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Bamford C H, Jenkins A D & Johnston R. Studies in polymerization. XI. Reactions between polymer radicals and ferric chloride in non-aqueous media. *Proc. Roy. Soc. London Ser. A* 239:214-29, 1957.
[Courtaulds, Limited, Research Laboratory, Maidenhead, Berkshire, England]

The free radical polymerizations of acrylonitrile, methacrylonitrile, and styrene in N,N-dimethylformamide in the presence of ferric chloride ($FeCl_3$) were studied. From such experiments the rate of chain initiation and the rate coefficients for reaction of the radicals with $FeCl_3$ may be deduced. A kinetic treatment is given. [The SCI® indicates that the papers in this series have been cited in over 800 publications.]

Beginnings and Ends of Polymer Chains

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The Courtauld Research Laboratory in Maidenhead, Berkshire, in which the work described in this paper was done, was established to carry out basic research allied to the synthetic textile industry and was particularly occupied with the synthesis and properties of high polymers. From the outset free-radical polymerization was included in the programme, although initially with some misgivings, but these were removed by the introduction (unfortunately by others!) of the "acrylic" synthetic fibres based on polyacrylonitrile.

We felt well prepared for studying the polymerization of acrylonitrile after earlier work on styrene and a few other conventional monomers. For some time we had been thinking about the influence of polarity on the reactivities of free radicals, and acrylonitrile with its relatively high polarity was of special interest. We argued that since reduction of transition metal cations by polymer radicals (already familiar in aqueous solution) is a highly polar process, comparison of acrylonitrile and styrene radicals should be revealing. This was the origin of the investigations described in the paper.

The actual systems were easily chosen. N,N-dimethyl formamide (DMF) is an excellent solvent for polyacrylonitrile and many other vinyl polymers, as well as for many metallic salts; ferric chloride ($FeCl_3$) is readily soluble, and its reduction product (Fe^{II}) is easily estimated. It soon became evident that $FeCl_3$ in DMF solution behaves as an ideal retarder of the polymerization of the three monomers examined (acrylonitrile, methacrylonitrile, and styrene), i.e., none of the reaction products interferes with any stage of the polymerization. Further, polystyrene radicals were found to react almost 10 times as rapidly as polyacrylonitrile radicals—clearly an observation relevant to the polarity question.

One result of the high reactivity of $FeCl_3$ towards polystyrene radicals is that the salt behaves effectively as an inhibitor of this polymerization. We were able to develop some new nonstationary kinetics of general applicability that led to evaluation of the rate coefficient (k_f) and also provided the basis of a new method of measuring rates of initiation in polymerizations, which we subsequently applied to four monomers.[1] The use of DMF as solvent enables the technique to be used with a wide variety of vinyl monomers. The kinetic algebra occupied Aubrey D. Jenkins, Dick Johnston, and me for an afternoon; I recall that it followed a minor celebratory lunch, but cannot remember the reason for the celebration—such occasions were not too uncommon. The kinetic treatment has proved useful in related investigations with derivatives of other metals[2] and other monomers, and the ideas in the paper have been incorporated into subsequent discussions.[3-5] Jenkins and B.H. Mustafa[6] have recently evaluated k_f by a different procedure involving the moderated copolymerization technique and obtained a very similar result.

One would expect an ideal retarder to have both kinetic and nonkinetic applications. A recent example of the latter was given by K. Ito[7] in connection with the existence and/or origin of a penultimate unit effect in copolymerization. D.H. Solomon and his colleagues[8] provided a nonkinetic example in their use of $FeCl_3$ in the purely thermal polymerization of styrene; they were thus enabled to isolate oligomers that could be characterized by nuclear magnetic resonance.

The work gave a great stimulus to our efforts in developing the patterns of radical reactivity scheme. In another context acrylonitrile polymerization also served us well by presenting us with many novel phenomena leading to ideas about radical occlusion, so that this monomer became a firm favourite.

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