Radicals and Radical Anions in Addition Polymerization, their Spectra and Reactivity

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CONVENTIONAL methods of polymer chemistry based on the measurement of either or both the rate and degree of polymerization as a function of various experimental variables permit one or more of the absolute rate constants of propagation, mutual termination, retardation, and transfer, to be determined. They do not allow the measurement of the rate constant for initiation. The recently developed technique of pulse radiolysis permits not only the measurement of the rate of addition of the initial radical or ion to the polymerizable monomer (m_1), but also other interesting properties of the initial monomer–initiator adduct to be elucidated. We report here some results obtained with acrylamide (AM), methacrylamide (MAM), *N*-t-butylacrylamide (*N*-t-BuAM), acrylic acid (AA), acrylonitrile (AN), and styrene (S), in water, and styrene and α-methylstyrene in organic solvents.

All the monomers investigated accelerate the rate of decay of the spectrum of the hydrated electron, such that the half-life is inversely proportional to the monomer concentration. In the case of acrylamide this leads to the value for $k(e_{aq}^{-} + \text{AM}) = (2\cdot0 \pm 0\cdot4) \times 10^{10}$ M^{-1} sec.$^{-1}$ (mean of 17 values). The position and intensity of the absorption due to the OH radical precludes the application of the above method to the determination of $k(\text{OH} + \text{AM})$. However, by studying the effect of added monomer in decreasing the yield of CNS radicals produced in solutions containing thiocyanate ion,[1] this constant was shown to be $(1\cdot9 \pm 0\cdot5) \times 10^{9}$ M^{-1} sec.$^{-1}$

When dilute aqueous solutions of AM, MAM, *N*-t-BuAM, AA, or AN are pulsed, the spectra shown in Figure 1 are obtained. When electron scavengers such as H^+, N_2O, and H_2O_2 are present, the intense short-wave absorption between 265 and 275 mμ is absent indicating that this peak is due to $m_{aq}^{-}\cdot$. In neutral solution addition of excess carbonate ion or thiocyanate ion, both of which react rapidly with OH but not with e_{aq}^{-}, reduces the 375 mμ peak, but does not affect the 275 mμ peak, confirming that the chromophore at 275 ± 25 mμ is $\bar{\text{C}}\text{H}_2\text{–}\dot{\text{C}}\text{xy}$ or $\dot{\text{C}}\text{H}_2\text{–}\bar{\text{C}}\text{xy}$ and for 375 ± 25 mμ is $\text{zCH}_2\text{–}\dot{\text{C}}\text{xy}$ or $\dot{\text{C}}\text{H}_2\text{–Cxyz}$ where x = H or Me, y = CONH_2, CONHBu^{t}, CN, or CO_2^{-}, and z = H or OH, except for adducts formed from acrylonitrile or the acrylate ion which have no detectable absorption at 375 mμ. In the absence of any solute the decay of these peaks follows second-order kinetics precisely. Using generally accepted yields of various primary products of radiolysis in water the extinction coefficients and rate constants given in the Table below have been obtained.

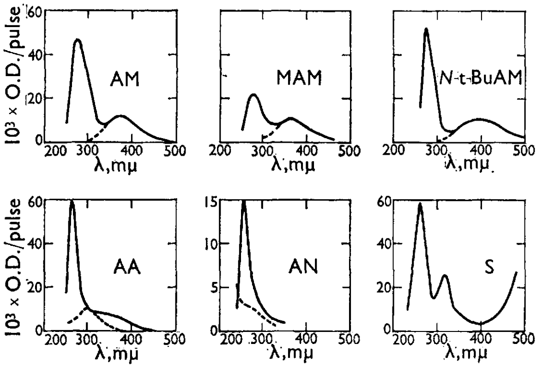

FIGURE 1

Transient absorption spectra obtained by pulse radiolysis of dilute aqueous solutions of monomers. Full line neutral or alkaline, broken line acidic. Dose per pulse varied in range 5—20 krad.

When oxygen is present both peaks decay at a rate proportional to the oxygen concentration corresponding to a rate constant in the case of AM $k(\text{O}_2 + \text{m}_1^{-}\cdot \text{ or } \text{HOm}_1\cdot) = (1\cdot9 \pm 0\cdot3) \times 10^{9}$ M^{-1} sec.$^{-1}$ (mean of 8 values). It is also possible to study the rate of reaction of these primary radical species with oxidizing or reducing inorganic salts which are known to act as retarders of polymerization, *e.g.*, measurements of the rate of decay of the absorption due to ferricyanide ion at 420 mμ when this solute is present in acidified 0·1 M-AM solutions leads to the conclusion that $k(\text{ferricyanide} + \text{Hm}_1\cdot \text{or HOm}_1\cdot) = (6\cdot8 \pm 0\cdot4) \times 10^{6}$ M^{-1} sec.$^{-1}$ (mean of 9 values), which is almost an order of magnitude larger than the value found for the reaction of polyacrylamide radicals with this retarding solute.[2]

If low-temperature aqueous glasses containing 0·1 M-AM are γ-irradiated the spectra shown in Figure 2 are obtained. We assign the absorption band at 325 mμ in acid glass to one of the uncharged chromophores referred to above, and the

TABLE

Extinction coefficients and bimolecular decay constants of radical anions ($m_1^{-}\cdot$) *and Radical adducts* ($Hm_1\cdot$ *or* $HOm_1\cdot$)

		$m_1^{-}\cdot$			$Hm_1\cdot$ or $HOm_1\cdot$	
m_1	λ_{max}(mμ)	ϵ(M^{-1}cm.$^{-1}$)	$2k$(M^{-1}sec.$^{-1}$)	λ_{max}(mμ)	ϵ(M^{-1}cm.$^{-1}$)	$2k$(M^{-1}sec.$^{-1}$)
AM	275	10,500	$4\cdot15 \times 10^9$	370	900	$1\cdot75 \times 10^9$
MAM	275	4,150	$4\cdot5 \times 10^9$	370	860	$1\cdot5 \times 10^9$
N-t-BuAM	275	10,200	$1\cdot06 \times 10^9$	400	800	$0\cdot7 \times 10^9$
AA	265	$\geqslant$16,000	$\geqslant 7\cdot4 \times 10^9$	—	—	—
AN	255	680	—	—	—	—

sharp peak at 290 mμ obtained in alkaline glass to the radical anion $m_1^{-}\cdot$.

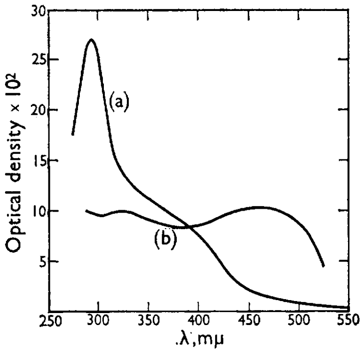

FIGURE 2

Spectra of 0·1 M-AM *in* (a) 8 N-KOH *and* (b) 5·3 M-H_2SO_4 *glass γ-irradiated to a dose of* 50 *krad at* 77°K. *The peak in* (b) *at* ca. 450 mμ *is that due to the* $\cdot SO_4^-$ *radical.*

Whilst the pulsing of styrene solutions in water gives similar double-peaked spectra, the spectrum obtained in very carefully purified organic solvents (cyclohexane, dioxan, tetrahydrofuran, and benzene) has only a single peak at 340 mμ. This differs from the spectra reported by Katayama,[3] and by Keene, Land, and Swallow,[4] and also differs from that of "living" polystyryl anions[5] in that it has no detectable absorption above 400 mμ. Whilst it is tempting to ascribe this to the radical anion S^-, the fact that the addition of sulphuric acid has no effect on this spectrum in cyclohexane solutions argues against this assignment. Since (a) the radical SH and also the triplet state S^T are both expected to absorb in this region, (b) the yields of this transient are very concentration-dependent, and (c) the half life of the decay at 320 mμ is at least a hundredfold less than that of the decay at 375 mμ, we think it is likely that two species are present and that neither is S^-.

(*Received, June* 15*th,* 1966; *Com.* 410.)

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[1] The principle of the method is described by G. E. Adams, J. W. Boag, and B. D. Michael, *Proc. Chem. Soc.*, 1964, 411.

[2] E. Collinson, F. S. Dainton, B. Mile, D. R. Smith, and S. Tazuke, *Nature*, 1963, **198**, 26.

[3] M. Katayama, *Bull. Chem. Soc. Japan*, 1965, **38**, 2208.

[4] J. P. Keene, E. J. Land, and A. J. Swallow, *J. Amer. Chem. Soc.*, 1965, **87**, 5284.

[5] D. N. Bhattacharya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, 1965, **69**, 612, and earlier papers cited therein.