Thermosensitive Imidazole-Containing Polymers as Catalysts in Hydrolytic Decomposition of *p*-Nitrophenyl Acetate

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ABSTRACT: Poly(*N*-vinylcaprolactam-*co*-1-vinylimidazole) (PVCL–Vim) and poly(*N*-isopropylacrylamide*co*-1-vinylimidazole) (PNIPA–Vim) are thermosensitive in water and water–2-propanol solutions. These copolymers are soluble at room temperature; however, they undergo phase transition at higher temperatures ($T_{\text{transition}} > 35$ °C). Catalytic properties of PVCL–Vim and PNIPA–Vim as well as of 1-methylimidazole and poly(1-vinylimidazole) (PVim) in hydrolysis of *p*-nitrophenyl acetate were studied. Variation of the reaction rate with temperature was investigated at constant concentrations of substrate and catalyst (imidazole groups). It was found that the reaction catalyzed by the copolymers does not follow Arrhenius-type behavior: as temperature is increased over the aggregation temperature, the reaction rate increases faster than it could be predicted from the Arrhenius law. This was explained via the assumption that the substrate having an affinity to polymer/solvent interface can be adsorbed at the surfaces of polymer aggregates. This leads to higher concentration of substrate around the catalytically active groups. Theoretical consideration supports such a possibility.

Introduction

The problem of mimicking the enzymes with the synthetic polymers bearing corresponding groups (for example, imidazole, acidic, or others) has received considerable attention starting from the 1960s and continued in the late 1990s due to both increasing interest to very selective enzyme catalysis and attempts to overcome limitations of the enzymes such as requirements of narrow pH range and subtle temperature control. $^{1\mbox{-8}}$ Recently, a polymeric catalyst for ester hydrolysis allowing one to switch on and off the catalytic activity was designed on the basis of a polymer gel consisting of two types of monomers: N-isopropylacrylamide (major component) and 4(5)-vinylimidazole (minor component).⁹ In that paper the authors used the ability of poly(N-isopropylacrylamide) (PNIPA) to swell or shrink reversibly with the change of temperature or solvent and observed significant increase of catalytic activity in the collapsed gel, suggesting that hydrophobic PNIPA network increases affinity for amphiphilic substrate, thus enhancing the catalytic activity. However, macrosized gel catalysts may be plagued with transport limitations and excessive sensitivity of properties to the synthesis conditions. In addition, a very low fraction of catalytically active units (1.6% mol) may limit the overall catalytic activity.

In this paper we explore the idea of controlling the catalytic activity of imidazole-bearing linear copolymers poly(*N*-vinylcaprolactam-*co*-1-vinylimidazole) and poly-

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(*N*-isopropylacrylamide-*co*-1-vinylimidazole) (Figure 1) by switching its morphological state via a phase transition in otherwise homogeneous solutions. Namely, upon temperature increase these macromolecules exhibit a coil-to-globule transition with subsequent formation of globular aggregates of submicrometer sizes. Normally these changes occur above 30-32 °C for homopolymers of *N*-vinylcaprolactam and *N*-isopropylacrylamide.^{10–12} Introducing hydrophilic units into the polymer backbone, one may increase the transition temperature.

The aggregates of thermosensitive copolymers are very stable in aqueous solutions and have developed surface areas, thus providing conditions of microheterogeneous catalysis with negligible diffusion limitations and with high concentration of the catalytically active

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groups at the aggregate interfaces. Also, 1-vinylimidazole units are amphiphilic, so they tend to position themselves in the polymer/water interfacial layers.

Experimental Section

Materials. *N*-Vinylcaprolactam and *N*-isopropylacrylamide (Polysciences) were recrystallized from ethanol solution, 2,2'azoisobisbutyronitrile (AIBN, Merck) was recrystallized from methanol solution, *p*-nitrophenyl acetate (NPA, Fluka) was recrystallized from 2-propanol solution, 1-vinylimidazole (Vim, Aldrich) was distilled under reduced pressure, and 1-methylimidazole (Aldrich) was used as received.

Polymer Synthesis. We synthesized two types of random copolymers containing both catalytically active 1-vinylimidazole and thermosensitive *N*-vinylcaprolactam or *N*-isopropylacrylamide units using free radical polymerization in solution. Also, 1-vinylimidazole homopolymer was synthesized in the same way.

Initial monomer solutions in absolute ethanol containing AIBN as initiator were incubated in argon atmosphere at 50 °C for 48 h. Then the reaction solution was 5-fold diluted with ethanol and poured into diethyl ether. White precipitate was collected. It was dissolved in deionized water and dialyzed for 72 h. Water was exchanged every 24 h. After dialysis, polymer solutions were freeze-dried for 20 h.

Kinetic Measurements. All kinetic measurements were performed at Vim and NPA concentrations of 2 mM in water–2-propanol solutions (10 vol %). The solutions were buffered with 2 mM of phosphate buffer (KH_2PO_4/Na_2HPO_4) at pH 7.4. The progress of catalytic reaction was monitored by tracing the rate of optical density increase at 402 nm due to the release of *p*-nitrophenol in a deprotonated form.

Some measurements were performed in turbid solutions. Hence, the optical density values were dependent on both turbidity and *p*-nitrophenol absorption. In the standard procedure of kinetic measurements (e.g. ref 13) a small amount of concentrated substrate solution is injected to the polymer solution and then mixed by shaking, and finally the optical density is recorded as a function of time. This method did not show good results, since injection and mixing made the turbidity and overall optical density values unstable during the measurement. To address this issue, a special procedure was developed to obtain constant and reproducible optical density values of turbid solutions.

Equal volumes (1 mL) of substrate solution (4 mM) and polymer solution (4 mM of Vim units and 4 mM of phosphate buffer) were kept at constant (to within 0.2 $^{\circ}$ C) temperature until full equilibration. The solutions of substrate were kept in quartz cuvettes. Both catalyst and substrate solutions were equipped with a stirrer.

Then the catalyst solutions were promptly injected into quartz cuvettes containing substrate. No changes of solution temperature were detected to within 0.2 °C after that procedure. After the injection, the solutions in quartz cuvettes were stirred at constant temperature for time t_n and the optical density at 402 nm of the solution was detected. A Hewlett-Packard 8452A single-beam spectrophotometer was used for that purpose. A solution stirred for $t_0 = 25$ s was used as a baseline solution. The initial slope of optical density D vs ($t_n - t_0$), which can be well fitted with linear model, was used to calculate the hydrolysis rate.

Constant stirring and recording of the baseline in 25 s after injection eliminated the possible influence of mixing and injection on absorbance values of turbid solutions. The studies of nonturbid solutions followed the same procedure.

Laser Light Scattering (LLS) Experiments. The laser light scattering experiments were performed with an ALV-Instruments ALV/CGS-8F laser goniometer system and an ALV-5000 multi- τ digital correlator. The light source was a JDS Uniphase helium/neon 22 mW laser operating at $\lambda = 633$ nm. In the dynamic light scattering (DLS) experiments time– intensity correlation functions in the beating mode were measured at a scattering angle of 90° as a function of

Table 1. Characteristics of the Polymers

	$M_{ m w}$,		Vim fraction, %,	Vim fraction, %,
	g/mol	$T_{\text{transition}}, ^{\circ}\text{C}$	titration	¹ H NMR
PVim	46 000			
PNIPA-Vim-11 ^a	48 000	35		11
PNIPA-Vim-13 ^a	79 000	35		13
PVCL-Vim-20 ^a	32 000	40	19	20
PVCL-Vim-29 ^a	41 000	42	28	30

^a The polymers are marked according to the Vim content.

temperature. The correlation functions obtained were analyzed using the CONTIN program.

All samples for light scattering studies were made by dissolution of the freeze-dried polymers in a water-2-propanol mixture (10 vol %) at room temperature for 12 h. The solutions were buffered with 2 mM of phosphate buffer (KH_2PO_4/Na_2-HPO_4) at pH 7.4.

Polymer solutions for LLS measurements were clarified by filtration through Millipore GS 0.22 μ m pore size filters before use. For DLS measurements, the polymer concentration was 0.5 mg/mL.

Static light scattering (SLS) measurements were carried out for $M_{\rm w}$ determination of the polymers using the Debye plot method. The scattering angle was 90°, and polymer concentrations varied from 0.7 to 3.0 mg/mL. Refractive index increments were measured with an Otsuka Photal RM-102 differential refractometer operating at $\lambda = 628$ nm.

Polymer Characterization. Polymer characteristics are given in Table 1. Average molecular weights of the synthesized polymers were determined by SLS. The Vim unit fraction in the copolymers was determined by standard titration and by ¹H NMR. Potentiometric measurements for titration were carried out with a HANNA pH-300 pH-meter at 25 °C. The solutions of nonionized copolymers with a concentration of Vim units of 0.002 M were loaded with an excess of NaOH and 0.2 M NaCl. They were titrated with 0.03 M HCl. NaCl was used for the increase of p_{K_a} of Vim units and better resolution of the equivalence point. The HCl/Vim concentration ratio was taken to be high since dilution is not beneficial for good resolution of the equivalence point.

The ¹H NMR spectra were recorded with a Bruker Avance DRX 400 MHz spectrometer using deuterated methanol as a solvent. A polymer concentration was 1 wt %. The spectra were collected at 25 °C. Chemical shifts for the proton spectra were referenced to deuterated methanol at 3.31 ppm. The results of the titration corroborated the ¹H NMR determination (Table 1).

Reaction Rate Calculation. The calculation of reaction rate was performed using eq 1:

$$V = \frac{\mathrm{d}D}{\mathrm{d}t} \frac{1}{\epsilon} \frac{1}{F} \tag{1}$$

where dD/dt is the initial slope of optical density variation with time, ϵ is the extinction coefficient of *p*-nitrophenol (deprotonated form), $\epsilon = 18500$ L/(mol cm), and *F* is the fraction of *p*-nitrophenol (deprotonated form) at pH 7.4 (*F* = 0.6, as was found by spectrophotometry).

Results and Discussion

As was already mentioned, PVCL–Vim and PNIPA– Vim are thermosensitive copolymers with the LCST in the interval 35–45 °C. It is challenging to compare the catalytic activity of these polymers in aggregated and nonaggregated states in order to understand how the aggregation affects catalytic properties. One cannot compare those properties directly since the increase of temperature normally leads to the enhancement of catalytic activity, and the effects due to the increase of temperature and aggregation can overlap.



Figure 2. Reaction rate of hydrolysis of NPA catalyzed with polymeric catalysts as a function of inverse temeperature. Concentrations of Vim groups and NPA are equal to 2 mM in each case.

Table 2. Parameters of Regression of the $log(V) - T^{-1}$ Dependencies for the Catalysts Studied (Linear Model Is
Applied)

catalyst	R^{a}	error, %	N, degrees of freedom
1-methylimidazole	0.996	6	3
PVim	0.988	11	3
PNIPA-Vim-11	0.945	24	3
PNIPA-Vim-13	0.937	26	3
PVCL-Vim-20	0.951	23	3
PVCL-Vim-29	0.943	20	4

 ^{a}R is the correlation coefficient.

It is well-known that for the majority of temperature activated reactions the reaction rate is an exponential function of inverse temperature (Arrhenius-type behavior). When plotted in semilogarithmic (Arrhenius) coordinates, reaction rate gives a linear plot. If there are some effects that can influence the reaction rate along with the temperature, we should be able to observe a deviation from the linear law. Our main interest is to obtain a temperature-responsive catalyst, which would stimulate the reaction rate growth which is faster than exponential due to more effective catalysis by polymer aggregates than by separate polymer chains.

Figure 2 shows the change of the reaction rate with a temperature increase for the four copolymer catalysts, 1-methylimidazole and PVim, at identical concentrations of imidazole groups (2 mM) for each catalyst. The dependencies are presented in Arrhenius coordinates.

From Figure 2 one can see that for 1-methylimidazole and PVim the dependencies are quite linear, showing that these catalysts follow Arrhenius type behavior. PVim appears to be less effective catalyst than its lowmolecular-weight analogue 1-methylimidazole.

The copolymer catalysts show different behavior: the rate-temperature dependencies are not linear in Arrhenius coordinates. In the temperature range 35–45 °C the growth law is faster than the linear one. However, when temperature is further raised, one may observe an opposite effect—the reaction rate slows down. This type of behavior can be seen in Figure 2.

In Table 2 statistical analysis of the curves of Figure 2 is performed. For each curve, a linear model is assumed, and the correlation coefficient together with the relative error of slope is presented. Both for 1-meth-



Figure 3. Distributions of hydrodynamic diameter for copolymers in water solutions at various temperatures: (a) PNIPA-Vim-11; (b) PVCL-Vim-29.

ylimidazole and PVim the correlation coefficient is close to 0.99, whereas for copolymers it normally does not exceed 0.95. It can also be seen that the relative error of the slope obtained by least-squares fitting is larger than 20% for copolymers whereas for 1-methylimidazole and PVim it is much lower. These facts mean that the linear model fit is less probable for the copolymers than for 1-methylimidazole and PVim in the temperature interval 20–55 °C due to deviations observed at temperatures around 35-45 °C.

To associate the catalytic properties of the copolymers with the aggregation properties, we have performed a DLS study of copolymer particle sizes as a function of temperature. Figure 3 shows the distributions of hydrodynamic diameter for several copolymers at various temperatures.

At the temperatures below 35 °C the copolymers exist in the form of coils whose hydrodynamic diameter does not exceed 20 nm at the average. The aggregates with a larger hydrodynamic diameter are formed upon heating (see Figure 3). Aggregation of PNIPA–Vim-11 starts at 35 °C, whereas for PVCL–Vim-29 aggregates emerge at 42 °C, as seen from Figure 3. The aggregates are growing larger with the temperature increase. When just formed (for both PNIPA–Vim-11 and PVCL–Vim-29), their size is about 200 nm. After temperature is further raised, the size attains 400 nm in diameter.

The measurements of cloud point values for PNIPA– Vim-13 showed that for this copolymer the aggregation temperature is close to that of PNIPA–Vim-11, whereas for PVCL–Vim-20 it was found to be 40 °C.

The comparison of the data presented in Figures 1 and 3 shows that the temperature intervals of aggregation precede the temperature interval of rapid growth of the reaction rate in the region of 35–45 °C. Indeed, for PNIPA–Vim the reaction rate starts growing faster than exponentially above 35 °C, whereas the reaction catalyzed by PVCL–Vim undergoes additional acceleration at temperatures higher than 40 °C.



Figure 4. Interfacial layer of copolymer aggregates as a catalytic nanoreactor.

Thus, we can state that the observed acceleration of the reaction is closely connected with the aggregation and is due to the higher catalytic activity of the aggregates compared to that of the coils.

The catalytic activity of the copolymers, however, does not exceed that of 1-methylimidazole at equal concentrations of Vim groups. For PVCL–Vim copolymers, at certain temperature it can be as high as that of 1-methylimidazole, and in all cases it is much higher than for PVim.

The property of enhanced catalytic activity in the presence of copolymer aggregates reveals itself under the conditions where the coil-to-globule transition followed by aggregation takes place. Since we observe the formation of aggregates rather than separate globules (Figure 3), catalysis is thus promoted by a microheterogeneous phase consisting of polymer aggregates. In this context, it is appropriate to explain the phenomenon of enhanced catalytic activity in the following terms.

Because of the existence of many hydrophobic copolymer/solvent interfaces in the solution of aggregates, one should expect that NPA will adsorb at these interfaces (Figure 4). The interfacial concentration of the substrate can be high since NPA is a good surfactant. We have investigated the interfacial activity of NPA at hexane/ water boundary, which can model the copolymer/solution interface. When NPA molecules are partitioned between hexane and water (log P = 0.87 at 25 °C), the free energy of adsorption of these molecules from water to hexane/water boundary is 9.7kT (24 kJ/mol), indicating that NPA has a significant affinity to water/organic interfaces.

Also, amphiphilic Vim units of the copolymer should be at the interface because they tend to interact with molecules of water and minimize the interfacial energy of aggregates. Indeed, the Vim units are capable of positioning themselves at interfaces. Our investigation of the interfacial activity of Vim monomer shows that if partitioned between hexane and water, it can be adsorbed at the hexane/water boundary with the free energy of adsorption equal to 5.8kT (14 kJ/mol). Furthermore, Vim has a larger affinity to water than to hexane (log P = -1.26 at 25 °C), and this can be an additional factor for Vim units to tend to leave partially the hydrophobic surrounding of the aggregates.

Thus, the interface appears as an area where the concentration of active species (both catalyst and substrate) is larger than in the bulk of the solution. At the interface the reaction progresses faster due to increase



Figure 5. Michaelis–Menten-type kinetics for decomposition of NPA by PNIPA–Vim-11 at 45 °C.

of both Vim and NPA local concentrations, thus leading to the effective growth of the catalytic activity of the copolymer. In this sense, the interfacial nanolayer of aggregates can be considered as a catalytic nanoreactor.

In enzymatic catalysis, the catalytic act is preceded by the complex formation between catalyst and substrate. Because of the complex formation, enzymatic reactions follow Michaelis–Menten-type kinetics:¹⁴

$$V = \frac{V_0[\mathbf{S}]}{K_{\rm m} + [\mathbf{S}]} \tag{2}$$

where $V_0 = k_{cat}[E_0]$, k_{cat} is the first-order rate constant for breakdown of the substrate–catalyst complex, $[E_0]$ is the concentration of catalyst, and [S] is the concentration of substrate.

One may expect that if the reaction rate vs substrate concentration measurements yields Michaelis-Mententype kinetics in our case, it can be a good indication that indeed NPA (substrate) adsorbs to the interfaces of aggregates, forming a kind of "complex" with surfaceactive catalytic groups. Such measurements were performed for PNIPA-Vim-11 at 45 °C (Figure 5). For that copolymer a kinetic curve was obtained which could be well fitted with eq 2, giving the parameters $V_0 = 8.6 \times$ 10^{-7} mol/(L s) and $K_{\rm m} = 0.0105$ M. The concentration of the catalyst was taken 10 times lower than in the temperature experiments (0.2 mM) to get an excess of substrate over catalyst, which is the condition for observing Michaelis-Menten kinetics. As one may see, the catalysis by PNIPA-Vim-11 indeed follows the kinetics of Michaelis–Menten type, although the $K_{\rm m}$ parameter is rather large when compared, for example, to that of α -chymotrypsin (for the same substrate, $K_{\rm m}$ $= 1.6 \times 10^{-4}$ M).¹⁵

Vasilevskaya et al.¹⁶ explored the theoretical possibility of acceleration of the reaction if both catalyst and substrate can adsorb at the oil/water interfaces in miniemulsions. It was shown that at certain optimum size of miniemulsion droplets (normally around several hundred nanometers) a significant acceleration of the reaction can take place compared to the case where the size of droplets is too small or too large as well as to the case of complete phase separation. Furthermore, it was shown that for the optimum size droplets a Michaelis-Menten profile of the reaction rate vs substrate concentration is typical when the surface of miniemulsion droplets is saturated with substrate species. Therefore, an increase of the reaction rate due to concentrating of the substrate at the interface of aggregates and the fact that the reaction at the interface of aggregates obeys Michaelis-Menten-type kinetics are theoretically justified.

There can be some additional factors that enhance catalytic activity at the surfaces of globules or aggregates. First, both catalyst and substrate are specifically oriented due to polymer concentration gradient in the interfacial layer. This factor can stimulate mutual orientation of the interacting species which in some cases can be beneficial for an elementary act of the catalytic reaction. Second, the substrate species are subjected to an additional high stress due to the polymer concentration gradient. The second factor obviously can decrease the activation energy of the reaction since the stress increases the ground state energy of the substrate, resulting in energy-rich species which can be more readily converted into the product.

Conclusion

Temperature-sensitive poly(N-vinylcaprolactam-co-1vinylimidazole) and poly(N-isopropylacrylamide-co-1vinylimidazole) are catalytically active in the reaction of hydrolysis of *p*-nitrophenyl acetate.

The reaction rate does not follow Arrhenius-type behavior upon temperature increase: in the temperature interval of 35-45 °C the growth is faster than exponential, while further increase of the temperature decreases the reaction rate. This type of behavior is observed when copolymers form aggregates in aqueous solution. The temperature of aggregation precedes the temperature of rapid growth of reaction rate. This phenomenon is associated with the adsorption of surfaceactive substrate at the interface of aggregates as well as with the enhancement of concentration of catalytically active imidazole groups in the surface areas.

In that context, this behavior has some common features with the catalytic action of enzymes. The active adsorption of the substrate at the surface of the catalyst

is similar to a stage of enzymatic catalysis. Indeed, before a catalytic act takes place substrate is usually sorbed by the active center of the enzyme. In some enzymes, like acetylcholinesterase, pepsin, and α -chymotrypsin, the substrate binding site contains hydrophobic structures which can effectively interact with hydrophobic moieties of the substrate, contributing to the formation of a relatively stable complex. However, in our system, that complex is somewhat less stable than those formed by enzymes, judging by Michaelis-Menten analysis of the kinetics of catalysis. Also, catalytic activity in our case is much lower than for enzymes: the catalytic activity of our most active polymer catalyst (PVCL-Vim-20) toward NPA hydrolysis at 43 °C is over 200 times lower than that of α -chymotrypsin at 25 °C. The latter was estimated from the data of ref 15. Indeed, other factors inherent to enzymes (e.g., geometric correspondence between active site of an enzyme and substrate) which increase the stability of the complex and catalytic activity of enzyme are not involved in the substrate-catalyst interactions in our system.

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