and sulfuric acids. A diminishing of the viscosity is also produced by adding natrium hydroxide or perchloric acid to the aqueous solutions, the effect being very accentuated in the case of perchloric acid. In Figure 6 are given some data that permit one to see that the direction and amount of the viscosity change depend on the nature of the added agents, but it is not possible to establish a dependence on pH or on the agents' being organic or inorganic.
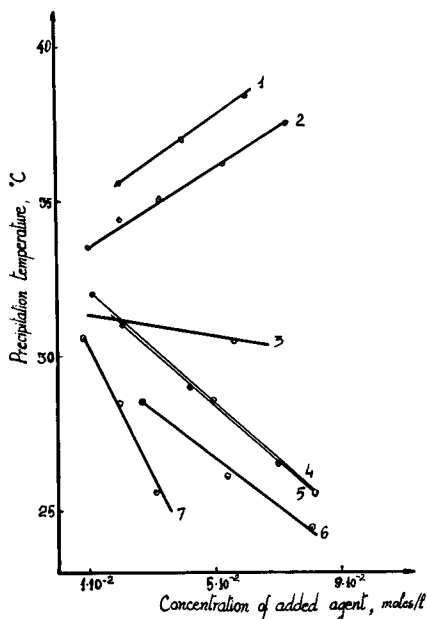
Fig. 7. Influence of acid and basic agents on temperature at which poly-*N*-vinyl-caprolactam precipitates from aqueous solutions: (*1*) sulfuric acid; (*2*) hydrochloric acid; (*3*) natrium hydroxide; (*4*) acetic acid; (*5*) lactic acid; (*6*) propionic acid; (*7*) trichloroacetic acid. For *1*, *2*, *3*, and *7* the polymer was that of Figure 3*A*; for *4*, *5*, and *6* it was that of Figure 3*B*.

The acids and bases modify, not only the viscosity of poly-*N*-vinylcaprolactam aqueous solutions, but also the temperature of precipitation of the polymer from solution. As one may see in Figure 7, hydrochloric and sulfuric acids produce an increasing in this temperature; natrium hydroxide and organic acids produce a decrease in it. Ammonium hydroxide has no effect on the phenomenon. A very strong effect was observed in the case of perchloric acid: 1.5×10^{-2} mole/l. of $HClO_4$ produces a diminishing of the precipitation temperature by 9°C. (from 31.5 to 22.5°C.). As one may see, it is again not possible to establish a dependence on pH or on the organic or inorganic nature of the agents.

As a general characteristic one may affirm that the substances that produce increasing viscosities of the aqueous polymer solutions also produce increasing precipitation temperatures; on the other hand, those which diminish this temperature can at the same time diminish the viscosity.

We suppose that the solubility in water of poly-*N*-vinylcaprolactam is a result of polar-group solvation; in aqueous solution the polymer contains an important number of water molecules bound to $C{=}O$ groups by hydrogen bonds. When the temperature increases, a diminishing of bound water molecules occurs, the solvation of the polymer diminishes, and, finally, the polymer precipitates.

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