

LETTERS TO THE EDITORS

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Preparation of Block and Graft Copolymers in Systems where the Life-time of the Kinetic Chain is Long

WE have reported¹ that block copolymers may be prepared by adding methyl methacrylate to a latex of polyvinyl acetate prepared by gamma-irradiation of the monomer emulsion. Polymer radicals trapped in latex particles initiate polymerization of the second monomer, forming linear block copolymer molecules.

It is apparent, however, that more copolymer is formed than can be accounted for by this mechanism. Latexes prepared from 1 gm. of vinyl acetate containing of the order of 10^{16} latex particles should, following the arguments of Smith and Ewart² that half the particles contain live radicals, give a yield of block copolymer of approximately 2 mgm. In fact these latexes have been found to yield 0.05–0.10 gm. of copolymer per gram of vinyl acetate together with large excesses of methyl methacrylate polymer.

During the polymerization of the second monomer no further radicals are generated, the propagating radicals remain trapped in the latex particles and so mutual termination reactions do not occur. The kinetic chain-length is thus essentially limited only by the amount of methyl methacrylate added. The molecular weight of the polymer molecules is, of course, limited by chain transfer reactions. During the course of the polymerization of a gram of methyl methacrylate by 10^{16} radicals, transfer to monomer and polymer must occur many times. Transfer to monomer will account for the pure polymethyl methacrylate found in the system. Transfer to polyvinyl acetate will lead to branched graft copolymer molecules which must form the preponderant part of the copolymer yield.

Transfer-limited molecules may also be obtained by adding styrene emulsions to previously irradiated polymethyl methacrylate films. Small amounts of block copolymer are found in the film, but the bulk of the polymerization occurs in the supernatant styrene emulsion. The characteristics are essentially similar to a true emulsion polymerization. The rate is given by $k_p n [M]$, where k_p is the propagation constant for styrene, $[M]$ the monomer concentration and n varies between the number of latex particles formed and half that number. The temperature increment of the rate is 7.2 kcal., which is close to the energy of activation of propagation for polystyrene. The molecular weight of the polystyrene is exceptionally high, measurements of viscosity indicating a range of $4\text{--}12 \times 10^6$. The samples of higher molecular weight have high Huggins constants³ and are probably highly branched.

Our suggestion is that polymerization proceeds in the polymer film until such time as transfer to monomer occurs and the resulting small radicals escape into the supernatant phase and initiate emulsion polymerization of styrene. The size of the polystyrene formed is, to a large extent, limited only by transfer. The measured molecular weights are in fact in excess of the limit to the number average set by the monomer transfer constant, but a dead

polymer molecule can resume growth as a branched molecule if another radical is transferred to it.

P. E. M. ALLEN
G. M. BURNETT
J. M. DOWNER
R. HARDY
H. W. MELVILLE

Department of Chemistry,
University of Birmingham.
May 31.

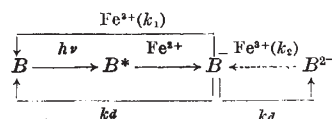
¹ Allen, P. E. M., Downer, J. M., Hastings, G. W., Melville, H. W., and Urwin, J. R., *Nature*, **177**, 910 (1956).

² Smith, W. V., and Ewart, R. H., *J. Chem. Phys.*, **16**, 592 (1948).

³ Huggins, M. L., *J. Amer. Chem. Soc.*, **64**, 2716 (1942).

Photo-reduction of Methylene Blue and Thionine by Ferrous Sulphate using Flash Irradiation

WHEN dilute solutions of methylene blue in 0.1 N sulphuric acid are subjected to flash photolysis with orange-red light in the presence of ferrous sulphate ($\sim 0.1 M$), the kinetic curves obtained by monitoring at various wave-lengths can all be interpreted in terms of the following reaction scheme:



By direct measurement, the rate constant (k_d) for the dismutation of the semiquinone radical ($B^{\cdot -}$) was found to be of the order 1.5×10^9 l. mole⁻¹ sec.⁻¹. By observing the degree to which the formation of leuco methylene blue (B^{2-}) was suppressed by the addition of ferric iron, the value of k_1/k_d and hence k_1 ($\sim 2.4 \times 10^5$ l. mole⁻¹ sec.⁻¹) was obtained. The latter is so much smaller than k_d that the quantity of ferric iron produced by the photochemical reaction has no appreciable effect on the dismutation of the semiquinone radical.

The reverse of the dismutation reaction, if sufficiently rapid, would lead to an appreciable equilibrium concentration of semiquinone in partly reduced methylene blue solutions. This would allow of two routes for the re-oxidation of the leuco-base, namely, by direct reaction with ferric iron, or by reaction of ferric iron with the equilibrium concentration of semiquinone. Rough observations of the rate of re-oxidation, taken in conjunction with the above value for k_1 , suggest that the equilibrium concentration of semiquinone must be very much less than the value reported by Michaelis and co-workers¹ for dilute acid solutions.

In view of the observations of Bridge and Porter^{2,3}, it is of particular interest to determine whether the semiquinone in the present experiments is produced via the triplet state or by direct reaction of the excited singlet state. This point has been investigated with thionine, the behaviour of which on flash photolysis is qualitatively similar to that of methylene blue. If the semiquinones were formed solely by reaction of the excited singlet states of the dyestuffs, the quenching of fluorescence by ferrous sulphate should be related to the yield of semiquinone by the expression:

$$\frac{\Phi_{ro}}{\phi} = 1 + \frac{1}{K[\text{Fe}^{2+}]}$$