Notes

Sequence Distribution and Solvolytic Activity of Copolymers Containing Imidazole Groups

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It has been shown that poly[4(5)-vinylimidazole] is an effective catalyst for the hydrolyses of *p*-nitrophenyl esters as compared to monomeric imidazole.[1] The enhanced catalytic activity of the polymer was attributed to bifunctional interactions between catalytically active imidazole groups along the polymer chain.[2-4] However, the steric relationship between the functional groups which interact cooperatively is not clear. Overberger and Shen have suggested that bifunctional interactions occur primarily between neighboring imidazole units rather than between remote groups brought together via contortion of the polymer coil.[5]

We investigated the catalytic activities of poly[4(5)-vinylimidazole-*co*-acrylamide] (PIm) and poly(*N*-acrylylhistamine-*co*-acrylamide) (PHis) for the solvolysis of 1-acetylbenzotriazole to elucidate the spatial relationship between cooperatively interacting imidazole groups in these copolymers. From plots of catalytic rate constant vs. neutral imidazole fraction (α) for monomeric imidazole-catalyzed solvolysis of this substrate, the catalytic activity of protonated imidazole as a general acid[6] was found to be much smaller than that of neutral species, ca. 1/20. Therefore, the catalysis is attributed mostly to neutral species at intermediate pH. At higher pH values, above α = 0.98, a trace amount of anionic species participates in the catalysis,[7] where the reaction mechanism is complicated in the case of polymeric imidazole.[1]

On the basis of these results, the catalytic activities of PIm and PHis were investigated. The solvolysis was followed spectrophotometrically. In Figure 1, the second-order catalytic rate constants calculated from pseudo-first-order kinetics are plotted as a function of copolymer composition, where k_0 is the rate constant for spontaneous solvolysis and $k_{\text{cat}} = (k_{\text{obsd}} - k_0)/[\text{imidazole group}]$. If multifunctional catalysis is not operative the plots should be flat. In the case that a bifunctional interaction between remote neutral groups on the polymer chain is predominant, the catalytic rate constant will increase linearly with increasing imidazole content, because the probability of such an intramolecular interaction is considered to be approximately proportional to the number of imidazole units in one polymer chain. During reactions catalyzed by PHis this seems to be the case. This is reasonable since the relatively long side chain connecting the imidazole group to the polymer would make it possible for this to occur. On the other hand, the rate constant–copolymer composition profile for PIm was different from that for PHis. Since the pendant imidazole of PIm is attached directly to the polymer backbone, concerted interactions between remote imidazole groups are less effective.[5] Accordingly, bifunctional catalysis by a combination of neighboring imidazole groups seems more likely for this polymer. Hence, the sequence distributions of these copolymers were calculated from copolymerization data, r_1 and r_2, according to the method of Harwood and Ritchey[8] (Figure 2), and compared with the catalytic activities.

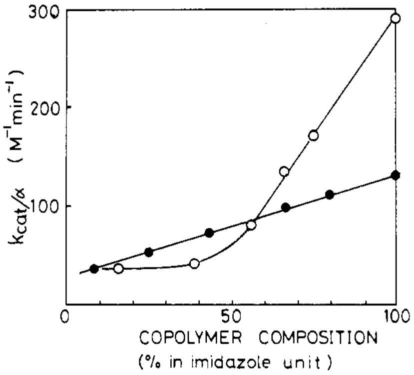

Figure 1. Effect of copolymer composition on k_{cat}: solvent 20% EtOH–water, ionic strength μ = 0.02(Tris-HCl + KCl), [substrate] = 4 × 10^{-4} M, at 20 °C. (○) PIm, pH 8.20, α = 0.95–0.97, [imidazole group] = 3 × 10^{-4} M; (●) PHis, pH 8.19, α = 0.95–0.97, [imidazole group] = 1.5 × 10^{-4} M.

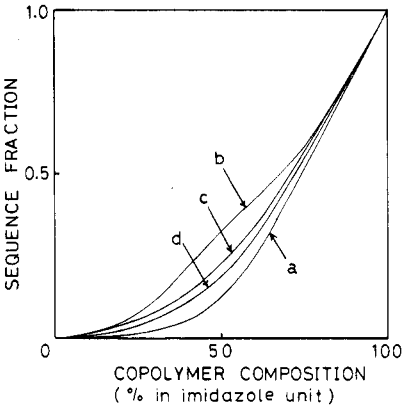

Figure 2. Sequence distribution calculated from r_1 = 0.13, r_2 = 0.76 for PIm and r_1 = 0.36, r_2 = 1.15 for PHis, where suffix 1 represents the imidazole-containing monomer; the copolymerizations were carried out in benzene for PIm and in ethanol for PHis with AIBN at 70 °C. (a) PIm, doublet (Im-Im); (b) PIm, triplet (Im-M-Im); (c) PIm, quartet (Im-M-M-Im); (d) PHis, doublet (His-His) [Im = 4(5)-vinylimidazole, M = Im or acrylamide, His = *N*-acrylylhistamine].

Although a small number of protonated imidazole groups are present under the solvolytic conditions employed (α = 0.95–0.97), the calculated values are approximately applicable. The curves for Im-Im and Im-M-M-Im sequences in PIm appear similar to the rate constant plot for this polymer in Figure 1. It is not entirely clear that catalytic rate constant vs. copolymer composition and sequence fraction vs. copolymer composition plots correspond; however, these results seem to indicate that the short-range imidazole–imidazole interactions are effective in the reactions catalyzed by PIm, while cooperative interactions between remote groups along the polymer chain predominate in the case of PHis. The higher catalytic activity of PIm at high imidazole contents could be reasonably explained by this mechanism. In a qualitative manner the enhanced catalytic rates might be attributed to both 1–2 and 1–4 cooperativities in the two sequences described above, and it is still obscure which is effective.

The close proximity of vicinal functions in PHis should be rather difficult because of the long side chain.[9] The linearity in the plot of PHis also indicates that terfunc-

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tional catalysis is unlikely, because if it takes place the plot should be parabolic, as shown in the following equation:

$$k_{\text{cat}}/\alpha = k_1 + k_2\alpha[\text{His}] + k_3\alpha^2[\text{His}]^2$$

where [His] is the local concentration of histamine residues in PHis (which corresponds to the copolymer composition), k_1 is the rate constant for the catalysis by isolated imidazole functions, k_2 is the rate constant for bifunctional catalysis, and k_3 is the rate constant for terfunctional catalysis. The last term must be negligibly small in the reactions studied by us.

Very similar results were obtained for the solvolysis of 2,4-dinitrophenyl acetate catalyzed by PIm and PHis.[7]

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References and Notes

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Ratios of Weight and Number Average Molecular Weights to be Expected in Ionic Polymerization with Chain Termination but No Chain Transfer

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Recent work in Kennedy's Laboratory[1] indicated that in cationic polymerization carried out under conditions where chain transfer is absent, the ratio of the weight average and number average degree of polymerization, $\bar{P}_w/\bar{P}_n$, is substantially lower than 2, as would correspond to a most probable chain length distribution. This ratio was also found to decrease when the reaction was discontinued at low conversion. It is shown below that two factors are expected to lead to this result: (1) $\bar{P}_w/\bar{P}_n < 2$ if the polymerization is discontinued at a time when part of the chains are still actively growing. (2) $\bar{P}_w/\bar{P}_n < 2$, even if the polymerization process is allowed to run its course, since the relative probability of chain termination and chain propagation as the monomer concentration is gradually reduced.

In the following we make the following assumptions: (a) The propagation of all chains is initiated simultaneously. (b) The Poisson distribution of the lengths of chains which were still actively growing at the time at which the polymerization was discontinued can be approximated by a single degree of polymerization P.

For polymerizations in which the ratio of the termination and propagation rate is independent of the length of the chain, the distribution function of the number of chains with a degree of polymerization P is given by[2]

$$N(P) = \epsilon \exp(-\epsilon P) \tag{1}$$

Table I

$\epsilon P_{\max}$	$\exp(-\epsilon P_{\max})$	$\bar{P}_w/\bar{P}_n$
0.1	0.905	1.033
0.2	0.819	1.067
0.5	0.606	1.165
1.0	0.368	1.322
1.5	0.223	1.465
2.0	0.135	1.589
2.5	0.082	1.692
3.0	0.050	1.774

where ϵ is the fractional probability that the chain will terminate rather than add a monomer unit. In our case $\epsilon = k_t/k_pM$ and we shall first assume that ϵ can be treated as constant, i.e., that the change in monomer concentration, M, can be neglected. If the growing chains have attained a degree of polymerization $P_{\max}$ at the time the reaction was discontinued, the fraction of "living" chains was $\exp(-\epsilon P_{\max})$. The number and weight average degrees of polymerization will then be

$$\bar{P}_n = \frac{\int_0^{P_{\max}} P\epsilon \exp(-\epsilon P)\,\mathrm{d}P + P_{\max}\exp(-\epsilon P_{\max})}{\int_0^{P_{\max}} \epsilon \exp(-\epsilon P)\,\mathrm{d}P + \exp(-\epsilon P_{\max})} = \frac{1}{\epsilon}[1 - \exp(-\epsilon P_{\max})] \tag{2}$$

$$\bar{P}_w = \frac{\int_0^{P_{\max}} P^2\epsilon \exp(-\epsilon P)\,\mathrm{d}P + (P_{\max})^2\exp(-\epsilon P_{\max})}{\int_0^{P_{\max}} P\epsilon \exp(-\epsilon P)\,\mathrm{d}P + (P_{\max})\exp(-\epsilon P_{\max})} = \frac{2[1 - (1 + P_{\max})\exp(-\epsilon P_{\max})]}{\epsilon[1 - \exp(-\epsilon P_{\max})]} \tag{3}$$

$$\frac{\bar{P}_w}{\bar{P}_n} = \frac{2[1 - (1 + \epsilon P_{\max})\exp(-\epsilon P_{\max})]}{[1 - \exp(-\epsilon P_{\max})]^2} \tag{4}$$

Note that $(\bar{P}_n)_\infty$, the number average molecular weight as $P_{\max} \rightarrow \infty$, i.e., when the polymerization is allowed to run its course, is equal to $1/\epsilon$, so that $\epsilon P_{\max}$ may be obtained from

$$\epsilon P_{\max} = \ln\{(\bar{P}_n)_\infty/[(\bar{P}_n)_\infty \bar{P}_n]\} \tag{5}$$

Also, since $P_{\max} = k_p(M)t$ (as long as (M) may be treated as constant), we have $\epsilon P_{\max} = k_t t$ where t is the polymerization time.

Table I shows how the fraction of living chains and $\bar{P}_w/\bar{P}_n$ depend on $\epsilon P_{\max}$.

It may be seen that even if only a rather small fraction of the chains is still growing at the time the polymerization is discontinued, the $\bar{P}_w/\bar{P}_n$ ratio falls substantially under the value of 2, corresponding to the most probable chain length distribution.

The variation in the monomer concentration during the polymerization can be taken into account in the following way: If the concentrations of actively growing chains and of the monomer were C_0 and M_0, respectively, at $t = 0$, then they will be at any time t

$$C = C_0 \exp(-k_t t) \tag{6}$$

$$M = M_0 \exp\left[-\int k_p C_0 \exp(-k_t t)\,\mathrm{d}t\right] \tag{7}$$

It is convenient to introduce the dimensionless parameters $X = k_pC_0/k_t$, $\tau = k_t t$, so that

$$M = M_0 \exp\left[-\int_0^{\tau} X \exp(-\tau')\,\mathrm{d}\tau'\right] = M_0 \exp[-X(1 - e^{-\tau})] = M_0 f(\tau) \tag{8}$$

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