

## LETTERS TO THE EDITORS

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## Synthesis of Branched Polymers

LITTLE is known about the behaviour of branched-chain polymer molecules either in solution or in the solid state. One of the difficulties hindering the acquisition of this knowledge is the lack of synthetic methods for building molecules to a predetermined pattern. This communication is concerned with one approach to a solution of this problem in the case of vinyl polymers. Polystyrene may be taken to illustrate the application of the method.

Polystyrene in solution in carbon tetrachloride is brominated photochemically at room temperature until the bromine content rises to about 5–10 per cent. The brominated polymer is dissolved in styrene monomer and the solution irradiated with ultraviolet light of such a wave-length that the bromine atoms are removed, leaving polymer radicals and free bromine atoms both of which initiate polymerization, branches growing from the polymer radicals. Unless the bromine content of the initiating polymer is very low the product is precipitated as a gel, showing that cross-linking has occurred by the radical branches combining<sup>1</sup>. However, cross-linking may be prevented by the addition of carbon tetrachloride, which then acts as a transfer agent and gives rise to shorter branches. By a judicious choice of conditions it is possible to obtain a mixture of branched-chain polystyrene and linear polystyrene so different in molecular weight that the two components may be separated by fractional precipitation. From the fractionation results, it is possible to estimate the weight fraction of high polymer molecules present as branches. The use of styrene monomer labelled with carbon-14 for the branch-growth polymerization makes possible an alternative determination of this quantity.

The determination of the number of branches per molecule is more difficult. From the observed rate of polymerization it is possible, with a knowledge of the velocity constants of propagation and termination and of the transfer velocity constant of the styrene radical for carbon tetrachloride, to calculate the average length of the branches.

Unfortunately, transfer constants are not known with a very high degree of precision. Determination of the average length of the branches and the weight fraction of the branches enables a simple calculation of the frequency of the branches. A second method is available for determining the frequency of the branches. The branched polystyrene will have a smaller bromine content than the starting material partly because of the dilution effect of the added branches and partly because each branch replaces a bromine atom. The bromine contents of a brominated polymer before and after branching were determined by the neutron activation technique and provided data for the calculation of the number of monomer units in the backbone of the polymer per branch. The results of a number of branching experiments are summarized in the accompanying table.

The branching figures given in the table have been calculated from the fractionation data. The molecular weights of the backbones of the polymers have been

Expt. No.	% branching	Chain-length of branches ( $P_n$ )	No. of monomer units of backbone/branch	$M_w$ of backbone	Branches per molecule
A1	37	130	220	300,000	14
B3	39	310	480	900,000	19
E4	25	95	290	900,000	31
F1	34	230	450	200,000	4.5
F2	37	230	390	200,000	5

estimated from viscosity measurements on the brominated linear polystyrene.

In the case of experiment F1, radioactive monomer was used. This tracer technique indicated that the product was 35 per cent branched, or one branch per 430 monomer units of backbone. Bromine analyses on the branched polymer F1 indicated one branch per 350 monomer units of backbone or 40 per cent branched.

Experiments with radioactive monomer and the determination of bromine by neutron irradiation were carried out in collaboration with Dr. J. C. Bevington, whose advice and assistance are gratefully acknowledged. The work is being extended to other vinyl polymers.

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<sup>1</sup> Bevington, J. C., Melville, H. W., and Taylor, R. P., *J. Polymer Sci.*, 12, 449 (1954).

### Chemical Action of Ionizing Radiations : Excitation of Optical Levels by Particles of Relatively Low Energy

IT is well known that the energy lost by the fast particles of ionizing radiations is ultimately used for the excitation of discrete states, for ionization and for giving to the secondary electrons kinetic energies less than the first excitation-level of the atoms or molecules present in the system<sup>1</sup>.

When the kinetic energy of the charged particles is large compared with the ionization and excitation potentials of the atoms or molecules present, excitation (and ionization) will be distributed among all the atoms and molecules in the system according to their relative proportions. However, as the particles are slowed down, they are no longer able to excite those species the excitation potentials of which are greater than the kinetic energy of the exciting particles. Therefore, from a certain point, excitation (and ionization) will be confined to atoms and molecules with a sufficiently low excitation (and ionization) potential; these processes will go on as long as the kinetic energy of the charged particles is greater than the lowest electronic excitation potential.

A case which is of particular interest is represented by dilute aqueous solutions of many organic and inorganic compounds. It is well known<sup>2</sup> that water itself does not absorb light of wave-lengths greater than about 1800 Å., as its first continuous absorption band stretches from 1430 to 1860 Å. with a maximum at 1665 Å. ( $\sim 7.5$  eV.). Therefore, in dilute aqueous solutions, at electron energies greater than about 7.5 eV., chemical effects will be due mainly to the action on the water ('indirect effect'), as most of the radiation energy will be absorbed by the solvent