

The Effect of Hydrogen Bonding Addends on the Dilute Solution Viscosity of Poly(methacrylamide)

We have recently reported on a study of the effect of hydrogen bonding agents, such as urea and lithium chloride, on the shape of the synthetic polymers in aqueous solutions.¹ The polymers were poly(acrylic acid) (PAA), poly(acrylamide) (PAAm), and poly(methacrylic acid) (PMA). This investigation has now been extended to poly(methacrylamide) (PMAm).

Nine grams of methacrylamide, supplied by Eastman Organic Chemicals and purified by recrystallization from toluene, were polymerized in 0.85% hydrogen peroxide solution at 50°C. for 24 hr. The resulting polymer was dialyzed and freeze-dried. The conversion was 30%. Its degree of polymerization of 920 was determined by light-scattering measurements carried out in a Bryce-Phoenix Light Scattering Photometer. The light-scattering slope parameter B was found to be $-2.1 \times 10^{-4} \text{g. (cc./g.)}^2$, and no dissymmetry in the scattering could be detected.

The intrinsic viscosity of the polymer was determined in water, 5M lithium chloride, 3–5M sodium chloride, 2M potassium thiocyanate, and 6.7M urea. The addends were Fisher Certified Reagents. The viscometers used were of the Ubbelohde dilution type, having a time flow of about 300 sec. for water at 30°C., at which temperature all the measurements were carried out. The results are given in Figure 1.

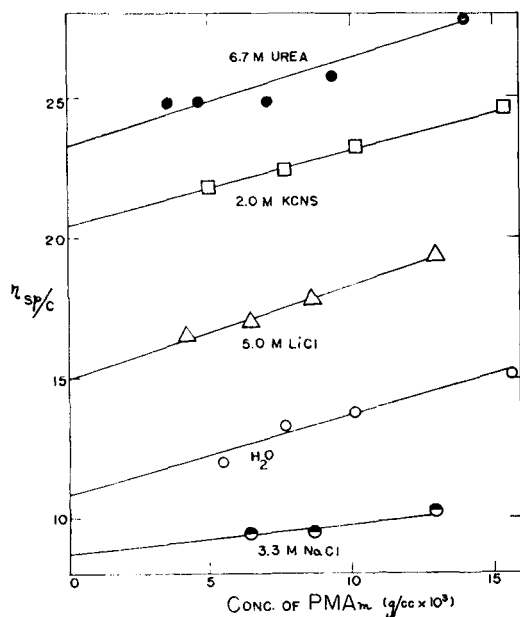


Figure 1.

In addition to the viscometric study it was observed that while the polymer is precipitated from its aqueous solutions on cooling to 0°C., its solutions in lithium chloride, potassium thiocyanate, and urea remain transparent at this tempera-

ture. On the other hand, the polymer was found to be insoluble in 5M sodium chloride at room temperature. It was also observed that the polymer is precipitated by addition of ethanol, methanol, and acetone.

Evaluating the viscometric data, the same assumptions are made as in the case of PAA, PAAm, and PMA. It is again assumed that changes in intrinsic viscosity reflect mainly an increase or decrease of intramolecular hydrogen bonding. Light-scattering and viscometric data indicate that PMAm is sparingly soluble in water at 30° and internally bonded to an appreciable degree.² The absence of any detectable dissymmetry in light scattering is a further indication of internal bonding. Now lithium chloride, potassium thiocyanate, and urea are well known hydrogen bond breakers, e.g., they prevent gelling of gelatin solutions.³ The increase of the intrinsic viscosity of PMAm caused by their addition can be interpreted as a replacement of intramolecular bonds by polymer-addend bonds and subsequent opening up of the polymer coil. Sodium chloride, which is not a hydrogen bond breaker, has a "salting out" action which causes a further coiling up of the molecule and eventual precipitation.

While PMAm is sparingly soluble in water and internally bonded to an appreciable degree, PAAm is very soluble in water, so that the amide groups are hydrated and intramolecular bonds are few or completely absent. This was concluded from light-scattering measurements reported previously² to which it may be added that while no dissymmetry could be detected in the light scattering in the PMAm polymer investigated here, a PAAm polymer of degree of polymerization 850 has a dissymmetry of 1.07.⁴ So even if on the addition of lithium chloride, potassium thiocyanate, and urea the addend molecules bind to the PAAm molecule, they probably do not cause the breaking of intramolecular bonds, but only displace water molecules. The change in molecule shape involved is apparently too small to be detected by viscosity measurements. The difference of solubility also explains the fact that PMAm is salted out by sodium chloride and PAAm is not. The action of ethanol on both polymers is the same.

Whereas the difference in behavior of the amides could be reasonably explained, there is no ready explanation for the difference in reaction of the polyacids. The most puzzling case is probably the addition of urea, which opens up the coil of both PMAm and PAA, but has the opposite effect on PMA, although this polymer is chemically close to the others.

References

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