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Nature of the "Hypercoiled" Form of Poly(methacrylic acid) in Water at Low pH

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It has long been known that poly(methacrylic acid) (PMA) responds in a strikingly different manner to increasing ionization than poly(acrylic acid) (PAA).[1] Whereas the chain molecules of PAA expand smoothly with an increasing charge of the polymer, the PMA chains resist expansion before a critical charge density is attained. Leyte and Mandel[2] showed that the dependence of the apparent ionization constant on the degree of polymer ionization indicates a cooperative transition between two chain conformations, and in their calorimetric study, Crescenzi et al.[3] have measured the endothermicity characterizing this transition.[22] Its nature has also been studied by Raman spectroscopy, which shows that the number of available conformations becomes more restricted in the contracted form.[4,5] However, it should be emphasized that molecules of the contracted form of PMA are far from being compact spheres from which the solvent is largely or entirely excluded, as in polysoaps.[6] In both 0.001 N aqueous HCl at 30 °C[7] and methanol at 26 °C[8] the intrinsic viscosity of PMA is proportional to the square root of the molecular weight, so that the chains behave as random coils in a Θ medium. The rms chain-end displacements are only 54% greater in methanol solution, so that the term "hypercoiling" seems to exaggerate the description of the state of PMA in water at low pH. It may also be noted that the existence of different Θ states of PMA is not unique. Flory's assumption[9] that the local conformational distribution in long-chain molecules is independent of the solvent medium does not seem to apply to chains with strong dipoles, where polar and nonpolar Θ solvents produce different chain extensions.[10]

In 1954 Oster discovered[11] that the dye Auramine O (AO), which fluoresces very weakly in aqueous solution, has its emission intensity greatly increased in the presence of PMA at low pH. He suspected that the phenomenon was due to a local rigidity of the medium which would prevent the quenching of the excited molecule by internal rotation and he showed that the fluorescence of AO increased, in fact, with the viscosity of solutions.[12] The rigidity of the microenvironment may, however, not be the only (or even the major) cause of the strong fluorescence of AO associated with the contracted PMA, since many dyes fluoresce strongly in organic media but have their fluorescence quenched by contact with water.[13]

Anufrieva et al.[14] showed that the fluorescence of AO can be used as an indicator of the transition of PMA from the contracted to the expanded state and interpreted the sharp decrease of AO fluorescence when methanol was added to the aqueous PMA solution as indicating that the contracted state depends on hydrophobic bonding between the methyl substituents of PMA. Changes in fluorescence intensity have also been used to study the kinetics of the conformational transition of PMA, using either noncovalently bonded pyrene[15] or dansyl labels attached to the polymer.[16]

Extensive fluorescence studies of labeled PMA in aqueous solution at low pH have led to more detailed interpretation of the molecular conformation. Tan and Treloar[17] studied PMA with 9-methylanthracene associated noncovalently to the polymer and concluded, on the basis of a biphasic decay of the fluorescence anisotropy, that "9-methylanthracene can exist either within large clusters of the chain that exist in the native structure of the chain and also within small structures that arise in response to the presence of the hydrocarbon". They estimated the size of the "clusters" assuming that the chain in these clusters has the extension characteristics of PMA in a Θ-solvent. Ghiggino and Tan,[18] who studied PMA with 9,10-dimethylanthracene incorporated into the chain backbone, concluded similarly that "the unionized form of PMA exists as several tightly packed clusters" connected by flexible chain segments. Here, the expression "tightly packed" is inconsistent with their estimated cluster size on the basis of the chain conformation in a Θ medium. More recently, Bednář et al.[19] studied the fluorescence lifetime and the decay of the fluorescence anisotropy of PMA carrying dansyl groups. The striking increase in the fluorescence lifetime and the rotational correlation time at low pH was interpreted by assuming that most of "the dansyl labels are firmly entrapped in a cluster of highly hydrophobic character" of low fluidity. This implies much tighter clusters than those postulated by Tan and Treloar or by Ghiggino and Tan. Bednář et al. conclude also that "at low pH the PMA chain forms highly compact clusters which are joined by short extended parts of the polymer chain". Similar conclusions were reached by Soutar and Swanson,[20] who employed copolymers of methacrylic acid containing small proportions of 1-vinylnaphthalene or acenaphthylene residues. Both Bednář et al. and Soutar and Swanson found that the mobility of the label is smallest near pH 4, increasing somewhat in more acidic media. This indicates that hydrogen bonding between ionized and un-ionized carboxyls contributes to the rigidity of the microenvironment of the fluorescent probe.

Is it legitimate to use results obtained with labeled PMA to reach conclusions on the state of the unlabeled polymer? Soutar and Swanson pointed out that this may not be warranted.[20] Some years ago, we studied the kinetics of fluorescence enhancement when a low-pH aqueous solution of PMA is mixed with a solution of AO in a stopped-flow apparatus.[21] We found that after a diffusion-controlled association of the dye with the polymer (too fast to be recorded by the stopped-flow technique) *the dye triggers a relatively slow conformational transition of the PMA* (fitted at pH 4.04 and 21 °C by biphasic kinetics with rate constants of about 4 and 0.1 s^{-1}, the fast rate accounting for two-thirds of the change) *which is responsible for the enhanced fluorescence intensity*. This result shows that models of chain conformation based on the fluorescence studies of labeled PMA, while convincing for the *labeled* polymer, cannot be used to infer the state of the *unlabeled* PMA.

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