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The "Template-Effect" of Water in Acrylonitrile Polymerization

G. Henrici Olivé and S. Henrici Olivé

Monsanto Triangle Park Development Center, Inc.,
Research Triangle Park, N.C. 27709, USA

Acrylonitrile (AN) is a particular case among vinyl monomers regarding the solvent dependence of the propagation rate constant (k_p) in homogeneous free radical polymerization. Whereas in dimethylformamide and dimethylsulfoxide k_p has values which one might expect from a comparison with other monomers and from the reactivity of the growing radical (400 and 1910 $l\ mol^{-1}s^{-1}$ respectively, at 25°C [1]), in water k_p is considerably higher (2.8×10^4 $l\ mol^{-1}s^{-1}$[1]), and almost approaching values reported for ionic polymerization [2]. Summarizing work concerning this phenomenon up to 1963, Dainton [3] indicated that the rate constants in water and in organic solvents could not be reconciled.

In 1973 Perec [4], in a study of the copolymerization of AN with acrylamide in water and other hydrogen bonding solvents, suggested associates of acrylamide (but not of AN) with itself and with the solvent as the cause of observed anomalies. However, it is well known that organic nitriles do also associate to dimers [5], which are decomposed by water, with the formation of heterodimers and -trimers, depending on the relative concentrations [6]:

$$R\text{-}C{\equiv}N \cdots H\text{-}O\text{-}H; \quad R\text{-}C{\equiv}N\cdots H\text{-}O\text{-}H\cdots N{\equiv}C\text{-}R$$

The interaction of water with the nitrile group leads to an increase of the stretching frequency of the C≡N bond ($\Delta\nu_{C\equiv N} = 7\ cm^{-1}$ [7]), indicating a moderate stabilization of this bond. The hypsochromic shift of the C≡N stretching frequency is diagnostic for interaction of the nitrogen lone pair electrons

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with the proton. (Interaction of the C≡N bonding π-orbitals with an electron acceptor would lead to a bathochromic shift [8].)

Organic nitriles interact in the same way with other Brønsted acids (e.g., phenol, where a hypsochromic shift of 9 cm^{-1} was found in the case of AN [9]), as well as with Lewis acids ($AlCl_3$, BF_3, $ZnCl_2$, $SnCl_4$; $\Delta\nu_{C\equiv N}$ = 30-90 cm^{-1}; similar shifts for AN and acetonitrile [10,11]).

The polymerization rate of AN in alcohols as solvent is comparable to that in dimethylformamide [12]; the rate in the presence of Lewis acids, however, has been reported to be higher than that of AN alone [11], although by far not attaining the extremely high rate observed in water. Taking into consideration the above-mentioned values of $\Delta\nu_{C\equiv N}$ as a measure of the degree of interaction of the C≡N group with the electron acceptor, it has to be concluded that the mere fact of this type of interaction alone can certainly not account for the water effect in AN polymerization.

We suggest that the important peculiarity of the water molecule resides in its ability to form simultaneously two hydrogen bonds, e.g., one with the ultimate C≡N group of a growing polymer radical, and one with a monomer. This arrangement not only would increase the effective local concentration of monomer in the neighborhood of the radical (cf. the "template effect" in coordination catalysis [13]), but also might activate the radical as well as the monomer by decreased delocalization of the free electron of the radical [14] and of the electrons of the vinyl double bond, on stabilization of the C≡N bond.

We have to consider the structure of water in order to estimate whether the vinyl double bond of an AN molecule, hydrogen-bonded to a water molecule via its nitrogen lone pair orbital, may come into reaction distance (say 300 pm = 3 Å) to the radical site of a growing chain coordinated to the same species.

According to present knowledge, water is made up of a continuous distribution of associates, whereby the ratio of particles with association number $K \leqslant 4$ to larger particles is 70/30 [15]. The lowest energy configurations of these associates have been reported by Stillinger [16]. For an estimate of the geometry of the possible reaction complexes we used literature data of bond lengths and bond angles, as summarized in Table 1.

Figure 1 shows polymer radical and monomer coordinated to a single water molecule. A simple, straightforward trigonometric evaluation, using the data of Table 1, indicates that both hydrogen bonds would have to be bent about 40° out of their lowest energy (linear) position, in order to bring the reacting ends into the required distance. This movement is relatively costly in terms of stabilization energy [16], and might therefore be prohibitive.

In the water dimer (Fig. 2), the situation appears to be somewhat more favorable. One of the hydrogens of molecule $H^1O^1H^2$ forms a hydrogen bond to the second molecule $H^3O^2H^4$. The plane of the latter molecule is perpendicular to that of the first, with an orientation angle δ. In the most stable configuration $\delta = 35°$, and molecule $H^1O^1H^2$ is in a position obtained from that shown in Fig. 2 by turning it by 180° about the O^1-O^2 axis (repulsion between hydrogens minimized). However, this rotation is relatively easy, and also an increase of the orientation angle is not very costly [16]. As shown in Fig. 2, an increase of this angle by 60° would be required; this value would, of course, be less, if also some bending of the hydrogen bonds $N^1H^1O^1$ and $N^2H^3O^2$ could be assumed.

An even more favorable situation is found with the water trimer (Fig. 3). The required increase of the orientation angle δ by only 23° should permit easy reaction of the radical (C^2) with the double bond (C^4-C^5).

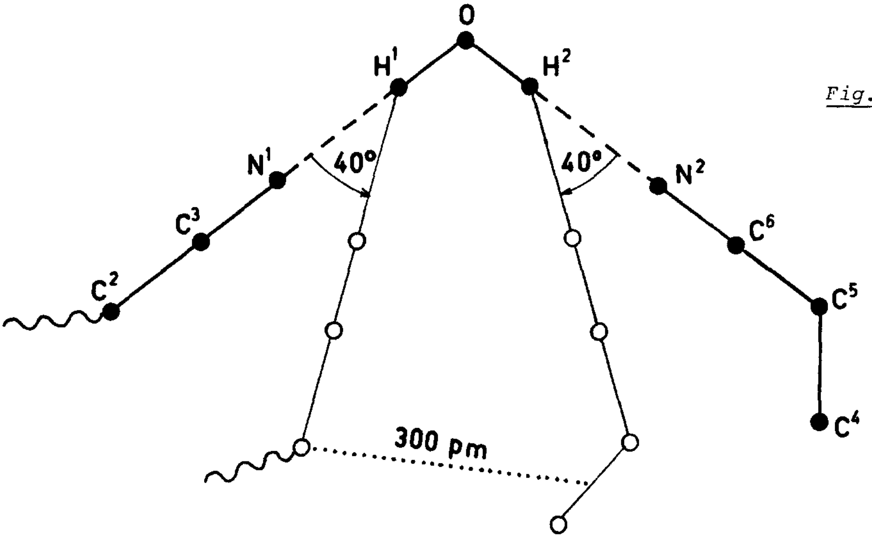

Fig. 1

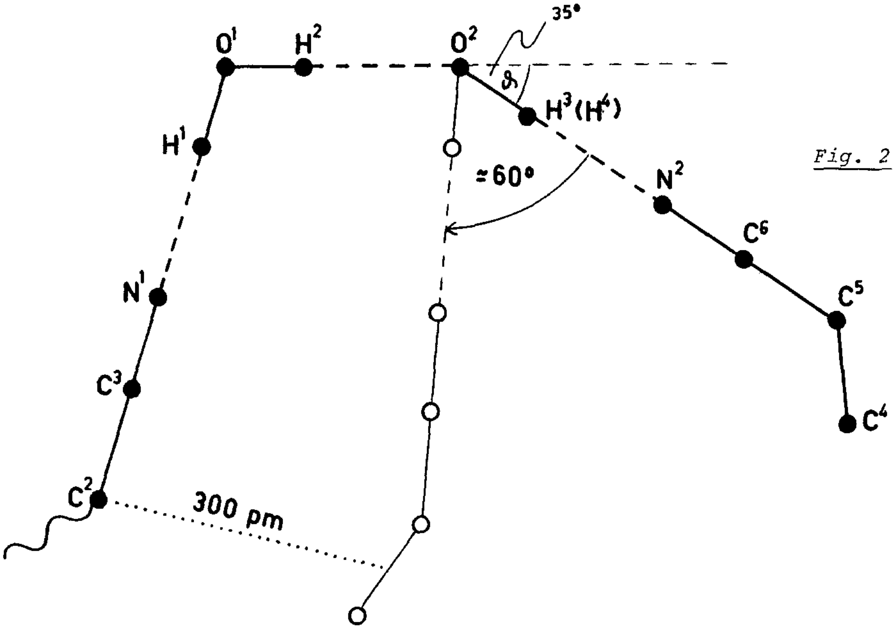

Fig. 2

Fig. 1. Growing chain and monomer coordinated to a single water molecule

Fig. 2. Growing chain and monomer coordinated to a water dimer.

Actually, the trimer structure represented in Fig. 3 is only one of the three most stable configurations as indicated by Stillinger [16], but the other two give the same result. A similar arrangement of three vicinal water molecules can be assumed to be present also in higher aggregates of water. Thus it can be concluded that water may well act as a "template", bringing together - and at the same time activate - the growing polymer radical and the monomeric acrylonitrile. This behavior of the water might also be one important aspect of its crucial role in biochemistry.

Fig. 3

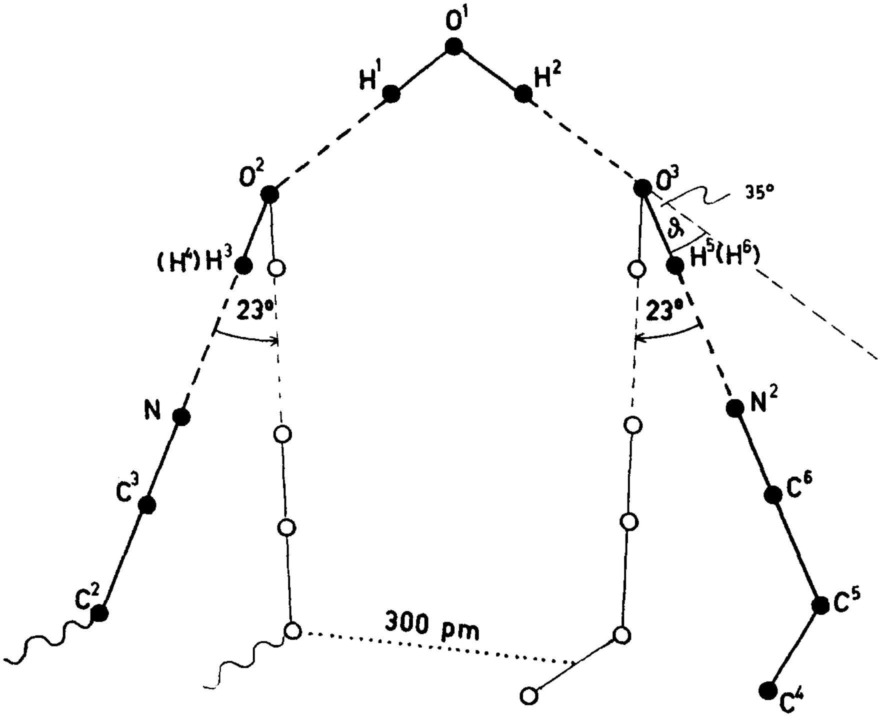

Fig. 3. Growing chain and monomer coordinated to a water trimer.

Table 1. Bond lengths and bond angles in acrylonitrile, water and hydrogen bonds.

Bond	Bond length (pm)	Bond angle	Degrees	Reference
$P_n\text{-}C^1H_2\text{-}HC^{2*}\text{-}C^3N^1 + C^4H_2{=}C^5H\text{-}C^6N^2 \longrightarrow P^*_{n+2}$				
$C^2\text{-}C^3$	143	$C^4\text{-}C^5\text{-}C^6$	122.4°	[17]
$C^5\text{-}C^6$	143	$C^2\text{-}C^3\text{-}N^1$	180°	
$C^4\text{-}C^5$	134	$C^5\text{-}C^6\text{-}N^2$	180°	
C - N	116			
H - O - H				
H-O	95.7	H-O-H	104.5°	[16]
O···H - O				
O···H	204	O···H-O	180°	[16]
N···H - O				
N···H	212	N···H-O	180°	[18]

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