# Liquid Ionization Mass Spectrometry for Studies on Reactions between Formaldehyde Oligomers in Aqueous Solution and Alcohols

Jun Saito, Takeo Kaneko, Peiming Yang, Yoshio Niwa,† and Masahiko Tsuchiya*
*Faculty of Engineering, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240*
*†National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba 305*

(Received January 8, 1996)

Reactions between poly(oxymethylene)glycol (POMG) in aqueous solution and methanol or ethanol were studied by liquid ionization mass spectrometry. Hemiformalization of POMG occurred soon after methanol addition to form monomethylethers of POMG and completed within 15 min. While hemiformalization by ethanol addition occurred slowly and it took time, about 30 min, before producing monoethylethers of POMG.

---

Since a small amount of methanol (0.5-15%) is added to formalin in order to suppress too much polymerization of formaldehyde, the formalin contains not only POMGs but also methylethers of POMG. Its composition varies depending on its temperature, pH and so on. Gas chromatography of TMS derivatives[1] and NMR[2] have been used to analyse POMGs in formalin, but these methods are not good enough for analysis of reaction products in an aqueous solution. Since Liquid ionization (LI) mass spectrometry[3-5] is useful for analysis of a mixture like reaction products in a solution without any derivatization, LI-MS was applied to study these reactions.

Paraformaldehyde (solid) was dissolved in water to prepare the primary aqueous solution (3% by weight) in order to avoid influence of hemiformals at start. After keeping the primary solution to reach its equilibrium at about 25 °C, an equal amount (by weight) of water or methanol or ethanol was added to the solution and mixed well for 1 min using a shaking machine. After mixing the solution, LI mass spectra of the mixture were measured at proper intervals, such as 5, 10 or 30 min. Mass spectra were obtained by scanning the mass range from m/z 30 to 530 or 830 in 2 s and were recorded repeatedly for about 1.5 min using a personal computer. LI mass spectra shown in this paper are all the average of mass spectra of 5-10 scans.

In the case of water addition, LI mass spectra of the mixture showed mostly the peaks corresponding to protonated molecules ($MH^+$) of POMG hydrates, represented as $HO(CH_2O)_nH(H_2O)_m H^+$, which are referred to as $A_nW_mH^+$ or n-m (around n= 1-15, m= 1-7). These peaks were observed only when the sample was heated. Larger oligomers were hydrated with more water molecules. LI mass spectra of the mixture measured later than 20 min after adding water to the solution resembled each other, indicating the solution reached equilibrium in about 20 min.

In the case of methanol addition to the primary solution, formation of hemiformals occurred soon after mixing, although it took about 10 min to complete the reactions. LI mass spectrum measured at 14 min after methanol addition (Figure 1) indicates that most of peaks were corresponding to solvated POMG monomethylether ions, $CH_3O(CH_2O)_nH(H_2O)_m(CH_3OH)_kH^+$ (referred to as $C_nW_mM_k$ or n-m-k). A dotted line in Figure 1 (right) indicates the temperature change of the sample, which was kept at ambient temperature between scan numbers 1-15 and then, was heated up to over 200 °C in final. All ions shown in Figure 1 were desorbed (=observed) without heating (scan number 1-5). Total ion profile (TIC: a solid line in Figure 1) indicates that the formation of hemiformals (observed without heating) were almost completed in 14 min, except for only a few POMG which were observed at elevated temperature (scan number 17-30). The hemiformals were separated to some extent from POMG by programming temperature of the sample.

In the case of ethanol, the formation of hemiformals also occurred to give monoethylethers of POMG, but the reactions proceeded slower than that in the case of methanol. Even 20 min after ethanol addition, the total amount of remained POMGs was much abundant than the products of hemiformals as shown in

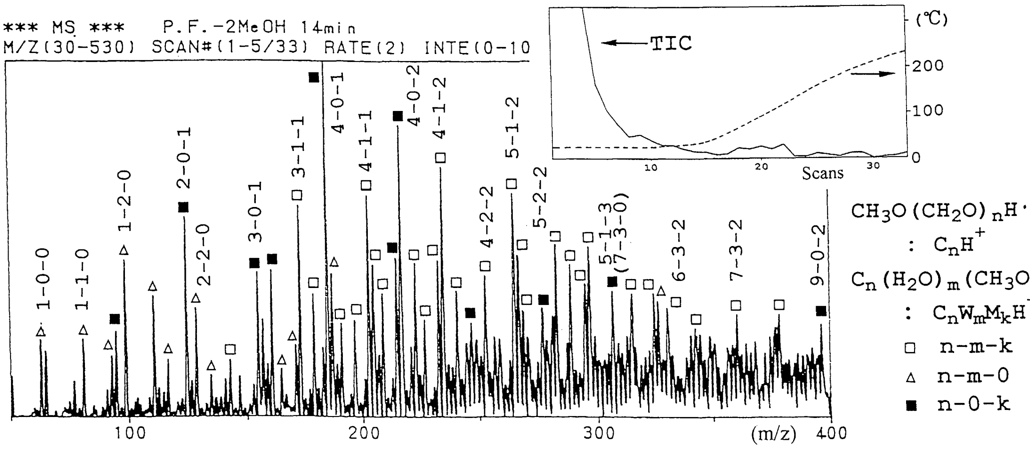

**Figure 1.** LI mass spectrum of paraformaldehyde aqueous solution mixed with methanol, measured at 14 min after methanol addition. TIC : total ion profile.

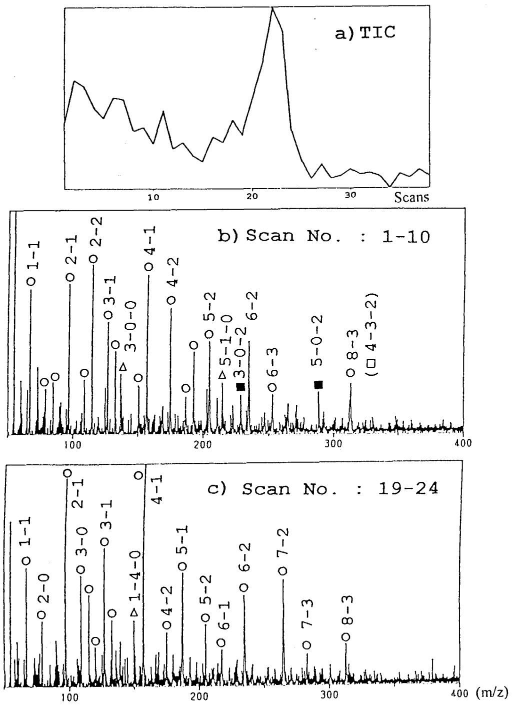

**Figure 2.** Total ion profile a) and LI mass spectra b) and c) of the POMG solution mixed with ethanol, measured at 20 min after ethanol addition.
O : $A_nW_mH^+$ ; n-m, △□■: $G_nW_mE_kH^+$ ; n-m-k

Figure 2. The upper mass spectrum (2b) is an average for scan numbers 1-10 and the lower mass spectrum (2c) is that for 19-24. Both spectra show mostly $A_nW_mH^+$ peaks even without heating (upper), except for only a few peaks corresponding to $C_2H_5O(CH_2O)_nH\ (H_2O)_m(C_2H_5OH)_kH^+$ (refer to as $G_nW_mE_kH^+$ or n-m-k), such as $G_3E_2H^+$ (3-0-2) and $G_5W_1H^+$ (5-1-0). Judging from the total ion profiles shown in Figure 2a (=the lowest column (TIC) in Figure 3), the total abundance of hemiformals appears to be less than that of POMGs.

Selected ion profiles are useful to obtain qualitative information about reaction products and the reaction mechanisms, as shown in Figure 3 for some of main ions measured at 20 min (a) and 44 min (b) after ethanol addition. Twenty minutes after ethanol addition (Figure 3a, left), the abundant hydrated POMGs ions were still observed at m/z 97-307 ($A_nW_1H^+$, n=1-9), 235 and 265 ($A_nW_2H^+$, n=6,7), and so on. Hemiformals were also observed at m/z 123-183 ($G_nE_1H^+$, n=1-3), 169-259 ($G_nE_2H^+$, n=1-4), 323 and 353 ($G_nW_1E_3H^+$, n=4,5). It is interesting to note that at 20 min after ethanol addition, abundant $A_nW_1H^+$ ions with n=1-4 were observed also without heating (at scan number 1-15), while at 10 min after ethanol addition, these ions were observed only by heating (data not shown). Probably because solvated ions like $A_nW_1E_kH^+$ were formed and these were more volatile to desorb without heating. At 44 min after ethanol addition (Figure 3b, right), almost all peaks observed were corresponding to hemiformals, except for m/z 97, 127, 157 and 265. LI mass spectrum of the mixture measured at 58 min after ethanol addition is similar to that at 44 min and indicates that the formation of hemiformals were completed.

Hydrated hemiformals, $C_nW_mM_kH^+$, were observed more abundantly by methanol addition. In contrast, $G_nE_kH^+$ ions (■) were much abundant than $G_nW_mE_kH^+$ ions in the case of ethanol addition. The results suggest that the substitution of water molecules in a hydrated POMG with ethanol is required prior to the formation of hemiformals.

Since proton affinities (PA) of solvents, such as water and small alcohols, are small compared with PAs of products, the solvents show no disturbance in measuring solute ions. LI-MS is useful to study chemical reactions occurred in a solution.

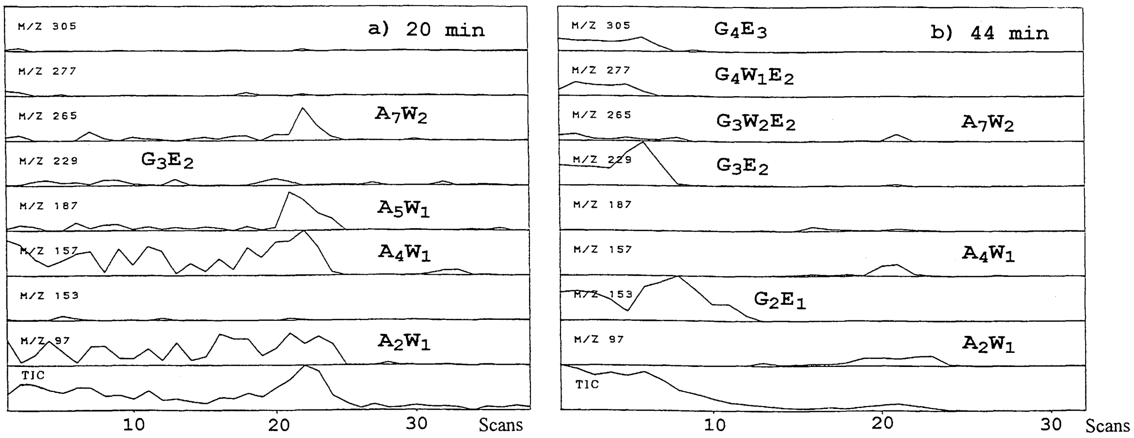

**Figure 3 .** Selected ion profiles (desorption profiles) of main ions for the paraformaldehyde aqueous solution mixed with ethanol, measured at 20 min (left) and 44 min (right) after ethanol addition. $G_n$ : $C_2H_5\,(CH_2O)_nH$

## References

1 D.F.Utterback, D.S.Millington, and A.Gold, *Anal. Chem.*, **56**, 470 (1984).
2 D.J.Le Botian, B.G.Mechin, and G.J.Martin, *Anal Chem.*, **55**, 587 (1983).
3 M.Tsuchiya and H.Kuwabara, *Anal. Chem.*, **56**, 14 (1984).
4 M.Tsuchiya, S.Teshima, T.Kaneko, and T.Hirano, *Nippon Kagaku Kaishi*, **1993**, 687.
5 M.Tsuchiya, "Advances in Mass Spectrometry," ed by I.Cornides, John Wiley & Son. (1995), Vol. 13, p.333.