Fig. 1. Effect of water on the polymerization of methyl methacrylate in *tert*-butyl alcohol at 60° C

Fig. 2. Effect of water on the polymerization of methyl methacrylate in acetic acid at 60° C

Johnston⁵ also report that water reduces the reactivity of solvent as a transfer agent. This is not surprising in view of the fact that alkyl radicals, $X-CH_2-CH\cdot R$, do not react with water², and as shown by Merz and Waters³ that even the highly reactive phenyl radical can persist in aqueous solution until it collides with a suitable solute radical or molecule. The unexpected increase in degree of polymerization

Table 1. POLYMERIZATION OF METHYL METHACRYLATE IN *tert*-BUTYL ALCOHOL-WATER MIXTURE

<i>t</i> -BuOH/Monomer = 1:1 by volume in each experiment.			
$[H_2O]/[M]$	$10^4/\bar{P}$	$10^5 R_p$ moles l. ⁻¹ sec. ⁻¹	$10^5 \left\{ \frac{1}{\bar{P}} - R_p \delta^2 / M^2 \right\}$
0.0000	3.45	9.24	3.25
0.1963	3.00	10.09	2.65
0.3529	2.53	8.93	2.02
0.5353	2.36	7.07	2.10
0.7089	2.29	6.40	2.00
0.8878*	2.14*	3.17*	2.00*

* Polymerization carried out in the heterogeneous phase. The initial mixture was slightly heterogeneous.

M , monomer concentration; $\bar{P}$, degree of polymerization; R_p , rate of polymerization; δ , the relation k_{tr}/k_p where k_t and k_p are rate constants for termination and propagation respectively.

$\bar{P}$ has been calculated from intrinsic viscosity data after Baxendale *et al.* (*J. Polymer Sci.*, 1, 237 (1946)).

Table 2. POLYMERIZATION OF METHYL METHACRYLATE IN ACETIC ACID-WATER MIXTURE

Acetic acid/Monomer = 1:1 by volume in each experiment.			
$[H_2O]/[M]$	$10^4/\bar{P}$	Optical density at 515 mμ using rhodamine reagent (polymer solution 0.2%)	Average No. of COOH per molecule
0.00	7.67	0.41	very low
0.29	8.56	0.46	0.922
0.58	5.72	0.50	1.75
1.16	5.19	0.50	1.93
2.90	6.11	0.50	1.65
5.80	7.67	0.55	1.79

as also the negative slope of the plot of $1/\bar{P} - R_p \delta^2 / M$ against $[H_2O]/[M]$ can be attributed to a tighter coiling of the polymer chain leading to a reduced termination rate.

A slightly different trend is noticeable in the polymerization of methyl methacrylate in acetic acid in the presence of water. In this system the quantity of water was varied over a wider range ($S/M = 0.29-5.8$). The results are tabulated in Table 2 and represented in Fig. 2. As in the previous case $1/\bar{P}$ decreases with addition of water and this might be presumed to be due to the same reasons as cited before.

In this case also from the point marked with an arrow the system starts to show heterogeneity. The new feature which appears here is that from about 1:1 (water/acetic acid) the curve takes an upward turn. It is believed that this complication is caused by the increasing ionization of acetic acid introducing in the system a new species, the acetate ion CH_3COO^- , which probably is a much better chain-transferring agent for poly(methyl methacrylate) radical than acetic acid. This also receives support from our results (Table 2, last col.) of the number of carboxyl end-groups per polymer chain as determined by the dye interaction method⁶ developed in this laboratory. The number of carboxyl end groups increases with the addition of water and remains more or less steady on further addition of water.

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Revision of the End Carbon Chain Concept in the Gas-Liquid Chromatography of Methyl Esters of Unsaturated Fatty Acids

THE 'end carbon chain', shown to be the key factor in relating the retention time of unsaturated fatty acids of differing chain-length but the same number of double bonds, was originally defined as the number of carbon atoms beyond the double bond farthest removed from the carboxyl group¹.

It would be advantageous to redefine this unit as the number of carbon atoms reckoned from the centre of the double bond farthest removed from the carboxyl group to, and including, the terminal methyl group. The end carbon chain is then simply the fatty acid chain-length less the familiar position number usually employed to identify this particular double bond position. Moreover, the revised 'end carbon chain' concept is immediately useful in assessing the biological activities of certain fatty acids as related through the terminal numbering system².

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