USES OF ISOTOPES IN ADDITION POLYMERIZATION

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CONTENTS

I. INTRODUCTION

This review deals with advances in our knowledge of addition polymerization of unsaturated monomers which have resulted from the use of isotopes. Discussion is limited to the uses of isotopes as tracers and to the mechanistic implications of the kinetic isotope effect. The effects of ionizing radiations on monomers and polymers are not discussed except in cases where the work has also involved isotopic tracers. Discussion of other physicochemical techniques is necessarily restricted, but their importance is acknowledged here; indeed polymerization systems provide some of the best examples of the interdependence of isotopic methods and other chemical techniques.

References to the use of isotopes in vinyl polymerizations date back to 1944 (176), and the literature survey is complete to the end of 1961. Later references are included but coverage may not be complete. The subcommittee of the Commission on Macromolecules of the International Union of Pure and Applied Chemistry has laid down certain rules regarding nomenclature in polymer science (119, 120), but in general no universal notation for polymer reactions and kinetics has been adopted. The notation used here is that used by Mayo (146–150), and Tobolsky (26, 27, 122), and several well known textbooks of polymer chemistry. Throughout the review the term "polymerization" refers only to addition polymerization of unsaturated monomers.

Chemical Abstracts does not follow the recommendations of the Commission on Inorganic Nomenclature of the I.U.P.A.C. as regards isotopic symbols, and British practice differs from American practice for the nomenclature of labeled compounds. However, *Chemical Abstracts'* terminology has been adopted for this review and the reader is referred to the book by Murray and Williams (159) for a concise summary of the rules.

It is hoped that this review will encourage more workers to enter a rewarding field of research. Much has been written about the difficulties, expense, and hazards of isotope techniques, and in many cases these aspects have been exaggerated. For radioactive isotopes in particular it is worth noting that many of the most useful ones are either Class III (moderate toxicity, *e.g.*, Br^{80}, I^{131}, S^{35}) or Class IV (low toxicity, *e.g.*, H^3, C^{14}), and at tracer levels require the minimum of additional facilities. An excellent paper by Catch expands this rational approach (82).

II. ADDITION POLYMERIZATION

Addition polymerizations of vinyl compounds are chain reactions and consequently proceed *via* three well defined stages, *viz.* (i) *initiation*, which is accomplished by introducing free radicals or ions into the system, either directly through heat, light, or high energy irradiations, or *via* intermediate compounds known as initiators or catalysts. Whatever the means, the product is always a reactive intermediate containing one monomer unit. (ii) *Propagation* follows, and is the growth of polymer molecules by successive addition of monomer units to the reactive site. Finally, (iii) *termination* occurs when the reactive site at the end of a growing polymer is rendered inactive.

It is convenient to illustrate the above processes by reference to polymerization initiated by means of a free radical initiator, since much of the work covered in this review is concerned with such reactions.

Initiation

$$\mathrm{I} \xrightarrow{k_\mathrm{d}} 2\mathrm{R}\cdot \quad \text{Decomposition of initiator} \tag{1}$$

$$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_\mathrm{i}} \mathrm{M}_1\cdot \quad \text{Attack on monomer} \tag{2}$$

Propagation

$$\mathrm{M}_1\cdot + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{M}_2\cdot$$

$$\mathrm{M}_2\cdot + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{M}_3\cdot$$

$$\vdots$$

$$\mathrm{M}_n\cdot + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{M}_{n+1}\cdot \tag{3}$$

Termination

$$\mathrm{M}_n\cdot + \mathrm{M}_m\cdot \xrightarrow{k_\mathrm{tc}} \mathrm{M}_{n+m} \quad \text{Combination} \tag{4}$$

$$\mathrm{M}_n\cdot + \mathrm{M}_m\cdot \xrightarrow{k_\mathrm{td}} \mathrm{M}_n\mathrm{H} + \mathrm{M}_m(-\mathrm{H}) \quad \text{Disproportionation} \tag{5}$$

$$\mathrm{M}_n\cdot + \mathrm{AS} \xrightarrow{k_\mathrm{tr}} \mathrm{M}_n\mathrm{A} + \mathrm{S}\cdot \quad \text{Chain transfer} \tag{6}$$

Reactions 1 to 5 are self-explanatory. In reaction 6 AS may be monomer, polymer, initiator, solvent, or added compounds such as thiols or halogenated hydrocarbons which readily react with free radicals. It is a general feature of chain transfer that the radical S· is able to replace R· in reaction 2, thus the kinetic chain length remains unaffected while the chain length of the formed polymer is reduced.

Where the radical S· has a reduced reactivity toward monomer, the polymerization rate is subject to retardation. This particular type of retardation is usually termed degradative chain transfer to distinguish it from the other form of retardation where a growing polymer radical adds on to the retarder molecule Z (reaction 7) to produce a polymeric radical with a reduced ability to add more monomer units in continuance of the propagation sequence (reaction 8), *i.e.*, $k_\mathrm{p} > k_\mathrm{zp}$.

$$\mathrm{M}_n\cdot + \mathrm{Z} \xrightarrow{k_\mathrm{z}} \mathrm{M}_n\mathrm{Z}\cdot \tag{7}$$

$$\mathrm{M}_n\mathrm{Z}\cdot + \mathrm{M} \xrightarrow{k_\mathrm{zp}} \mathrm{M}_n\mathrm{ZM}\cdot \tag{8}$$

Where a retarder becomes so efficient that it completely suppresses polymerization it is known as an inhibitor. Clearly, inhibition occurs when $k_\mathrm{zp} \doteq 0$ though it should be noted that usually there is no sharp division between retardation and inhibition.

The reactions described in this section involving interactions between initiator radicals, polymer radicals, and their environmental molecules and radicals, are particularly amenable to investigation by isotopic tracer techniques.

III. Initiation

A full understanding of the mechanisms and kinetic characteristics of initiation reactions such as 1 and 2 requires knowledge of (i) the initiator species, (ii) the rate of initiation, (iii) the efficiency of the initiator or catalyst, and, since efficiencies are usually less than 100%, of the wasteful side reactions involved.

A. NATURE OF THE INITIATING SPECIES

1. *Free Radical Polymerization in Organic Media*

In reaction 2 the product $\mathrm{M}_1\cdot$ requires definition. It seems usual to assume that radical R· formed from the initiator (reaction 1) adds to the double bond of a monomer (reaction 9) to give a radical which then enters the propagation sequence.

$$\mathrm{R}\cdot + \mathrm{CH_2{=}CXY} \rightarrow \mathrm{R{-}CH_2{-}\dot{C}XY} \tag{9}$$

In some cases there is evidence to substantiate this assumption (14, 15, 33, 38), and it probably is the most important reaction. Nevertheless, the alternative of labile atom abstraction by R· (H–, Cl–, etc.) needs to be borne in mind, particularly when reactive radicals such as methyl or phenyl are involved. For example, there is evidence that in the dibenzoyl peroxide or *p,p′*-dimethoxydibenzoyl peroxide initiated polymerization of acrylonitrile, hydrogen abstraction is an important mode of initiation (3, 20).

A popular free radical source, 1,1′-azoisobutyronitrile (AIBN) undergoes thermal or photochemical decomposition to give nitrogen and 2-cyano-2-propyl radicals (reaction 10), and several groups have established that the cyanopropyl radicals are mesomeric with a ketene imine structure $(\mathrm{CH_3})_2\mathrm{C{=}C{=}N}\cdot$. Use of C^{14}-labeled AIBN has provided abundant evidence that radicals resulting from this decomposition initiate polymerizations solely by addition to the double bond (14, 15, 32, 33, 36–38), but as yet the relative importance of the two mesomeric structures in reaction 9 has not been determined. In the absence of monomer the ketene–imine radical can combine with a 2-cyano-2-propyl radical to form dimethylketenecyanoisopropylimine, $(\mathrm{CH_3})_2\mathrm{C(CN){-}N{=}C{=}C(CH_3)_2}$, which is also

$$(\mathrm{CH_3})_2\mathrm{C(CN){-}N{=}N{-}(CN)C(CH_3)_2} \rightarrow 2(\mathrm{CH_3})_2\dot{\mathrm{C}}(\mathrm{CN}) + \mathrm{N_2} \tag{10}$$

thermally unstable and able to initiate polymerization of styrene (62).

A second mode of decomposition of AIBN into a cyanopropyl radical and an azo radical $(CH_3)_2C(CN)-N{=}N\cdot$ was proposed to account for apparent differences in the efficiencies of initiation of different monomers (9). It was supposed that only the azo radical was capable of initiating polymerization of methyl methacrylate. There seems little justification for this postulate, which requires that polymers should have thermally unstable azo end groups, since there is no evidence of loss of C^{14} when polymers prepared using labeled AIBN are heated or subjected to ultraviolet irradiation (33).

Diaroyl peroxides are widely used as polymerization initiators. With the possible exception of a few unsymmetrical peroxides, thermal or photochemical decomposition results in the formation of two aroyloxy radicals (reaction 11).

$$ArCO{-}O{-}O{-}CO{-}Ar \rightarrow 2ArCO{-}O\cdot \qquad (11)$$

Subsequently the aroyloxy radicals may decompose into aryl radicals and CO_2 (reaction 12).

$$ArCO{-}O\cdot \rightarrow Ar\cdot + CO_2 \qquad (12)$$

Temperature, substituent groups on the aryl nucleus, and possibly solvent, all affect the stability and reactivity of the peroxides and their derived radicals; consequently, the relative contributions of aroyloxy and aryl radicals to the initiation reaction 9 may be expected to vary widely.

Early experiments were designed to show that initiation resulted from addition of radicals to the monomer double bond. Thus, Pfann, Salley, and Mark used *p,p'*-dibromodibenzoyl peroxide to initiate styrene polymerization at 140° and subsequently determined the number of bromine atoms combined in the polymer by radioactivation analysis $Br^{81}(n,\gamma)Br^{82}$ (176). This work was of limited quantitative significance but is historically important as the first reported application of radiochemical methods to mechanistic studies of polymerization reactions. Use of deuterated dibenzoyl peroxide in styrene polymerization has indicated that fragments of the peroxide become incorporated in the polymer (217); however, Russian workers first published definite evidence that unsubstituted benzoyloxy radicals are involved in initiation of styrene polymerization. Dibenzoyl peroxide-di-*carboxyl*-C^{14} was used in varying concentrations to initiate polymerizations at various temperatures, and it was found that with increasing temperature the contribution due to benzoyloxy radicals in reaction 9 decreased, and the yield of $C^{14}O_2$ increased. This trend indicates increased dissociation of benzoyloxy radicals into phenyl radicals with increasing temperature, but the fate of the phenyl radicals was not investigated. An interesting feature of this work, in which polymerizations were continued to high conversions, was that at constant temperature, increased initiator concentration resulted in a decrease in the number of benzoyloxy radicals per polymer molecule (135, 136). The same trend is not observed in low conversion polymers (45, 47, 50).

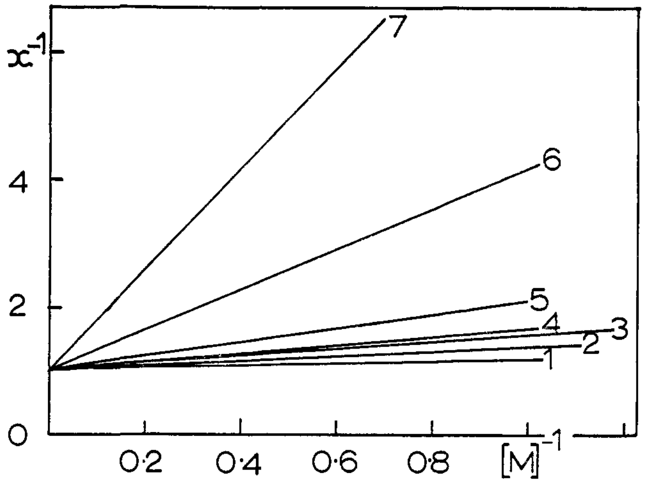


Fig. 1.—Relative reactivities of monomers toward the benzoyloxy radical at 60°: 1, 2,5-dimethylstyrene; 2, styrene; 3, 2,4,6-trimethylstyrene; 4, styrene at 80°; 5, vinyl acetate; 6, methyl methacrylate; 7, acrylonitrile.

The roles of both phenyl and benzoyloxy radicals in methyl methacrylate polymerization at 60° were clearly defined by the use of two labeled initiators (14, 15). Firstly, polymerizations were initiated using dibenzoyl peroxide-di-*ar*-C^{14} and the total number of initiator fragments per polymer molecule, phenyl or benzoyloxy, was determined. Secondly, polymerizations were initiated with dibenzoyl peroxide-di-*carboxyl*-C^{14} and the number of benzoyloxy radicals per polymer molecule determined. Comparison of the first system with AIBN-initiated polymerizations indicated that initiation by hydrogen abstraction was unimportant; hence, comparison of the results for the two peroxides showed that phenyl radicals were responsible for 43% of the initiating events.

Exactly the same result may be calculated from the more comprehensive data of Bevington (45, 49) who, in a series of papers has provided extensive data on initiation reactions. Thus, labeled dibenzoyl peroxides and substituted dibenzoyl peroxides have been used to initiate polymerization of several monomers under a variety of conditions. The roles of the different initiating species were determined either by using two labeled peroxides, as described above, or by using ring labeled peroxide alone followed by removal of aroyloxy groups by hydrolysis.

For dibenzoyl peroxide it was shown that at constant temperature, the fraction x of the initiating radicals which are benzoyloxy radicals increases with increasing monomer concentration (Fig. 1). This is seen to be logical when the reactions involved are considered.

TABLE I

REACTIVITIES OF MONOMERS TOWARD AROYLOXY RADICALS

Radical	Monomer	Temp., °C.	k_1/k_2	Ref.
$C_6H_5CO{-}O\cdot$	2,5-Di-Me-styrene	60	0.2	(59)
	Styrene	60	0.4	(47)
	Styrene	80	0.7	(50)
	2,4,6-Tri-Me-styrene	60	0.6	(59)
	Vinyl acetate	60	1.1	(22)
	Me methacrylate	60	3.3	(49)
	Acrylonitrile	60	$\geqslant 8.0$	(20)
p-MeO-$C_6H_4CO{-}O\cdot$	Styrene	60	0.022	(52)
	Styrene	80	0.053	(52)
	Vinyl acetate	60	0.05	(3)
	Me methacrylate	60	0.16	(3)
	Me methacrylate	80	0.39	(3)
	Acrylonitrile	60	$\geqslant 1.8$	(3)
m-MeO-$C_6H_4CO{-}O\cdot$	Styrene	60	0.3	(55)
	Styrene	80	0.6	(55)
m-Br-$C_6H_4CO{-}O\cdot$	Styrene	60	>0.3	(57)
	Styrene	80	>0.5	(57)
3,5-di-Br-4-MeO-$C_6H_2CO{-}O\cdot$	Styrene	60	>0.06	(57)
	Styrene	80	>0.4	(57)

$$C_6H_5{-}CO{-}O\cdot \xrightarrow{k_1} C_6H_5\cdot + CO_2 \tag{13}$$

$$C_6H_5{-}CO{-}O\cdot + CH_2{=}CXY \xrightarrow{k_2} C_6H_5{-}CO{-}O{-}CH_2{-}\dot{C}XY \tag{14}$$

As the concentration of monomer is reduced, more benzoyloxy radicals will lose CO_2 *via* reaction 13 before they can be captured by monomer (reaction 14). The fraction x may be expressed as

$$x = \frac{k_2[C_6H_5CO{-}O\cdot][M]}{k_1[C_6H_5CO{-}O\cdot] + k_2[C_6H_5CO{-}O\cdot][M]} \tag{15}$$

where $[C_6H_5CO{-}O\cdot]$ is the stationary concentration of benzoyloxy radicals and [M] is the concentration of monomer, so that

$$\frac{1}{x} = \frac{k_1}{k_2[M]} + 1 \tag{16}$$

Since k_1 is almost certainly independent of the nature of the monomer, Fig. 1 gives a clear picture of the relative reactivities of different monomers toward the benzoyloxy radical, 2,5-dimethylstyrene being the most reactive monomer and acrylonitrile the least reactive monomer investigated. These differences are expressed quantitatively in Table I.

Similar studies to those described above have been carried out with p,p'-dimethoxydibenzoyl peroxide (3, 52, 54), m,m'-dimethoxydibenzoyl peroxide (55), m,m'-dibromodibenzoylperoxide (57), and di(3,5-dibromo-4-methoxy)dibenzoyl peroxide (57, 60). The conclusions to be drawn from these studies are that electron-donating groups (MeO–) increase the stability of the aroyloxy radical while electron-withdrawing groups (Br–) decrease stability in accordance with accepted views on aromatic reactivity.

In general, the methoxy-substituted peroxides behave normally, in the sense that they do not take part in complicating side reactions, the effect of p-substitution on the stability of the aroyloxy radical being much more marked than that of m-substitution. On the other hand, the bromine-substituted peroxides appear to engage in transfer reactions which render the determinations of k_1/k_2 uncertain. The main evidence for these transfer reactions was nonlinearity of plots of reciprocal kinetic chain length $1/\nu$ against rate of polymerization R_p. At high initiator concentrations, more initiator fragments appeared in the polymer than were expected from the low values of ν, and also the value of x increased. These observations indicate that transfer occurred either by abstraction of an atom from the initiator or by an induced decomposition such as reaction 17.

$$M_n\cdot + (ArCO{-}O{-})_2 \rightarrow M_n{-}O{-}COAr + ArCO{-}O\cdot \tag{17}$$

Radical-induced decompositions such as reaction 18

$$M_n{-}CH_2{-}CH(C_6H_5) + (ArCO{-}O{-})_2 \rightarrow M_n{-}CH{=}CH(C_6H_5) + ArCO{-}OH + ArCO{-}O\cdot \tag{18}$$

were rejected since they would not cause the observed dependence of x upon initiator concentration.

So far discussion has related to peroxides undergoing thermal decomposition. When the dissociation into radicals is promoted photochemically there is evidence of a change in the mechanism whereby aryl radicals are generated (54). Either (i) aroyloxy radicals are generated in an unstable, electronically excited state which loses CO_2 very rapidly before reaction with monomer can occur or (ii) an electronically excited peroxide molecule dissociates directly into aryl radicals. Either situation can be represented by equation 19, where $y < 1$.

$$C_6H_5CO{-}O{-}O{-}COC_6H_5 \xrightarrow{h\nu} 2(1-y)C_6H_5CO{-}O\cdot + 2yC_6H_5\cdot + 2yCO_2 \tag{19}$$

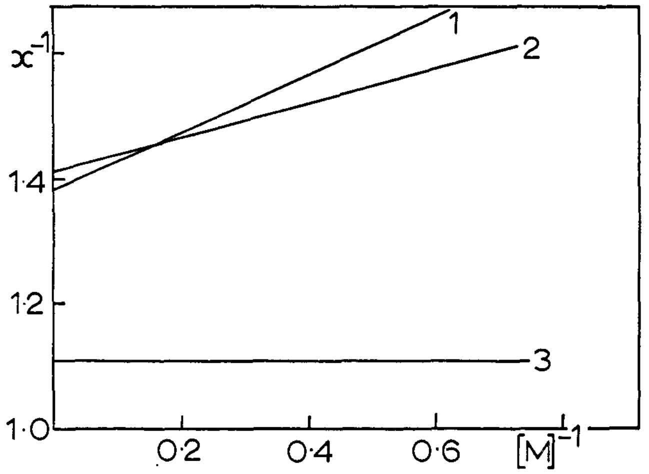


FIG. 2.—Photolysis of aroyl peroxides in the presence of styrene: 1, dibenzoyl peroxide at 40°; 2, dibenzoyl peroxide at 25°; 3, *p,p'*-dimethoxydibenzoyl peroxide at 25°.

An expression analogous to equation 16 may then be derived as

$$\frac{1}{x} = \frac{1}{1 - y} + \frac{k_1}{k_2[\mathrm{M}](1 - y)} \tag{16a}$$

where k_1 and k_2 refer to reactions 13 and 14 as before. If y is zero, as with thermal decomposition, equation 16a reduces to equation 16. However, for the photochemically initiated polymerization of styrene at 25° and 40°, plots of $1/x$ against $1/[\mathrm{M}]$ (Fig. 2) yield values of $y = 0.29$, $k_1/k_2 = 0.21$, and $y = 0.3$, $k_1/k_2 = 0.25$, respectively. The fraction y is independent of temperature as would be expected if production of phenyl radicals resulted from electronic excitation of the initiator molecule. Further, in an Arrhenius plot of log k_1/k_2 against $1/T$ for the benzoyl peroxide–styrene system, the values obtained at 60° (47), and 80° (50), and values obtained during photolysis at 25 and 40° fall on a reasonably straight line, which suggests that benzoyloxy radicals formed photochemically are not in an excited state but behave in the same way as radicals produced thermally. Thus, the available evidence seems to favor production of phenyl radicals by direct electronic excitation of the peroxide molecule.

Photo-initiation of methyl methacrylate *via* benzoin methyl ether remains obscure. Earlier experiments indicated that the most probable locus for free radical formation was the carbonyl group, though the mechanism of polymerization initiation was not resolved. Attempts to solve the problem using benzoin methyl-C^{14} ether were only partially successful when it was found that under the conditions used, 12.3–14.7 labeled groups were combined per average polymer molecule (156). Normal copolymerization was ruled out by the fact that polymer produced by thermal initiation using AIBN contained no radioactivity, thus the observations were consistent with either a diradical initiation followed by predominant termination by combination or copolymerization of "excited" benzoin molecules. Kinetics, and the fact that some termination by disproportionation is known to occur in methyl methacrylate polymerization, favor the latter explanation, but the problem certainly merits further examination.

The nature of the initiating species in the polymerization of styrene using di-*t*-butyl peroxide at 80° and 130° has been investigated (2, 59). The problem is very similar to that of the diaroyl peroxides in that the initial dissociation products of di-*t*-butyl peroxide, *t*-butoxy radicals, may undergo subsequent decomposition into methyl radicals and acetone (reactions 20 and 21).

$$(\mathrm{CH_3})_3\mathrm{C{-}O{-}O{-}C(CH_3)_3} \rightarrow 2(\mathrm{CH_3})_3\mathrm{C{-}O}\cdot \tag{20}$$

$$(\mathrm{CH_3})_3\mathrm{C{-}O}\cdot \rightarrow \mathrm{CH_3}\cdot + (\mathrm{CH_3})_2\mathrm{CO} \tag{21}$$

Use of methyl-labeled and *t*-carbon-labeled peroxides established that initiation is chiefly by *t*-butoxy radicals except at low concentrations of styrene and high temperatures. When cyclohexane or dimethylformamide were used as diluents, initiation tended to be by an indirect process in which the primary radicals abstracted hydrogen from the solvent to give the initiating species. Thus, much less radioactivity appeared in the polymer. One other point discussed was the effect of isotopic substitution on the rate of reaction 21. It was estimated that the rate of rupture of a C^{12}–C^{14} bond was about 7% less than the rate for a C^{12}–C^{12} bond. This value for the isotope effect, however, must be regarded as approximate.

Finally, it is of interest to consider radical polymerization initiated thermally in the absence of added initiator. For styrene a plausible mechanism has been postulated which involves a termolecular initiation step (reaction 22) (151).

$$\begin{gathered}
2\mathrm{CHPh{=}CH_2} \rightarrow \mathrm{\dot{C}HPh{-}CH_2{-}CH_2{-}\dot{C}HPh} \\
\mathrm{\dot{C}HPh{-}CH_2{-}CH_2{-}\dot{C}HPh} + \mathrm{CHPh{=}CH_2} \rightarrow \\
\mathrm{CHPh{=}CH{-}CH_2{-}\dot{C}HPh} + \mathrm{CH_3{-}\dot{C}HPh}
\end{gathered} \tag{22}$$

Reaction 22 must now be regarded with suspicion since it has been shown that styrene-β-$\mathrm{H}^2{}_2$ polymerizes at exactly the same rate as undeuterated styrene. Consequently the rate-determining step cannot involve hydrogen transfer from the 2-position (110).

2. *Free Radical Polymerization in Aqueous Media*

Several groups have attempted to study the initiation process in aqueous polymerization but, strangely, almost the only initiator used has been sulfur-35-labeled persulfate. Systems tend to be experimentally difficult, and consequently, the results obtained are less conclusive than those of the preceding section. Thus, in the absence of detergent, considerable difficulty was experienced when attempts were made to reproduce earlier experiments (134).

Thermal polymerization of styrene using labeled persulfate at temperatures from 30–70° yielded polymers containing approximately two sulfur atoms per polymer molecule except where very high molecular weight polymer was obtained when the number of combined sulfur atoms decreased. This effect was interpreted in terms of the termination reaction rather than the initiation process (134, 192, 193). Though not specified the initiation species are presumably sulfate radical ions produced by decomposition of persulfate (reaction 23).

$$S_2O_8^{-2} \rightarrow 2SO_4^{-}\cdot \qquad (23)$$

When an oxidation–reduction system (reaction 24) was used in the presence of a detergent, results were re-

$$S_2O_8 + Fe(II) \rightarrow SO_4^{-2} + Fe(III) + SO_4^{-}\cdot \qquad (24)$$

producible, and it was demonstrated that initiation efficiency was greatly improved though the detergent had no part in the initiation process (134).

An oxidation–reduction system consisting of perchlorate–bisulfite was used for the polymerization of vinyl chloride (95). Both components were labeled, respectively, with chlorine-36 and sulfur-35, and it was found that fragments from both became bound in the polymer. The S^{35} content was found to be some four times the Cl^{36} content and was explained in terms of the mechanism (reactions 25 and 26).

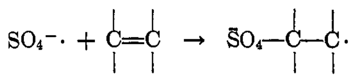
$$SO_3^{-2} + \text{oxidant} \rightarrow \cdot SO_3^{-} + \text{oxidant}^{-} \qquad (25)$$

$$\cdot SO_3^{-} + CHCl{=}CH_2 \rightarrow \dot{C}HCl{-}CH_2{-}SO_3^{-} \qquad (26)$$

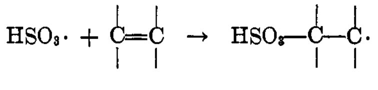
However, only one tenth of the bound Cl^{36} originated in the hypochlorite intermediate formed during the reaction; hence, most of the bound chlorine enters the polymer molecule *via* unidentified species.

Acrylonitrile has been polymerized at 60° using persulfate-S^{35} initiator. Conditions were varied to give polymers with molecular weights varying from 1.67×10^4 to 9.9×10^4, and in all cases the number of initiator fragments per polymer molecule was about 0.9 (204). When the oxidation–reduction system persulfate–bisulfite was used with either $K_2S^{35}{}_2O_8$ or $NaHS^{35}O_3$ the results were more complex (204), both sulfonate and sulfate groups appeared in the polymer (reactions 27–29), and the proportion of sulfonate

$$S_2O_8^{-2} + HSO_3^{-} \rightarrow SO_4^{-2} + SO_4^{-}\cdot + HSO_3\cdot \qquad (27)$$



$$SO_4^{-}\cdot + C{=}C \rightarrow \bar{S}O_4{-}C{-}C\cdot \qquad (28)$$



$$HSO_3\cdot + C{=}C \rightarrow HSO_3{-}C{-}C\cdot \qquad (29)$$

groups to sulfate groups increased with increasing monomer concentration. This ratio was measured by comparing the specific activity of the initial sulfur in the radioactive initiator component with the specific activity of the sulfur isolated from the polymer. The latter specific activity was lower by a factor dependent upon the contribution of the unlabeled species in the initiation reaction. At high monomer concentrations, the ratio approached the theoretical 1:1 but side reactions such as reaction 30 caused a reduction in the

$$M_n\cdot + HSO_3^{-} \rightarrow M_nH + SO_3^{-}\cdot \qquad (30)$$

number of sulfonate groups at low monomer or high bisulfite concentrations.

Persulfate initiation of chloroprene polymerization was investigated using S^{35}-labeled initiator, and combined S^{35} was located in the polymer. However, the quantity of combined S^{35} varied considerably and as the authors indicate was subject to various uncertainties, not least of which was the removal of uncombined inorganic persulfate residues without hydrolysis or ester interchange of the combined sulfate groups. Also, the possibility of initiation by hydroxyl radicals, formed by reaction of persulfate with water (reaction 31), cannot be excluded (155). Indeed, a study of the

$$SO_4^{-}\cdot + H_2O \rightarrow H^{+} + SO_4^{-2} + \cdot OH \qquad (31)$$

polymerization of tetrafluoroethylene provides definite evidence that such complications can arise; polymerization initiated by persulfate-S^{35} activated thermally or by reaction with ferrous ions or bisulfite yielded polymer with no combined S^{35}. Thus either initiation was *via* hydroxyl radicals or bound perfluoroalkyl sulfuric ester groups were rapidly hydrolyzed during the polymerization and subsequent isolation of the polymer. When labeled bisulfite was used, however, some S^{35} became bound with the polymer and could not be hydrolyzed off again, presumably because it was present as sulfonate groups (30).

Most of the work discussed in this section is subject to the uncertainties described above and there is considerable scope for further quantitative investigation.

3. Ionic and Stereoregular Polymerization

Labeled initiators have been used in homogeneous anionic and cationic polymerizations and labeled Ziegler type catalysts have also been studied.

Grignard reagents are thought to initiate polymerization *via* an anionic mechanism, but their mode of action is complex and not fully understood. However, when methyl methacrylate polymerization was initiated with butylmagnesium bromide-Br^{82}, bromine was shown to be attached to the polymer (138). Also, phenyl-C^{14} groups were found in polystyrene prepared using phenyl-C^{14}-magnesium bromide and titanium tetrachloride or butyl orthotitanate as initiator (4).

Bromine-82-labeled stannic bromide was used to initiate cationic polymerization of styrene at −5° and at 25°, and activity was said to be combined with the polymer (138). In view of our present knowledge of cationic polymerization, however, it seems unlikely that the bromine was introduced during initiation. Most probably bromination of the formed polymer occurred. Confirmation of this view was obtained when antimony-124 pentachloride was used to initiate styrene polymerization at 25° and no radioactivity was found in the polymer (84). In these experiments, the important role of co-catalysts was not determined; however, water was definitely shown to have some part in the initiation of polymerization of isobutene gas by boron trifluoride (85). Deuterated water was used as co-catalyst, and deuterium was found to be combined in the polymer, presumably entering *via* reaction 32. Similarly, it was shown that when D_2O was used as

$$BF_3OD^-D^+ + CH_2{=}C(CH_3)_2 \rightarrow CH_2D{-}\overset{+}{C}(CH_3)_2BF_3OD^- \quad (32)$$

co-catalyst in the stannic chloride-initiated polymerization of α-methylstyrene the resultant polymer contained C–D linkages (86).

More recently, methyl-C^{14} chloride has been used as solvent for the aluminum trichloride-initiated polymerization of isobutene. Approximately one polymer molecule in four had a labeled methyl group attached indicating the importance of the solvent as a co-catalyst (reaction 33). A likely termination reaction in this

$$C^{14}H_3{}^+AlCl_4^- + CH_2{=}C(CH_3)_2 \rightarrow C^{14}H_3{-}CH_2{-}\overset{+}{C}(CH_3)_2AlCl_4^- \quad (33)$$

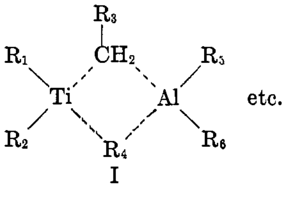
system is chain transfer to monomer which accounts for the polymer chains with no bound carbon-14 (128). Similar work using boron trifluoride etherate-C^{14} to initiate isobutylvinyl ether polymerization has established that the complexing ether has some role in the initiation process (reaction 34). However, since only 0.7% of the polymer molecules contained a labeled end

$$BF_3OR^-R^+ + CH_2{=}CH(OR') \rightarrow R{-}CH_2{-}\overset{+}{C}H(OR')BF_3OR^- \quad (34)$$

group, the paramount role of chain transfer to monomer must be conceded (129).

In the vast field of Ziegler catalysts, Natta and his group have used tracers to examine the polymerization of propene in the presence of triethylaluminum and the crystalline α-form of titanium trichloride (165, 172). Consequently, only Natta's mechanism is discussed here. For a fuller discussion of the relative merits of various suggested mechanisms the reader is referred to a recent review (25).

According to Natta the process is a coordinated anionic type. An electron-deficient initiator complex containing a transition metal has the tendency to attract olefin molecules whose π-electrons tend to compensate the deficiency of electrons in the complex. The structure may be loosely represented as I.

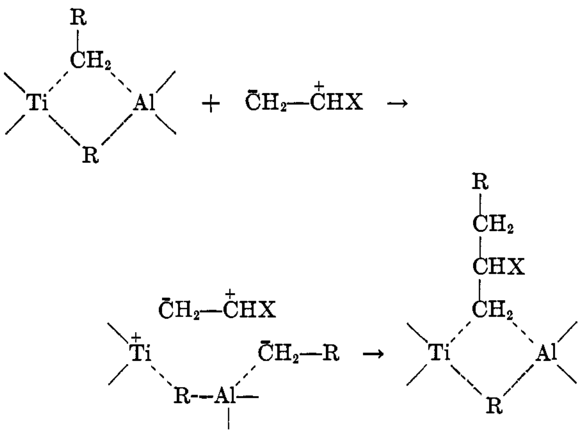


I

In the first stage, an olefin molecule is strongly polarized by the catalyst (reaction 35). At the same time an ionic dissociation of a bridge bond in I takes place and

$$CH_2{=}CHX \rightarrow \bar{C}H_2{-}\overset{+}{C}HX \quad (35)$$

the monomeric unit is introduced between the electronegative CH_2 and the electropositive metal (reaction 36). Subsequently the complex bond of the aluminum



(36)

ion shifts from the carbanion which is now part of a polymer chain to the carbanion on the newly added monomeric unit, as shown, and then the process repeats along the propagation sequence.

The above mechanism requires that alkyl groups originally present in the catalyst should appear as terminal groups on the polymer chains, and this has been demonstrated by use of triethyl-C^{14}-aluminum in propene polymerization (162). Very similar results were obtained when diethyl-C^{14}-aluminum chloride was used, and it was demonstrated that all the active sites present were utilized initially (163). Radiochemical determination of the number of alkyl groups present in the organometallic complexes adsorbed on $TiCl_3$ allowed estimation of the active centers present. The number of active centers varied from 0.3 to 1.0 mole % per mole of $TiCl_3$ dependent upon the type of aluminum compound. The value was independent of temperature (below 60°) but two types of adsorption were detected: the first was reversible and played no part in initiation, and the second was irreversible and was responsible for the polymerization process (164). Reaction 36 is definitely the subject of controversy (25), but there is no doubt that alkyl groups become chemically bound in the polymer. This was confirmed when a soluble catalyst consisting of bis(cyclopentadienyl)titanium dichloride and dimethyl-C^{14}-aluminum chloride was used to initiate polymerization of ethylene (83). Also, the duality of alkyl groups in the complex has been confirmed in a study of the reaction between titanium trichloride and trimethylaluminum, trimethyl-H^2_9-aluminum, or trimethyl-C^{14}-aluminum. It was shown that the proportion of CH_3- groups which do exchange is 0.43 of the total hydrolyzable carbon present in the complex, and that the nonexchangeable carbon must have the empirical composition CH since the over-all composition of the hydrocarbon groups is CH_2 (181).

B. RATES OF INITIATION

For free radical initiation according to equations 1 and 2 the rate of initiation is given by equation 37

$$R_i = R_p/\nu \qquad (37)$$

where R_p is the rate of polymerization and ν is the kinetic chain length. Various methods have been used to determine R_i but all are subject to uncertainties which are not readily disposed of. The labeled initiator method is no exception to this, but in many instances it is probably the best method available. The principle of the method is quite simple. According to equation 9 a kinetic chain is initiated by the addition of an initiator radical to monomer; therefore, the number of monomers reacting as a result of this primary event is the kinetic chain length. Thus, ν is readily obtained by using a radioactive initiator of known specific activity and determining the specific activity of a portion of the resultant purified polymer. The method requires no knowledge of the mode of termination (combination or disproportionation) or of the existence of transfer to monomer, polymer, or solvent. The essential conditions are: (i) initiation must be solely by addition of the radicals R· to the monomer double bond, *i.e.*, no initiation by hydrogen abstraction or by direct thermal, photochemical, or radiochemical means; (ii) other reactions of the initiator with polymer molecules or radicals must be negligible; and (iii) there must be no loss of low molecular weight polymer molecules during the removal of uncombined initiator. In practice it is often possible to satisfy these conditions or to apply small corrections when necessary (15, 33).

Even when transfer to initiator or induced decomposition becomes appreciable, it has been found possible to obtain reliable values for R_i by using mixtures of initiators. The method depends upon the observation that the rate and efficiency of initiation by AIBN are unaffected by the addition of peroxide initiators to the system (60). Thus, susceptibility to transfer of a labeled initiator may be revealed by maintaining its concentration and that of the monomer constant, while increasing the concentration of a second unlabeled initiator (AIBN) through a series of experiments. As the stationary concentration of polymer radicals increases, so do the number of transfer events, and the apparent rate of initiation (R_i') increases (Fig. 3). The intercept on the R_i' axis represents the unattainable conditions where the concentration of $[M_n\cdot]$ radicals is zero, hence transfer is nonexistent, and gives the true value of R_i. It is of interest to note that di(3,5-dibromo-4-methoxy)dibenzoyl peroxide-C^{14} undergoes considerable induced decomposition during styrene polymerization but not during methyl methacrylate polymerization. For methyl methacrylate, k_p (equation 3) is approximately four times that for styrene, but, even allowing for this, there is still a remarkable difference in reactivity between the two types of polymer radical (60).

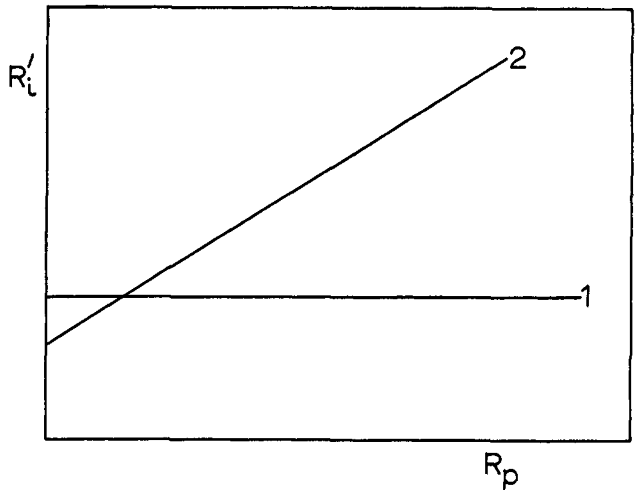


Fig. 3.—Apparent rates of initiation: 1, for an initiator not susceptible to transfer; 2, for an initiator undergoing transfer.

C. INITIATOR EFFICIENCIES

If the rate of initiation has been measured and the rate constant for decomposition of the initiator k_d (equation 1) is known, then it is a simple matter to calculate the initiator efficiency f from equation 38 where [I] represents the concentration of initiator and

$$R_i = 2fk_d[I] \qquad (38)$$

f is the fraction of initiator radicals produced which initiate polymerization.

Before the advent of the radioisotope method for determination of R_i, erroneous values of R_i had led to the conclusion that initiator efficiencies close to unity obtained for both benzoyl peroxide and AIBN in either methyl methacrylate or styrene. Subsequently it has been shown that, with the azo compound in particular, such high efficiencies are extremely unlikely (Table II). Low efficiencies in bulk polymerization may be explained in terms of a cage effect, wherein pairs of primary initiator radicals react with each other before they have diffused out of their cage of surrounding molecules. The products of these wasteful side reactions are present in extremely minute quantities, but if they are labeled, they are conveniently measured by isotope dilution procedures (2, 37, 38, 40). Such studies confirm the low efficiency of AIBN as an initiator, and it has further been shown that even the free-radical scavenger diphenylpicrylhydrazyl (DPPH) is unable to interrupt reactions within a cage (41, 43). Thus, rates of decomposition (k_d, equation 1) are likely

TABLE II

RATES AND EFFICIENCIES OF INITIATION MEASURED BY TRACER METHODS

Initiator	Monomer^{a}	Temp., °C.	R_i/[I] (× 10^6)	f	Ref.
AIBN	St	50	...	0.70	(10)
AIBN	St	50	3.06	0.52	(115)
AIBN	St	50	2.70^{b}	0.50^{b}	(115)
AIBN	St	50	2.24^{c}	0.55^{c}	(115)
AIBN	St	50	1.98^{d}	0.51^{d}	(115)
AIBN	St	60	14.2	0.61	(40)
AIBN	St	60	12.5	...	(59, 60)
AIBN	St	60	11.6	0.48	(36)
AIBN	St	60	15.3	0.64	(38)
AIBN	St	60	15	0.7	(72)
AIBN	St	66	...	0.80	(10)
AIBN	St/MM	60	10.9	0.46	(36)
AIBN	St/BA	60	11.2	0.52	(33)
AIBN	St/BA	60	12	0.6	(72)
AIBN	*p*-MeOSt	60	12.3	0.54	(16)
AIBN	*p*-ClSt	60	14.4	0.61	(16)
AIBN	MM	50	...	0.56	(10)
AIBN	MM	60	10.2	0.43	(36)
AIBN	MM	60	12.4	0.52	(38)
AIBN	MM	60	11.7	0.50	(15)
AIBN	MM	77	...	0.63	(10)
AIBN	AN	50	...	1.03	(10)
AIBN	AN	60	12.4	0.47^{e}	(56)
AIBN	AN	60	12.0	0.50^{f}	(56)
AIBN	BA	60	11	0.5	(72)
AIBN	VA	50	..	0.72	(10)
AIBN	VC	50	...	0.74	(10)
AIBN	VC	50	3.60	1.0	(89)
AIBN	MM/MA	60	g	g	(66)
Dibenzoyl peroxide	St	60	3.87	h	(49)
Dibenzoyl peroxide	St	60	4.0	h	(47)
Dibenzoyl peroxide	St	60	4.7	h	(1)
Dibenzoyl peroxide	St	60	4.56	(0.75)^{i}	(14, 15)
Dibenzoyl peroxide	St	80	51.0	h	(50)
Dibenzoyl peroxide	MM	60	3.63	h	(49)
Dibenzoyl peroxide	MM	60	5.15	(0.82)^{i}	(14, 15)
Dibenzoyl peroxide	VA	60	5.09	h	(20)
Di(4-MeO-benzoyl) peroxide	St	60	10.9	h	(52)
Di(4-MeO-benzoyl) peroxide	St	80	139	h	(52)
Di(4-MeO-benzoyl) peroxide	MM	60	10.8	h	(3)
Di(4-MeO-benzoyl) peroxide	MM	80	166	h	(3)
Di(4-MeO-benzoyl) peroxide	VA	60	16.0	h	(3)
Di(3-MeO-benzoyl) peroxide	St	60	5.20	h	(55)
Di(3-MeO-benzoyl) peroxide	St	80	61.0	h	(55)
Di(3-Br-benzoyl) peroxide	St	60	2.2^{j}	h	(57)
Di(3-Br-benzoyl) peroxide	St	80	24.4^{j}	h	(57)
Di(3,5-diBr-4-MeO-benzoyl) peroxide	St	60	1.22^{j}	h	(57)
Di(3,5-diBr-4-MeO-benzoyl) peroxide	St	80	18.8^{j}	h	(57)
Di(3,5-diBr-4-MeO-benzoyl) peroxide	St	60	2.04	h	(59)
Di(3,5-diBr-4-MeO-benzoyl) peroxide	St	60	1.88	h	(60)
Di(3,5-diBr-4-MeO-benzoyl) peroxide	MM	60	2.04	h	(59)
Di(3,5-diBr-4-MeO-benzoyl) peroxide	MM	60	1.88	h	(60)
Di-*t*-butyl peroxide	St	80	15.6^{k}	h	(2)
Di-*t*-butyl peroxide	St	130	60.9^{k}	h	(2)
2-Cyano-2-propyl-azoformamide	St	100	21.6	1.0	(63)

[a] St = styrene, *p*-MeOSt = *p*-methoxystyrene, *p*-ClSt = *p*-chlorostyrene, MM = methyl methacrylate, BA = butyl acrylate, AN = acrylonitrile, VA = vinyl acetate, VC = vinyl chloride, MA = maleic anhydride. [b] In bromobenzene. [c] In benzene, toluene, or pyridine. [d] In dioxane. [e] Homogeneous in dimethylformamide. [f] Heterogeneous in benzene. [g] Varies with monomer feed. [h] Assumed $f = 1$, see text. [i] Calculated using $k_d = 3.2 \times 10^{-6}$ sec.$^{-1}$ (197). [j] Estimated by comparison with dibenzoyl peroxide. [k] Assuming no initiation *via* hydrogen abstraction.

to be underestimated if these rates are measured by following the rate of decoloration of DPPH solutions.

With regard to peroxide initiators, the position is not fully explored, through circumstantial evidence suggests that efficiencies close to one are obtained. Thus, carbon dioxide formation can be almost completely suppressed by the presence of radical scavengers which cannot suppress the cage reactions of AIBN, and it is argued, therefore, that cage reactions are unlikely to operate (19, 47). Compelling though this argument is, the experimental facts, relating to dibenzoyl peroxide only, are not entirely convincing, particularly when applied to other peroxides. It may be significant that values of k_d obtained from equation 38, using values of R_i from Table II, and assuming $f = 1$, are often appreciably lower than other values reported in the literature. This difference is probably due to incomplete suppression of induced decomposition when working at the higher concentrations required for conventional analysis, but more facts are required.

Independent checks on the efficiency of peroxide initiators *via* isotope dilution analysis for decomposition products have not yet been reported except in the rather special case of di(benzoyl-4-H^3) peroxide decomposition in cyclohexane at 91° (198). Styrene was used to suppress induced decomposition, and it was found that, for styrene concentrations in the range 0.0–0.12 *M*, the yield of benzoic acid remained constant at 0.5 mole per mole of peroxide. Evidently styrene cannot compete with cyclohexane for benzoate radicals under these conditions. In the same experiments, yields of benzene, phenyl benzoate, and biphenyl increased with 0.0 to 0.015 *M* styrene but decreased with 0.015 to 0.12 *M* styrene. At concentration of 0.015 *M* styrene, over 92% of the phenyl groups of the peroxide were accounted for in the four stated products. Clearly the major initiating species for styrene polymerization are cyclohexyl radicals. However, the main point to be made is that even in the moderately reactive solvent cyclohexane, phenyl benzoate and biphenyl were formed. Furthermore, their yields were independent of peroxide concentration and extent of reaction at a 5:1 styrene–peroxide ratio—strong evidence for the occurrence of cage reactions. The fall in yield of phenyl benzoate and biphenyl was much less than that of benzene with increasing styrene concentration, which may be explained in terms of a more effective competition between styrene and cyclohexane for phenyl radicals outside the cage. Clearly, the conditions were not strictly comparable with normal polymerizations where monomer concentrations range from 1 to 9 *M* and reactive solvents are absent. In inert solvent, it has been clearly demonstrated that initiator efficiency falls off rapidly below monomer concentrations of about 1 *M* (72) and that initiator radicals from AIBN are wasted in reactions outside the cage (Table III) (40). At present, therefore, the importance of cage reactions during peroxide initiation requires further definition.

TABLE III

INITIATOR EFFICIENCY IN THE AIBN-INITIATED POLYMERIZATION OF STYRENE AT 60° (40)

Monomer concn., moles/l.	Efficiency (*f*)
6.17	0.64
4.18	0.63
2.32	0.68
0.86	0.57
0.37	0.52
0.20	0.52
0.08	0.38
0.015	0.17

IV. PROPAGATION

The propagation reaction 3 has not been extensively studied by tracer methods, though a few isolated observations have been made. Perhaps the most interesting work was a demonstration of the reversibility of this step (reaction 39)

$$M_n\cdot \xrightarrow{k_{-p}} M_{n-1}\cdot + M \tag{39}$$

This reaction has an activation energy of about 20 kcal./mole compared with 5 kcal./mole for the forward reaction; its importance therefore, increases rapidly as the temperature of polymerization is raised. Thus, we arrive at the concept of a ceiling temperature where $k_p = k_{-p}$. For methyl methacrylate deviations from the expected kinetics are observed at temperatures above 100° (80), and at 125° it was shown that polymerization was probably reversible (140). Labeled polymethyl methacrylate was prepared from methyl-C^{14} methacrylate and the resultant polymer purified. Subsequently unlabeled monomer was polymerized in the presence of the labeled polymer, and at the end of the reaction period, residual monomer was isolated and found to contain activity. There is, however, a subtle distinction between depropagation of an unterminated kinetic chain and depolymerization of previously formed polymer which may also explain the formation of labeled monomer.

In solutions of low dielectric constant, the propagation step in ionic polymerization requires little or no energy of activation. The contrast between this and the 5 kcal./mole or so required for free-radical propagation is illustrated by a study of the magnitude of C^{12}–C^{14} isotope effects. The Bigeleisen equation (65) predicts that for two related reactions, the reaction with the lower activation energy will show the smaller isotope effect. This prediction is in accord with the experimental findings (Table IV).

TABLE IV

ISOTOPE EFFECTS IN POLYMERIZATIONS OF C^{14}-LABELED MONOMERS

Monomer	Initiator	Temp., °C.	$k_{p,14}/k_{p,12}$	Ref.
Styrene-β-C^{14}	Thermal	99	0.918	(117)
	Bz_2O_2	51	0.915	(117)
	Stannic chloride	25	0.950	(117)
	$TiCl_3/AlEt_3$	0	0.970	(169)
Styrene-β-C^{14}/maleic anhydride	Bz_2O_2	80	0.95	(117)
Styrene-α-C^{14}	Thermal	99	0.970	(117)
	Stannic chloride	25	1.00	(117)
Ethylene-C^{14}	$TiCl_3/AlEt_3$	0	0.966	(169)
Propylene-C^{14}	$TiCl_3/AlEt_3$	0	0.965	(169)

The higher value of $k_{p,14}/k_{p,12}$ for styrene–maleic anhydride copolymerization is also explainable in terms of a lower activation energy of propagation due to participation in the transition state of resonance structures in which electron transfer has occurred between radical and olefin.

The similarity between the values obtained for three monomers using the coordinated anionic catalyst is considered to be evidence that the same mechanism holds in each case. The additional similarity between these values and that for stannic chloride-initiated polymerization of styrene-β-C^{14} might possibly be cited as further evidence of the ionic nature of these polymerizations and as one more nail in the coffin for postulated mechanisms of Ziegler catalysis which involve free radicals.

The whole concept of stereospecific propagation has been queried and the suggestion made that isotactic polymers are merely linear, whereas atactic and syndiotatic polymers are branched. Isotactic polypropene was subjected to deuterium exchange on a nickel–kieselguhr catalyst and it was claimed that up to 18% of the tertiary carbon atoms were racemized without significant alteration of the nature of the polymer. Evidence for this racemization was given as the incorporation of up to 3% deuterium in the polymer (81). Stronger evidence is required if widely accepted ideas are to be modified, particularly since it has been elegantly demonstrated that *cis*-propene-1-H^2_1 and *trans*-propene-1-H^2_1 give different polymers, respectively, *threo*-diisotactic and *erythro*-diisotactic polypropenes, when polymerized on triethylaluminum–α-titanium trichloride (161).

V. TERMINATION

Tracer studies of the termination reaction in free radical polymerizations involve the use of labeled initiators. Many polymerizations show a dependence of the rate of polymerization on the square root of the initiator concentration, and kinetic analysis (96) establishes that polymer radicals are terminated by mutual reaction of pairs. Thus, if the polymer radicals were initiated *via* reaction 9 and then terminated by combination (reaction 4) or disproportionation (reaction 5), then polymer molecules would contain two initiator fragments or one initiator fragment, respectively. In general, the fraction $(2 - n)/n$, where n = the number of initiator fragments per polymer molecule, represents the fraction of radicals being terminated by disproportionation. The validity of this simple deduction is dependent upon several stringent requirements: (i) As stated previously, polymer radicals must terminate solely by reaction in pairs. (ii) Chain transfer reactions between polymer radicals and monomer, solvent, or initiator must not occur. Absence of significant amounts of such transfer reactions may be demonstrated by the fact that a plot of $1/\bar{P}_n$ against R_p has a negligible intercept and is not curved, since kinetic analysis predicts the dependence of number average degree of polymerization $\bar{P}_n$ upon R_p will follow equation 40.

$$1/\bar{P}_n = C_M + C_S[S]/[M] + (k_t/k_p)^2 R_p/[M]^2 + C_I(k_t/k_p^2 f k_d) R_p^2/[M]^2 \quad (40)$$

where transfer constants are defined by $C_M = k_{tr,M}/k_p$; $C_S = k_{tr,S}/k_p$; $C_I = k_{tr,I}/k_p$; and $k_t = k_{tc} + k_{td}$ (reactions 4 and 5); and M = monomer; S = solvent; I = initiator (96). (iii) Finally, initiation must be solely *via* reaction 9 as discussed previously in the section on rates of initiation.

It must be stressed here that studies of this sort are dependent upon accurate measurements of the rate of polymerization, specific activity of initiator, specific activity of pure polymer, *and* polymer number average molecular weight. The latter quantity is subject to the largest uncertainties and must be determined with care (5).

Early experiments in emulsion polymerization of styrene with persulfate-S^{35} indicated that styrene radicals terminate by combination (192, 193). As discussed earlier, however, these heterogeneous systems are experimentally difficult and rigorous kinetic analysis was not undertaken. For homogeneous polymerizations, the initiator AIBN is ideal since it is not susceptible to induced decomposition and initiates solely *via* reaction 9. It is unfortunate, therefore, that the first attempt to utilize AIBN-C^{14} in a study of the termination reaction led to an erroneous conclusion (10), which has justifiably been criticized (32). Subsequently the method has been used with considerable success in several investigations, though the need to satisfy the above requirements, or establish satisfactory corrections in lieu, has not always been appreciated.

There is now no doubt that polystyrene free radicals terminate exclusively by combination at temperatures up to 60° (14, 15, 32, 36, 99, 112, 134). Similarly it has been clearly demonstrated that polymethyl methacrylate radicals undergo substantial disproportionation, and that the importance of disproportionation increases with increasing temperature (5, 14, 15, 32, 36, 184, 185). There has, however, been slight disagreement as to the extent of disproportionation which undoubtedly arises from differences in interpretation of osmotic pressure data (5). It has been suggested that $\bar{M}_n$ determinations on unfractionated polymers are subject to errors which can be avoided if the polymer is first fractionated (184, 185). Determination of $\bar{M}_n$ of sharp fractions is more precise, but it is then necessary to allow for the fact that high molecular weight fractions contain more molecules formed by combination while low molecular weight fractions contain more molecules formed by disproportionation, and it seems debatable whether any over-all gain in precision is achieved.

For copolymerization of styrene and methyl methacrylate it was shown that a cross-termination reaction was highly favored and that this reaction was almost exclusively one of combination (36).

In the case of acrylonitrile it has been inferred that in homogeneous polymerizations at 60°, termination is predominantly by combination (56), and this has been confirmed in a study which made due allowance for the fact that chain-transfer reactions were important (18). On the other hand, polymerization of acrylonitrile in water using persulfate-S^{35} initiator yielded polymers with $n \simeq 0.9$ over a range of molecular weights from 1.67×10^4 to 9.9×10^4. These results were taken to mean that termination was exclusively by disproportionation, and no account was taken of possible chain-transfer reactions or other complicating features of this type of system (204).

Similar confusion exists in the case of vinyl chloride. Thus, it has been claimed that when polymerization is initiated with AIBN-C^{14} at 50°, 50% of the radicals terminate by combination and 50% by disproportionation. Graphs are given, however, which demonstrate the importance of chain transfer to monomer in accordance with the known behavior of this system (29). It must also be noted that the unlikely initiator efficiency, $f = 1$, was observed in this work (89). More plausible results were obtained using AIBN-C^{14} and dibenzoyl peroxide-di-*carboxyl*-C^{14} in bulk and suspension polymerization at 45° (179). The value of n was found to vary somewhat between 0.19 and 0.40, but it was clear that chain transfer was the main reaction governing the size of the molecule.

It has been claimed that polyvinyl acetate radicals terminate by disproportionation, but again no corrections were made for transfer reactions which seem highly probable with such reactive free radicals (99).

The possibility of termination of polymer radicals by primary radicals derived from the initiator has been considered for the styrene system only (112), and in the case of dibenzoyl peroxide-C^{14} it was clearly established that the combination reaction between polymer radicals and benzoyloxy radicals is insignificant except at low monomer concentrations and high peroxide concentrations (1).

In ionic polymerizations, acetic acid-H^3 and carbon dioxide-C^{14} have been used to deliberately terminate polymeric anions (reactions 41 and 42) (104, 107, 203). With this technique it was possible to show that methyl

$$M_n—\bar{C}HR + AcOH \rightarrow M_n—CH_2R + AcO^- \quad (41)$$

$$M_n—\bar{C}HR + CO_2 \rightarrow M_n—CHR—COO^- \quad (42)$$

methacrylate chains initiated by 9-fluorenyllithium or sodium naphthalene in tetrahydrofuran at −78° or in toluene at −50° and −78° retained their active ends for considerable periods after completion of polymerization. In other words additional support for the concept of "living polymers" was obtained, and it was shown that no new polymer chains were formed when additional monomer was polymerized by systems in which the initial polymerization was effectively complete. When styrene was the initial monomer the active chain ends would polymerize either more styrene or methyl methacrylate. On the other hand, polymethyl methacrylate anions would not polymerize styrene which acted as an inert diluent and did not terminate the chains. In the course of this work the isotope effect for hydrogen ion transfer k_H/k_T was estimated to be of the order of 1.58–1.73 and results had to be corrected accordingly. The possibility of CO_2 terminating two chains was disproved by comparison of molecular weights of polymers terminated with CO_2, Michler's ketone, and water (203). Similar techniques using ethanol-H^3, butanol-H^3, and $I^{131}{}_2$ were used to determine the active centers on Ziegler catalysts (64, 83, 94). There is some difference of opinion regarding the magnitude of the tritium isotope effect, and it seems plausible that this may vary from system to system. It should certainly never be ignored. The results obtained using $I^{131}{}_2$ with a soluble Ziegler catalyst established, somewhat unexpectedly, that the termination step was second order in active centers and that polymer chains reacted in pairs by disproportionation (83).

Ethylene-$H^2{}_4$ polymerized on a Ziegler catalyst consisting of triisobutylaluminum–titanium tetrachloride gave a polymer with identical viscosity to that of a polymer formed from unlabeled ethylene indicating that no isotope effect was operating in the termination step of this polymerization (130, 180). In contrast, isoprene-$H^2{}_8$ with a similar catalyst was found to polymerize faster and gave a higher molecular weight than unlabeled monomer (186). Three possible termination reactions have been proposed for this type of system (165) (reactions 43–45), and it would seem that

$$[cat]—(CH_2—CHR)_n—R' + AlR_3'' \rightarrow [cat]R'' + R_2''Al—(CH_2—CHR)_n—R' \quad (43)$$

$$[cat]—CH_2—CHR—(CH_2—CHR)_n—R' + CH_2{=}CHR \rightarrow [cat]—CH_2—CH_2R + CH_2{=}CR—(CH_2—CHR)_n—R' \quad (44)$$

$$[cat]—CH_2—CHR—(CH_2—CHR)_n—R' \rightarrow [cat]—H + CH_2{=}CR—(CH_2—CHR)_n—R' \quad (45)$$

in the two systems described these reactions have varying importance. Thus, the fact that no isotope effect is observed in the ethylene polymerization implies that reactions involving proton transfer (reactions 44 and 45) are less important than chain transfer with aluminum alkyl (reaction 43), while the reverse is true for isoprene polymerization.

VI. CHAIN TRANSFER

Termination of polymer chains *via* chain transfer (reaction 6) may occur if the chain ends are able to abstract a labile atom or group from initiator, monomer, polymer, solvent, or added impurities. Examples of chain transfer to initiator and to monomer have already been mentioned in earlier sections and examples of transfer to polymer will be discussed in section IX.

In certain polymerizations, transfer agents are deliberately added as "short-stops" to regulate the molecular weight of the polymer produced (155). Thiols are frequently used for this purpose in free radical polymerizations, and use of sulfur-35-labeled thiols has established that they become incorporated in the polymer (reactions 46 and 47) (134, 155). Clearly,

$$M_n\cdot + RSH \rightarrow M_nH + RS\cdot \quad (46)$$

$$RS\cdot + M \rightarrow M_1\cdot \text{ etc.} \quad (47)$$

intelligent use of thiols as short-stops requires a knowledge of the chain-transfer constant $k_{tr,RSH}/k_p$ for particular systems. A useful method for measurement of transfer constants using sulfur-35-labeled thiols has been described and realistically assessed. The tracer method enjoys its greatest advantage in systems having a high transfer constant and in which labeled reagent is readily prepared. On the other hand, systems with low transfer constants are best studied by molecular weight methods (210).

Measurement of the isotope effect in chain transfer reactions can be a useful test to determine the site of attack. Thus, both 2-propanol and 2-methyl-2-propanol act as transfer agents in styrene polymerization. However, the tertiary alcohol reacts at the hydroxyl hydrogen whereas the secondary alcohol reacts at the secondary hydrogen. This is clearly indicated from the results recorded in Table V (158).

TABLE V

CHAIN-TRANSFER CONSTANTS IN STYRENE POLYMERIZATION (158)

Transfer agent	Chain-transfer constants 100°	130°
2-Propanol	1.7×10^{-4}	2.7×10^{-4}
2-Propanol-H^2	1.6×10^{-4}	
2-Propanol-2-H^2	0.78×10^{-4}	
2-Methyl-2-propanol	5.0×10^{-5}	18×10^{-5}
2-Methyl-2-propanol-H^2	2.9×10^{-5}	7.8×10^{-5}

In the case of *n*-butanethiol-H^2 the isotope effect in styrene polymerization was found to be 3.8 at 70° and 4.0 at 60° showing that thiol hydrogen was involved in the transfer process (207). The transfer constant obtained for butanethiol at 60° was in good agreement with that recorded previously (210). Similarly, it was shown that degradative chain transfer to 1-naphthol in styrene polymerization occurs by abstraction of the hydroxyl hydrogen. The ratio of transfer constants for 1-naphthol and 1-naphthol-H^2 was 6.4 at 60° (105).

Isotope effect studies have also clarified the mechanism of degradative chain transfer in the polymerization of allyl acetate. Allyl-1-H^2 acetate was observed to polymerize two to three times as fast as allyl acetate and gave a polymer with a molecular weight 2.38 times that of the undeuterated monomer. These observations confirm that chain termination involves transfer of hydrogen from the 1-position (reaction 48) to give a resonance-stabilized allyl radical with reduced reactivity for initiation (22).

$$\begin{aligned} M_n\cdot + CH_2{=}CH{-}CH_2{-}OCO{-}CH_3 &\rightarrow \\ M_nH + CH_2{=}CH{-}\dot{C}H{-}OCO{-}CH_3 & \quad (48) \\ \updownarrow \qquad\qquad & \\ CH_2{-}CH{=}CH{-}OCO{-}CH_3 & \end{aligned}$$

In the stereoregular polymerization of propene, zinc diethyl has been shown to act as a chain-transfer agent, a few mmoles per liter causing a threefold drop in molecular weight. It was shown that zinc diethyl-C^{14} was consumed during polymerization and that C^{14}-labeled ethyl groups appeared in the polymer (reactions 49 and 50) (165, 167). Reaction 49 is analogous to the termination reaction 43 discussed earlier.

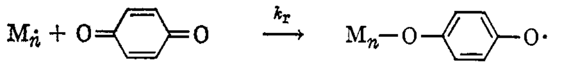
$$\begin{aligned} [\text{cat}]{-}(CH_2{-}CHMe)_nR + ZnEt_2 &\rightarrow \\ [\text{cat}]{-}Et + EtZn{-}(CH_2{-}CHMe)_nR & \quad (49) \\ [\text{cat}]{-}Et + CH_2{=}CHMe \rightarrow [\text{cat}]{-}CH_2{-}CHMe{-}Et & \quad (50) \end{aligned}$$

VII. RETARDATION AND INHIBITION

In section II it was stated that there is no sharp distinction between retardation and inhibition; the difference is one of degree and depends upon the reactivities and concentrations of different species in different systems. Thus, *p*-benzoquinone can act as either a retarder or a partial inhibitor[1] in methyl and ethyl methacrylate polymerizations, the transition occurring quite sharply at a critical concentration of quinone (100, 101). Similarly, under comparable conditions *p*-benzoquinone acts as a retarder for methyl methacrylate, as an inhibitor for styrene polymerizations, and has intermediate properties in styrene–methyl methacrylate copolymerizations (39, 42, 61). The specific role of the quinone has been investigated using *p*-benzoquinone-C^{14} and AIBN-C^{14}, and though much information was obtained which could not have been obtained by other means, there is scope for further investigation.

In styrene polymerization at 60° it was shown that the quinone was almost entirely consumed in the induction period and, though polymerization was not entirely suppressed during this period, the polymer formed had low molecular weight when compared with polymer formed afterward. At the end of inhibition, the rate of initiation and mode of termination were quite normal.

During the induction period, isotope dilution analysis showed that reaction between initiator radicals and quinone was of only minor importance, and about 90% of the quinone was incorporated into polymeric material. Thus, in this system the quinone acts largely by reaction with polymer radicals at an early state in their growth. Treatment of polymer molecules containing quinone residues with the specific reagent trifluoroacetic anhydride considerably reduced the C^{14} content of the polymers as a result of cleavage of ether linkages most probably formed *via* reaction 51. Other possible minor



(51)

reactions between polymer radicals and quinone were not investigated. Consideration of the initiator fragment–quinone residue balance led to the conclusion that removal of phenoxy radicals occurred almost entirely by combination with a polymer radical (reaction 52), but there was some evidence that a few

$$M_n{-}O{-}C_6H_4{-}O\cdot + M_n'\cdot \rightarrow M_n{-}O{-}C_6H_4{-}O{-}M_n' \quad (52)$$

phenoxy radicals could add to styrene leading to a small amount of copolymerization (42).

Similar studies of the retardation of methyl methacrylate polymerization by benzoquinone at 25 and 60° led to similar conclusions regarding the fate of the quinone and the phenoxy radicals, though at 60° some disproportionation reaction between phenoxy radicals and polymer radicals could be detected. In addition the tendency toward copolymerization was even less marked than with styrene (39). In the work described above, reaction between two phenoxy radicals (reaction 53) was discounted on the grounds that formation of

$$\begin{aligned} M_n{-}O{-}C_6H_4{-}O\cdot + \cdot O{-}C_6H_4{-}O{-}M_n' &\rightarrow \\ M_n{-}O{-}C_6H_4{-}O{-}O{-}C_6H_4{-}O{-}M_n' & \quad (53) \end{aligned}$$

the unstable peroxide linkage was unlikely (42).

---

[1] Classical definition regards an inhibitor as a substance which reacts with primary radicals until it is used up, then the chain reaction proceeds at a similar rate to reaction in the absence of inhibitor. Under this definition the substances discussed in this section are not truly inhibitors.

The fact that at higher concentrations of benzoquinone ($>3.2 \times 10^{-3}$ mole/l.) methyl methacrylate and ethyl methacrylate polymerizations show an induction period before retarded polymerization occurs has been cited as evidence that interaction with primary radicals must occur. This argument is reinforced by the observation that rates of initiation fall with increasing quinone concentration up to the point where inhibition is first observed. The rates observed at the end of the induction period are said to indicate that some of the adduct formed from initiator and quinone must subsequently decompose and initiate further chains. This led to the suggestion that initiator radicals react with quinone to form phenoxy radicals (reaction 51, where M_n is replaced by R) which combine to give a peroxide capable of subsequent decomposition and concomitant initiation (100, 101). It is not clear why phenoxy radicals formed originally should not react with monomer, while identical radicals formed by subsequent decomposition of the hypothetical peroxide should! Further, although in one experiment the concentration of quinone ($\sim 5 \times 10^{-3}$ mole/l.) was in excess of the initiator ($\sim 1.2 \times 10^{-3}$ mole/l.), the length of the induction period (~100 min.) was sufficient to account for less than 10% decomposition of the initiator. Thus at least 90% of the initiator was available to initiate the much retarded polymerization, and there seems little need to invoke the hypothetical peroxide to aid this initiation process. On the other hand, the peroxide, if formed, would subsequently yield radicals eminently suitable for termination of polymer chains.

The above criticism should not be taken as a categorical denial of the existence of products resulting from reaction between initiator radicals and quinone molecules, but rather should suggest that there is considerable scope for fuller investigation of these low molecular weight materials by specific reagent and isotope dilution procedures.

Some stable free radicals are inhibitors of polymerization and in the past have been used to evaluate rates of initiation from the length of the induction period they produced. The use of labeled reagents has shown that this technique is unreliable. Thus, diphenylpicrylhydrazyl is unable to scavenge all the free radicals produced by decomposition of AIBN. Further, about 10% of the hydrazyl is converted to the corresponding hydrazine. When styrene is polymerized in the presence of diphenylpicryl-C^{14}-hydrazyl, there is an induction period which roughly corresponds to full utilization of the hydrazyl, but subsequent polymerization is considerably retarded and C^{14} residues become combined with the polymer (41, 43). The stable free radical obtained by oxidation of N-(3-N-hydroxyanilino-1,3-dimethylbutylidene)aniline N-oxide behaves much more like an ideal inhibitor for styrene and methyl methacrylate, but again the stoichiometry of the reaction is uncertain (44).

The reduction products of the two stable free radicals discussed above, diphenylpicrylhydrazine and N-(3-N-hydroxyanilino-1,3- dimethylbutylidene)aniline N-oxide, were shown to be retarders for the polymerization of styrene, and when sufficient retarder was present each polymer molecule contained one initiator fragment and 0.5 retarder fragment. Possibly the mode of initiation was normal, and termination occurred *via* reactions 54 and 55, though it seems improbable that the system

$$M_n\cdot + HX \rightarrow M_nH + X\cdot \qquad (54)$$

$$M_{n'}\cdot + \cdot X \rightarrow M_{n'}X \qquad (55)$$

is as simple as this. Nevertheless, for certain cases, this work suggests an alternative method for measuring rates of initiation by using a labeled retarder instead of a labeled initiator (53).

Aromatic nitro compounds act as retarders or inhibitors of some polymerizations, and it has been shown that *m*-dinitrobenzene-C^{14} and picric acid-C^{14} become combined in polystyrene at 60°. Use of trifluoroacetic anhydride provided evidence that the nitro compounds were attached through C–O– linkages rather than C–C– linkages (58).

It has often been stressed that chemical purity is not the same as radiochemical purity and that it is essential to demonstrate that the latter is satisfactory. Infinitesimal amounts of impurity having high specific activity relative to the main compound can lead to completely misleading results in tracer experiments.

A classic example of misinterpretation resulting from radiochemical impurities is to be found in the retardation by "copolymerization" of benzene. Thus, when vinyl acetate was polymerized in the presence of benzene-C^{14} it was found that the C^{14} content of the resultant polymers required that about 20 benzene nuclei were combined in each polymer molecule (195, 196). Other workers claimed to demonstrate that even the unreactive styrene radical could attack benzene and found C^{14} activity equivalent to 17 benzene molecules per polystyrene molecule (113). Recently, however, these results were queried, particularly when it was found that retardation of vinyl acetate polymerization by chlorobenzene or *m*-dichlorobenzene could be explained in terms of a simple chain-transfer process. Careful examination of certain tracer experiments revealed that benzene-C^{14} prepared by catalytic trimerization of acetylene-C^{14} gave very similar results to those described above. However, a second sample of benzene-C^{14}, prepared by dehydrogenation of cyclohexane-C^{14} and rigorously purified by inclusion in extensive vinyl acetate polymerization followed by redistillation, failed to confirm these results (73). In fact, with radiochemically pure benzene-C^{14}, only about one molecule of benzene per polymer molecule was found (73, 114).

TABLE VI

MONOMER REACTIVITY RATIOS DETERMINED WITH THE AID OF LABELED MONOMERS

Monomer 1[a]	Monomer 2[a]	Initiator	Temp., °C.	r_1	r_2	Ref.
MM-C^{14}	Maleic anhydride	AIBN	60	3.46	0.03	(66)
MM-C^{14}	St	Bz_2O_2	60	0.46	0.52	(1)
MM-C^{14}	St	Bz_2O_2	60	0.49	0.53	(215)
St-C^{14}	MM	Bz_2O_2	60	0.46	0.48	(212)
St-C^{14}	MM	Bz_2O_2	132	0.60	0.55	(212)
St-C^{14}	EGDM	Bz_2O_2	60	0.35	0.65	(213)
St-C^{14}	*m*-DVB	Bz_2O_2	60	0.65	0.60	(213)
St-C^{14}	*p*-DVB	Bz_2O_2	60	...	...	(213)
St-C^{14}	*p*-MeSt	Bz_2O_2	60	0.83	0.96	(214)
St-C^{14}	*o*-MeSt	Bz_2O_2	60	0.90	0.81	(208)
St-C^{14}	*m*-MeSt	Bz_2O_2	60	0.83	0.93	(208)
St-C^{14}	*p*-MeSt	Bz_2O_2	60	1.02	1.21	(208)
St-C^{14}	*α*-MeSt	Bz_2O_2	60	0.71	0.14	(208)
St-C^{14}	2,5-diClSt	Bz_2O_2	70	0.38	1.77	(216)
St-C^{14}	2,5-diClSt	$TiCl_3/Al(i\text{-}Bu)_3$	70	1.0	1.0	(168)
St-C^{14}	2,5-diClSt	$TiCl_3/Al(i\text{-}Bu)_3$	40	0.90	1.15	(90)
St-C^{14}	*p*-*t*-BuSt	$TiCl_3/Al(i\text{-}Bu)_3$	70	...	...	(168)
St-C^{14}	*p*-*n*-BuSt	$TiCl_3/Al(i\text{-}Bu)_3$	70	...	...	(168)
St-C^{14}	*o*-MeSt	$TiCl_3/Al(i\text{-}Bu)_3$	40	12.5	0.10	(90)
St-C^{14}	*m*-MeSt	$TiCl_3/Al(i\text{-}Bu)_3$	40	2.0	0.50	(90)
St-C^{14}	*p*-EtSt	$TiCl_3/Al(i\text{-}Bu)_3$	40	0.95	1.05	(90)
St-C^{14}	*p*-FSt	$TiCl_3/Al(i\text{-}Bu)_3$	40	1.50	0.60	(90)
St-C^{14}	*p*-ClSt	$TiCl_3/Al(i\text{-}Bu)_3$	40	2.20	0.50	(90)
St-C^{14}	*p*-BrSt	$TiCl_3/Al(i\text{-}Bu)_3$	40	1.75	0.55	(90)
St-C^{14}	1-VN	$TiCl_3/Al(i\text{-}Bu)_3$	40	3.3	0.35	(90)
St	Cinnamic acid-C^{14}	AIBN	60	1.85	0	(21)
Ethylene	Propene-1-C^{14}	*t*-Bu_2O_2 or acetone oxime	130–220	3.43	...	(70)
Ethylene	1-Butene-1-C^{14}	*t*-Bu_2O_2 or acetone oxime	130–220	3.25	...	(70)
Ethylene	1-Octene-1-C^{14}	*t*-Bu_2O_2 or acetone oxime	130–220	3.66	...	(70)

[a] MM = methyl methacrylate; St = styrene; EGDM = ethylene glycol dimethacrylate; DVB = divinylbenzene; MeSt = methylstyrene; diClSt = dichlorostyrene; BuSt = butylstyrene; EtSt = ethylstyrene; FSt = fluorostyrene; ClSt = chlorostyrene; BrSt = bromostyrene; VN = vinylnaphthalene.

VIII. COPOLYMERIZATION

In copolymerizations of two monomers, the simple propagation step (reaction 3) has to be expanded to include four possible reaction sequences (reactions 56–59)

$$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1\cdot \tag{56}$$

$$M_1\cdot + M_2 \xrightarrow{k_{12}} M_2\cdot \tag{57}$$

$$M_2\cdot + M_2 \xrightarrow{k_{22}} M_2\cdot \tag{58}$$

$$M_2\cdot + M_1 \xrightarrow{k_{21}} M_1\cdot \tag{59}$$

where $M_1\cdot$ and $M_2\cdot$ represent active chains having monomers M_1 and M_2, respectively, as their terminal units. Monomer reactivity ratios are defined as $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, and for the ideal case of random copolymerization $r_1r_2 = 1$ (96).

Evaluation of monomer reactivity ratios involves some form of analysis of the copolymer to determine the relative abundances of the two monomeric units. Such analyses are frequently very difficult by conventional methods, particularly if the monomers are very similar, or if one monomer is present in very small amounts. Use of a labeled monomer overcomes these problems since the composition of the copolymer may readily be determined by radioactive assay. The method has only recently become popular, but where the results recorded in Table VI can be checked against other data, agreement is good (1, 66, 212, 215).

IX. BRANCHING

When polymer molecules act as chain-transfer agents during polymerization a special situation arises in which branched or even cross-linked polymers are formed. Branched structures have markedly different properties from linear structures, and a knowledge of the frequency of branching and of the length of branches is of considerable interest, particularly when this knowledge can be correlated with physical properties.

One of the first attempts to determine the extent of branching during styrene polymerization involved the use of styrene-α-H^2 and styrene-β-$H^2{}_1$. These monomers were polymerized thermally at 70° and their polymers compared with polystyrene prepared in the same way. Isotope effect studies with butanethiol-H^2

showed that hydrogen atom abstraction involved an appreciable isotope effect, therefore, had such a process occurred with polystyrene, there would have been an appreciable reduction in branching when deuterated polymer was involved. Since there was no significant difference between the three polymers it was concluded that chain transfer to polymer was unimportant in styrene polymerization (207).

The same conclusion was reached by an entirely different technique. Styrene-β-C^{14} was polymerized in the presence of a high molecular weight fraction of inactive polystyrene and conditions were chosen such that comparatively low molecular weight C^{14}-labeled polymer was produced. Separation of the high and low molecular weight fractions showed that very little C^{14} became attached to the inactive polymer. Only at high temperatures (154°) and high conversions was there evidence of significant numbers of branches (35).

A claim that 2-cyano-2-propyl radicals (from AIBN) initiate branching by direct attack on polystyrene molecules seems unrealistic, particularly since it has been shown that such radicals cannot abstract labile hydrogen from toluene (37, 38) or polyisoprene (7, 14). The claim is based upon the fact that at high conversions n becomes greater than 2 (112). A more plausible explanation is that at high conversions, copolymerization with methacrylonitrile-C^{14} can occur. The methacrylonitrile-C^{14} is most probably formed in "cage" disproportionation reaction of pairs of 2-cyano-2-propyl radicals (reaction 60). At low conversions,

$$2(CH_3)_2CCN \rightarrow CH_2{=}C(CH_3)CN + (CH_3)_2CHCN \quad (60)$$

copolymerization is insignificant because of the extremely low concentration of methacrylonitrile-C^{14}, but as the polymerization proceeds, its concentration increases due to increased initiator decomposition and decreased styrene monomer concentration.

Branched polystyrene has been prepared by photolysis of partially brominated polystyrene in the presence of styrene-β-C^{14}. The number of branches was calculated from the change in bromine content, which was determined by neutron activation analysis, and the average length of the branches determined from the C^{14} content of the branched polymer. Carbon tetrachloride had to be used as a chain transfer agent to prevent excessive cross linking (125, 126). Similarly prepared polymers have been used in a light scattering study of branched polystyrene (194).

Polyvinyl acetate free radicals are much more reactive than polystyrene radicals and are more likely to partake in self-branching reactions. The process has been investigated using polyvinyl acetate-1-C^{14} and techniques similar to those described for styrene. The difficulty of preparing pure labeled monomer was overcome by preparing a linear high molecular weight polymer in the usual way and then labeling by exchange with sodium acetate-1-C^{14}. The high molecular weight labeled polymer was included in a system containing inactive vinyl acetate which was polymerized to give low molecular weight polymer. The lowering of the specific activity of the high molecular weight fractions could be used to calculate the extent of branching which had occurred, and it was shown that at low conversions at 40° branching is not of very great significance, but at high conversions there may be several branches on each polymer molecule (31, 34).

Similar general conclusions were reached when polyvinyl acetate, photo-initiated by AIBN-C^{14}, was fractionated. For the high molecular weight fractions, $n \simeq 3$ and fell to $\simeq 0.5$ in the low molecular weight fractions. It was surmized that the high molecular weight fractions were extensively branched, since mutual termination of radicals is mainly by disproportionation, and values of n higher than 1 would arise from rather infrequent combination reactions (153).

Tailor-made branched polyvinyl acetate has been prepared by reaction of partially hydrolyzed polyvinyl acetate backbone polymer with low molecular weight polymer containing acid chloride end groups. The backbone was labeled by acetate-1-C^{14} exchange as described above and the number of branching sites (*i.e.*, number of –OH groups) calculated from the drop in specific activity after partial hydrolysis. The advantage of this technique was that the length of the branches could be determined before they were coupled to the backbone (152).

The method of polymerizing a labeled monomer in the presence of a high molecular weight inactive polymer has been used to investigate branching in persulfate-initiated polymerization of acrylamide. At 50° there was no evidence of self-branching but at 78° polymers with from one to seven branches were formed. The number of branches determined by the tracer method was in good agreement with the number calculated from physical data (103).

X. GRAFT COPOLYMER FORMATION

Closely allied to self-branched polymers are graft copolymers in which branches of one polymer are attached to a backbone of a second polymer. It has been repeatedly suggested that polymer formed from one monomer may act as a chain-transfer agent in the solution polymerization of a second monomer with resultant graft copolymer formation. There is little evidence for this generalization; indeed what evidence exists tends to rule against it (7, 14, 154, 191), and it may well be that the mutual incompatibility of many polymers in solution (evidenced by the occurrence of phase separation) prevents such chain-transfer events. What has become apparent is that the nature of the initiator in graft copolymerization is an important factor. Thus, polymethyl methacrylate–polystyrene grafts and polymethyl methacrylate–polyisoprene grafts are formed when dibenzoyl peroxide is used as initiator but not when AIBN is used (7, 14, 154, 191).

The process of grafting polymethyl methacrylate chains onto polyisoprene has been investigated using dibenzoyl peroxide-di-*ar*-C^{14} and dibenzoyl peroxide-di-*carboxyl*-C^{14}, and it was shown that grafting results from prior reaction of phenyl and benzoyloxy radicals with the polyisoprene either by addition to the double bond (reaction 61) or by abstraction of α-methylenic hydrogen (reaction 62) to give polyisoprenic alkyl and alkenyl radicals which act as loci for methyl methacrylate polymerization. At 60°, 90% of the radicals R· in reaction 61 are benzoyloxy, and this reaction accounts for about 60% of the grafting events. The growing grafted chains terminate mainly by disproportionation (see section V), but use of a mixed initiator consisting of AIBN-C^{14} and inactive dibenzoyl peroxide demonstrated the occurrence of cross-termination reactions between free and bound polymethyl methacrylate radicals since some C^{14} became bound in the graft copolymer (7, 14).

$$\mathrm{M}_n\mathrm{{—}CH_2C(Me){=}CHCH_2{—}M}_{n'} + \mathrm{R}\cdot \rightarrow \mathrm{M}_n\mathrm{{—}CH_2\dot{C}(Me)CH(R)CH_2{—}M}_{n'} \quad (61)$$

$$\mathrm{M}_n\mathrm{{—}CH_2C(Me){=}CHCH_2{—}M}_{n'} + \mathrm{R}\cdot \rightarrow \mathrm{M}_n\mathrm{{—}CH_2C(Me){=}CH\dot{C}H{—}M}_{n'} + \mathrm{RH} \quad (62)$$

In mixed polymerization systems of this type, separation of the homo- and grafted- polymers often presents problems, but when a suitable technique has been developed its efficacy is readily tested with labeled polymers (7, 14).

When polymers are subjected to ionizing radiation, reactive species are produced which are capable of initiating polymerization of a second monomer which becomes bound to the original polymer. If the sample is irradiated *in vacuo*, the reactive centers remain active for days after removal of the radiation, and this has been confirmed by introducing acrylonitrile-C^{14} into systems containing polystyrene, polyacrylonitrile, polyethylene terephthalate, and nylon (46, 48). Whether graft or block copolymers are formed will depend upon whether side-chain or main-chain fracture occurs during irradiation, though most probably both types are present in many systems.

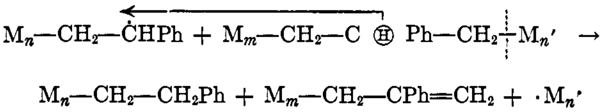
XI. Degradation and Irradiation

Polymers may be degraded by the action of heat, light, high energy radiation, and also mechanically, and isotopes have been used to study all these processes.

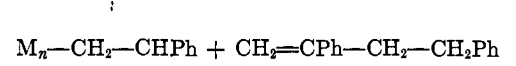
Thermal degradation of polystyrene has been studied using polystyrene-α-H^2 and polystyrene-β-$H^2{}_1$. The mechanism proposed is formally similar to the mechanism of polymerization and involves initiation, propagation, inter- and intramolecular chain transfer, and termination by disproportionation (reactions 63–67).

$$\mathrm{M}_n\mathrm{{—}CH_2{—}CHPh{—}CH_2{—}CHPh{—}M}_{n'} \rightarrow \mathrm{M}_n\mathrm{{—}CH_2{—}\dot{C}HPh} + \cdot\mathrm{CH_2{—}CHPh{—}M}_{n'} \quad (63)$$

$$\mathrm{M}_n\mathrm{{—}CH_2{—}CHPh{—}CH_2{—}\dot{C}HPh} \rightarrow \mathrm{M}_n\mathrm{{—}CH_2{—}CHPh} + \mathrm{CH_2{=}CHPh} \quad (64)$$



$$\mathrm{M}_n\mathrm{{—}CH_2{—}\dot{C}HPh} + \mathrm{M}_m\mathrm{{—}CH_2{—}C}\ \text{Ⓗ}\ \mathrm{Ph{—}CH_2{—}M}_{n'} \rightarrow \mathrm{M}_n\mathrm{{—}CH_2{—}CH_2Ph} + \mathrm{M}_m\mathrm{{—}CH_2{—}CPh{=}CH_2} + \cdot\mathrm{M}_{n'} \quad (65)$$

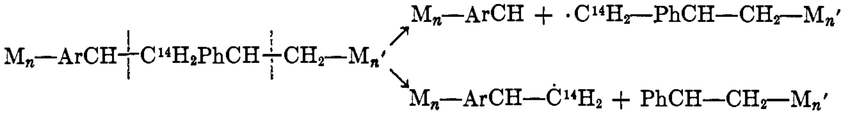


$$\mathrm{M}_n\mathrm{{—}CH_2{—}CHPh{—}CH_2{—}C}\ \text{Ⓗ}\ \mathrm{Ph{—}CH_2{—}\dot{C}HPh} \rightarrow \mathrm{M}_n\mathrm{{—}CH_2{—}CHPh} + \mathrm{CH_2{=}CPh{—}CH_2{—}CH_2Ph} \quad (66)$$

$$\mathrm{M}_n\mathrm{{—}CH_2{—}\dot{C}HPh} + \cdot\mathrm{CH_2{—}CHPh{—}M}_{n'} \rightarrow \mathrm{M}_n\mathrm{{—}CH_2{—}CH_2Ph} + \mathrm{CH_2{=}CPh{—}M}_{n'} \quad (67)$$

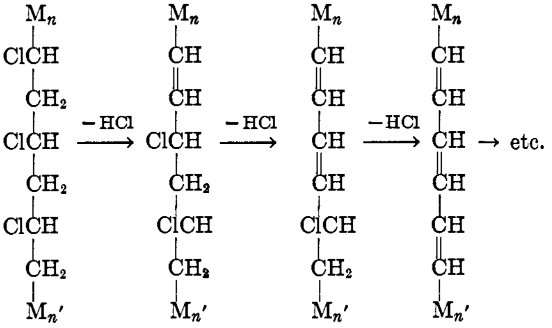
The importance of transfer reactions was assessed by observation of the effects of deuterium substitution. Polystyrene-α-H^2 showed a 50% decrease in the rate of the transfer process and an increase in the rate of propagation. Polystyrene-β-$H^2{}_1$ produced an increase in rates of both transfer and propagation reactions. This data showed that the α-hydrogen was the site of the transfer process as shown in reactions 65 or 66. However, data on the decrease in viscosity accompanying degradation indicated that only intermolecular transfer (reaction 65) was important (208).

When copolymers of styrene-β-C^{14} and *m*-methylstyrene or *p*-methylstyrene were thermally degraded, monomers were obtained in which C^{14} exchange had occurred. The distribution of C^{14} between the two monomers depends upon the nature of the copolymer, and in the cases studied closely approximated to the theoretical ratio (3:1) for randomly constructed polymers. Thus, the degradation process was not one of spallation from the original chain ends; the initial chain breaks (reaction 68) produced odd and even fragments with equal probability, and no repolymerization of the monomers occurred (157).



$$\mathrm{M}_n\mathrm{{—}ArCH{—}C^{14}H_2PhCH{—}CH_2{—}M}_{n'} \rightarrow \begin{cases} \mathrm{M}_n\mathrm{{—}ArCH} + \cdot\mathrm{C^{14}H_2{—}PhCH{—}CH_2{—}M}_{n'} \\ \mathrm{M}_n\mathrm{{—}ArCH{—}\dot{C}^{14}H_2} + \mathrm{PhCH{—}CH_2{—}M}_{n'} \end{cases} \quad (68)$$

The deterioration of polyvinyl chloride (PVC) is said to be due to a zipper-like elimination of hydrogen chloride (reaction 69) which results in the formation of colored, easily oxidizable, conjugated polyene structures.



(69)

The most probable sites of initiation are those which appear during termination or transfer reactions, *viz.* chlorine atoms situated on carbon atoms alpha to terminal double bonds or tertiary because of transfer events. Stabilization of PVC can be achieved by mixing and heating with barium, zinc, or cadmium salts of 2-ethylhexanoic acid. This stabilizing effect may well be due to the replacement of labile chlorine atoms by more stable carboxylate groups since it has been shown that 2-ethylhexanoate-C^{14} groups become chemically bound in the polymer (98).

Photodegradation of methyl methacrylate *in vacuo* proceeds with the formation of gaseous products, and use of specifically labeled polymers enabled one of these products, methyl formate, to be related to the elimination of ester side chains (97).

High energy radiations cause polymers to degrade, and in many cases to cross link to form insoluble networks. A few aspects of this vast field have been investigated using isotopic tracers. For example, the yields of free radicals per 100 e.v. absorbed energy [*G*(radical) values] are of considerable interest and various attempts have been made to estimate these yields with varying degrees of success. It has now been shown that labeled radical scavengers are likely to be of considerable value for this purpose. A doubly labeled scavenger, phenyl-H^3-*sec*-butyl-$S^{35}{}_1$-disulfide was used in polyisobutene irradiation, and it was shown that the *G* (radical) value of 7.3 for the polymer was very similar to values obtained in more mobile substances. However, the concentration of scavenger required in the highly viscous polymer was about ten times that required in mobile hydrocarbons, presumably because of higher concentrations of radicals in clusters which were unable to diffuse apart (17).

γ-Irradiation of polystyrene has received considerable attention. The effect of deuteration on the cross linking produced by γ-rays is not large or specific, and the isotopic composition of the hydrogen from differently deuterated polymers indicated that 22.3% comes from the α-position, 39.2% from the β-position, and 38.5% from the aromatic ring. In other words no simple mechanism can be pictured operating through a specific position in the monomer unit. However, with the exception of polystyrene-β-$H^2{}_1$, increasing deuteration leads to greater energy requirements for hydrogen formation, *i.e.*, lower yields of hydrogen. The isotope effect calculated from these results (2.2–2.8) may indicate an average maximum local temperature of about 400°.

Lack of correlation between cross links and deuterium content suggested that the cross-linking process involved phenyl groups as well as hydrogen atoms on the chain, and the argument is strengthened by the fact that the number of cross links is greater than the number of hydrogen molecules produced (209). Further evidence for this view is obtained from the observed differences in electron spin resonance spectra of polystyrenes reacting with hydrogen atoms and deuterium atoms, which indicate a possible addition of these moieties to the aromatic ring (121). Much the same conclusion has been reached from a study of the irradiation of toluene-1-$H^2{}_3$ at $-196°$, and it is concluded that at least some of the cross links are formed by combination of polymer radicals with cyclohexadienyl radicals formed by addition of hydrogen atoms to benzene rings on adjacent polymer molecules (178).

Copolymers of deuterated styrenes and methyl methacrylate have been irradiated and it was concluded that the styrene residues were attacked mostly at the α-position by radical fragments produced by decomposition of the ester side chain. With deuterated polystyrenes it was confirmed that radiation-initiated damage is not a simple function of the stability of a particular bond in the molecule although in this work rather higher values were obtained for the deuterium isotope effects (78). Irradiation of polymers of styrene-α-H^2, *p*-methylstyrene-α-H^2, and *p*-methoxystyrene-α-H^2 revealed that the backbones of substituted polystyrenes are less susceptible to radiation damage than polystyrene, but this could not be attributed to any enhanced susceptibility of the α-C–H bond (79).

The results obtained on irradiation of deuterated polyethylene are such that they must arise from a fundamentally different mechanism to that in polystyrene (209). It has been proposed that initially formed free-radical centers are able to migrate through the solid polyethylene, and evidence cited in favor of one mechanism for such migration is the exchange between gaseous deuterium and irradiated polymer (reactions 70, 71). These reactions occur during

$$M_n\cdot + D_2 \rightarrow M_nD + D\cdot \qquad (70)$$

$$D\cdot + M_n'H \rightarrow M_n'\cdot + HD \qquad (71)$$

irradiation (206), and subsequently, if irradiation is carried out *in vacuo* and then deuterium is admitted (92). The observed effects have been shown to depend upon the magnitude of polymer surface area, on dose, on deuterium pressure, on temperature, and also on the polymer. Thus polyethylene showed a maximum effect while polymethyl methacrylate showed a minimum effect (77).

Mechanical degradation can be achieved by ultrasonic vibrations or by shear. Degradation of polymethyl methacrylate and polystyrene by the former produces free radicals which will react with radical scavengers such as $I^{131}{}_2$, and the number of chain scissions can be related to the amount of scavenger combined (111).

Similarly, the plasticization of natural rubber by cold mastication is a degradation process which involves mechanical rupture of the polymer chains to give polymer radicals which have been detected by their reaction with 1:1′-dinaphthyl disulfide-S^{35}. The amount of radical acceptor incorporated in the polymer could be accounted for in terms of the decrease in number average molecular weight (13).

XII. OXIDATION

Technologically, the oxidative deterioration of polymers, particularly those of butadiene and isoprene and their copolymers, is of great interest, and improved means of protection against such deterioration are constantly sought. It is appropriate, therefore, that this review should include an account of certain uses of isotopes in this field despite the fact that the work has not always involved polymers. The nature of autoxidation reactions has been reviewed (23), and it is sufficient to note here that the process is a chain reaction involving hydroperoxides and their radicals and, consequently, is susceptible to inhibition and retardation by antioxidants.

There has been some controversy concerning the action of certain antioxidants, since originally it was thought that the antioxidants methylaniline-H^2 and diphenylamine-H^2 showed no isotope effects when compared with their hydrogen analogs (109). A similar observation was made in the case of N,N′-diphenyl-*p*-phenylenediamine-$H^2{}_2$ (173). However, when precautions were taken to continuously exclude water and other compounds containing exchangeable hydrogen from the system, isotope effects could be observed. The magnitude of these effects could be varied considerably by varying experimental conditions, but it was clear that N–H bond scission was the rate-controlling step of the reaction with peroxy radicals (187, 188). Similarly, definite isotope effects have been demonstrated in the reaction of peroxide radicals with phenols and the corresponding deuterated phenols, indicating that their antioxidant action is *via* O–H bond cleavage (187, 211).

In the case of butadiene–styrene copolymers, the effect of variable experimental conditions has been investigated. Four factors appear to be important: (i) The system involved. Thus, N-phenyl-2-naphthylamine showed an isotope effect while, under the same conditions, diphenylamine did not. (ii) The concentration of antioxidant. At higher concentrations a reverse isotope effect was observed. This can only be explained if a direct reaction between oxygen and antioxidant (reaction 72) be assumed to produce radicals capable of initiating oxidation. (iii) Temperature. The fate of the radical A· could be either termination of a kinetic chain by coupling with a peroxy radical (reaction 73) or initiation of a new kinetic chain (reaction 74). The second of these two reactions will have the higher activation energy and consequently will increase in importance with increasing temperature, an effect which would explain the observed increase in reverse isotope effect with increased temperature. (iv) Experimental conditions. These must be carefully chosen to exclude unwanted side reactions such as the exchange of labile hydrogen.

$$\mathrm{AH} + \mathrm{O_2} \rightarrow \mathrm{A}\cdot + \mathrm{HO_2}\cdot \qquad (72)$$

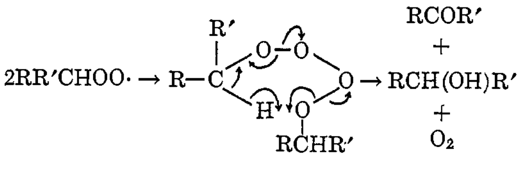
$$\mathrm{A}\cdot + \mathrm{RO_2}\cdot \rightarrow \text{stable products} \qquad (73)$$

$$\mathrm{A}\cdot + \mathrm{RH} \rightarrow \mathrm{AH} + \mathrm{R}\cdot \qquad (74)$$

These results show that earlier failures to observe significant isotope effects are readily explainable and that this type of antioxidant activity is due to hydrogen abstraction reactions (189).

The autoxidation of polystyrene at 175–235°, and in the presence of ozone at 65–154°, was studied using variously deuterated polystyrenes. It was found that reactivities decreased with increasing deuteration but that the most marked effects were observed when deuterium was bound to the tertiary carbon atoms. Thus, it was concluded that breaking of tertiary C–H bonds is the rate-controlling step during formation of the hydroperoxide intermediate (28).

It has been known for some time that termination of the kinetic chains in autoxidation involved pairs of peroxy radicals (23), but the precise mechanism for this termination process could not be formulated without recourse to isotopic methods. It now seems likely that, for primary and secondary alkyl peroxy radicals, termination occurs *via* reaction 75. The evidence for this is twofold. Firstly, it has been shown that the kinetic chain length of oxidation decreased somewhat from ethylbenzene to ethyl-1-$H^2{}_1$-benzene and that the hydroperoxide yield decreased similarly. A low isotope effect of $k_H/k_D = 1.9$ for 1-phenylethyl peroxy radicals is consistent with an exothermic reaction between peroxy radicals involving breaking of an α-C–H bond (182, 183). Secondly, when cumene was



(75)

oxidized with a mixture of O^{16}_2 and O^{18}_2 the residual oxygen, after oxidation, was found to contain isotopically mixed molecules of oxygen $O^{16}O^{18}$ in proportions which could only be accounted for in terms of reaction 75 (202).

XIII. MOLECULAR WEIGHT DETERMINATION

Once the mode of termination of a polymerization reaction has been precisely defined (see section V) the use of labeled initiators or terminating agents gives a precise and fairly rapid means of molecular weight determination. Thus, polystyrene which has been prepared with labeled free-radical initiators contains exactly two initiator fragments per polymer molecule, and its molecular weight can be computed from its specific activity and the specific activity of the initiator. The method is especially useful for low molecular weight polymers which are capable of diffusion through the usual osmotic membranes and provides a useful means of checking on such diffusion (6).

An alternative technique exists where polymers are known to contain terminal hydroxyl groups. In this case the hydroxyl groups may be esterified with *p*-toluenesulfonyl chloride-S^{35} and the molecular weight determined from combined S^{35} (118). Use of a C^{14}-labeled acid chloride would extend the useful life of the reagent which, in the example cited, is limited by the 87-day half-life of S^{35}.

Polychlorobutyl acrylate-Cl^{36} dissolved in acetone has also been used to study osmotic membrane phenomena, and it was found that for cellophane membranes (i) about 200 hr. was necessary to reach an equilibrium steady state, (ii) the fraction of polymer diffusing through the membrane in a given time was independent of the concentration, (iii) the amount of polymer diffusing was related to the permeability of the membrane, (iv) a practically irreversible adsorption of polymer on the membrane (30–40 μg./cm.^{2}) was observed (75).

Finally, a technique for relating viscosity average molecular weight $\bar{M}_v$ to $\bar{M}_n$ without recourse to osmotic pressure determination has been described, and labeled polystyrenes have been used to demonstrate the reliability of the method (116).

XIV. MISCELLANEOUS

Specific deuterium labeling is very useful for assigning frequencies to particular R–H bonds by observing shifts of bands in infrared spectra. The technique has been fairly widely applied to various systems including isotactic polypropenes (141, 142, 143, 175), isotactic polystyrenes (131–133, 199, 200), isotactic and atactic polymethyl methacrylate (160), polyacrylonitrile (144), polyvinyl alcohol (137), and *cis*- and *trans*-polybutadienes (106).

The mechanism of biosynthesis of polyisoprenes, of considerable interest to the natural rubber industry, will eventually be solved only with the aid of labeled precursors (8, 71, 123, 124, 127, 171, 201).

Sulfur vulcanization of synthetic and natural rubbers has been investigated using sulfur-35 (11, 67, 68, 91, 174). Also, deuterated polybutadienes and polyisoprenes have been used in an infrared study of the vulcanization process (190). The results are in general accord with the detailed mechanism of the sulfur–olefin reaction which has recently been extensively and critically investigated by nonisotopic techniques (24).

Diffusion of polymers in polymers, and solvents and solutes in polymers are difficult processes to follow, but many difficulties are avoided if the diffusion process is followed by means of labeled components (12, 74, 76, 170, 177).

The stability of certain polymers toward hydrolytic reagents has been investigated using C^{14}-labeled polymers (51). Isoprene-C^{14} was used to prepare butyl rubbers with known amounts of unsaturation, and it was found that the standard analytical methods for unsaturation were not satisfactory (145). Similarly, styrene-C^{14} was used to investigate analytical methods for styrenated oil acids and esters (69). Cross linking of a polyester by copolymerization of styrene has been studied using maleic anhydride-C^{14} (102). Sodium oleate-C^{14} and sodium nonadecanoate-C^{14} were used to determine distribution of these emulsifiers in emulsion polymerization of styrene (108). Oxidation of styrene produces a polymeric styrene oxide, and it was shown that benzaldehyde-C^{14} had no part in this polymerization (93). Szilard–Chalmers bombardment of ethyl bromide with slow neutrons in the presence of styrene results in polystyrene with bound Br^{82} (139). The radiochemical assay of ethylene-C^{14} has been achieved by polymerization on a Ziegler catalyst followed by counting of the polyethylene as a foil (87, 88).

XV. REFERENCES

(1) Allen, J. K., and Bevington, J. C., *Trans. Faraday Soc.*, **56**, 1762 (1960).
(2) Allen, J. K., and Bevington, J. C., *Proc. Roy. Soc.* (London), **A262**, 271 (1961).
(3) Allen, J. K., and Bevington, J. C., *Polymer*, **2**, 265 (1961).
(4) Allen, P. E. M., and Harrod, J. F., *Makromol. Chem.*, **32**, 153 (1959).
(5) Allen, P. W., Ayrey, G., Merrett, F. M., and Moore, C. G., *J. Polymer Sci.*, **22**, 549 (1956).
(6) Allen, P. W., and Place, M. A., *J. Polymer Sci.*, **26**, 386 (1957).
(7) Allen, P. W., Ayrey, G., Moore, C. G., and Scanlan, J., *J. Polymer Sci.*, **36**, 55 (1959).
(8) Archer, B. L., Ayrey, G., Cockbain, E. G., and McSweeney, G. P., *Nature*, **189**, 663 (1961).
(9) Arnett, L. M., *J. Am. Chem. Soc.*, **74**, 2027 (1952).
(10) Arnett, L. M., and Peterson, J. H., *J. Am. Chem. Soc.*, **74**, 2031 (1952).

(11) Auerbach, I., *Ind. Eng. Chem.*, **45**, 1526 (1953).

(12) Auerbach, I., and Gehman, S. D., *Anal. Chem.*, **26**, 685 (1954).

(13) Ayrey, G., Moore, C. G., and Watson, W. F., *J. Polymer Sci.*, **19**, 1 (1956).

(14) Ayrey, G., Ph.D. Thesis, University of London, 1957.

(15) Ayrey, G., and Moore, C. G., *J. Polymer Sci.*, **36**, 41 (1959).

(16) Ayrey, G., Mazza, R. J., and Levitt, G. F., unpublished work.

(17) Ayrey, G., and Turner, D., *J. Polymer Sci.*, **B1**, 185 (1963).

(18) Bailey, B. E., and Jenkins, A. D., *Trans. Faraday Soc.*, **56**, 903 (1960).

(19) Barson, C. A., and Bevington, J. C., *Tetrahedron*, **4**, 147 (1958).

(20) Barson, C. A., Bevington, J. C., and Eaves, D. E., *Trans. Faraday Soc.*, **54**, 1678 (1958).

(21) Barson, C. A., *J. Polymer Sci.*, **62**, S128 (1962).

(22) Bartlett, P. D., and Tate, F. A., *J. Am. Chem. Soc.*, **75**, 91 (1953).

(23) Bateman, L., *Quart. Rev.* (London), **8**, 147 (1954).

(24) Bateman, L., and Moore, C. G., "Organic Sulphur Compounds," Vol. 1, Pergamon Press, New York, N. Y., 1961, p. 210.

(25) Bawn, C. E. H., and Ledwith, A., *Quart. Rev.* (London), **16**, 361 (1962).

(26) Baysal, B., and Tobolsky, A. V., *J. Polymer Sci.*, **8**, 529 (1952).

(27) Baysal, B., and Tobolsky, A. V., *J. Polymer Sci.*, **11**, 471 (1953).

(28) Beachell, H. C., and Nemphos, S. P., *J. Polymer Sci.*, **25**, 173 (1957).

(29) Bengough, W. I., and Norrish, R. G. W., *Proc. Roy. Soc.* (London), **A200**, 301 (1950).

(30) Berry, K. L., and Peterson, J. H., *J. Am. Chem. Soc.*, **73**, 5195 (1951).

(31) Bevington, J. C., Guzmann, G. M., and Melville, H. W., *Nature*, **170**, 1026 (1952).

(32) Bevington, J. C., Melville, H. W., and Taylor, R. P., *J. Polymer Sci.*, **12**, 449 (1954).

(33) Bevington, J. C., Bradbury, J. H., and Burnett, G. M., *J. Polymer Sci.*, **12**, 469 (1954).

(34) Bevington, J. C., Guzmann, G. M., and Melville, H. W., *Proc. Roy. Soc.* (London), **A221**, 437 (1954).

(35) Bevington, J. C., Guzmann, G. M., and Melville, H. W., *Proc. Roy. Soc.* (London), **A221**, 453 (1954).

(36) Bevington, J. C., Melville, H. W., and Taylor, R. P., *J. Polymer Sci.*, **14**, 463 (1954).

(37) Bevington, J. C., *J. Chem. Soc.*, 3707 (1954).

(38) Bevington, J. C., *Simp. Intern. Chim. Macromol.* (Milan), **3** (1954).

(39) Bevington, J. C., Gahnem, N. A., and Melville, H. W., *Trans. Faraday Soc.*, **51**, 346 (1955).

(40) Bevington, J. C., *Trans. Faraday Soc.*, **51**, 1392 (1955).

(41) Bevington, J. C., *Nature*, **175**, 477 (1955).

(42) Bevington, J. C., Gahnem, N. A., and Melville, H. W., *J. Chem. Soc.*, 2822 (1955).

(43) Bevington, J. C., *J. Chem. Soc.*, 1127 (1956).

(44) Bevington, J. C., and Gahnem, N. A., *J. Chem. Soc.*, 3506 (1956).

(45) Bevington, J. C., and Brooks, C. S., *J. Polymer Sci.*, **22**, 257 (1956).

(46) Bevington, J. C., and Eaves, D. E., *Nature*, **178**, 1112 (1956).

(47) Bevington, J. C., *Proc. Roy. Soc.* (London), **A239**, 420 (1957).

(48) Bevington, J. C., *Chem. Ind.* (London), 411 (1957).

(49) Bevington, J. C., *Trans. Faraday Soc.*, **53**, 997 (1957).

(50) Bevington, J. C., and Toole, J., *J. Polymer Sci.*, **28**, 413 (1958).

(51) Bevington, J. C., Eaves, D. E., and Vale, R. L., *J. Polymer Sci.*, **32**, 317 (1958).

(52) Bevington, J. C., Toole, J., and Trossarelli, L., *Trans. Faraday Soc.*, **54**, 863 (1958).

(53) Bevington, J. C., and Gahnem, N. A., *J. Chem. Soc.*, 2254 (1958).

(54) Bevington, J. C., and Lewis, T. D., *Trans. Faraday Soc.*, **54**, 1340 (1958).

(55) Bevington, J. C., Toole, J., and Trossarelli, L., *Makromol. Chem.*, **28**, 237 (1958).

(56) Bevington, J. C., and Eaves, D. E., *Trans. Faraday Soc.*, **55**, 1777 (1959).

(57) Bevington, J. C., Toole, J., and Trossarelli, L., *Makromol. Chem.*, **32**, 57 (1959).

(58) Bevington, J. C., and Gahnem, N. A., *J. Chem. Soc.*, 2071 (1959).

(59) Bevington, J. C., *Makromol. Chem.*, **34**, 152 (1959).

(60) Bevington, J. C., and Lewis, T. D., *Polymer*, **1**, 1 (1960).

(61) Bevington, J. C., and Gahnem, N. A., *Makromol. Chem.*, **43**, 61 (1961).

(62) Bevington, J. C., and Troth, H. G., *Trans. Faraday Soc.*, **58**, 186 (1962).

(63) Bevington, J. C., and Wahid, A., *Polymer*, **3**, 585 (1962).

(64) Bier, G., Hoffmann, W., Lehmann, G., and Seydel, G., *Makromol. Chem.*, **58**, 1 (1962).

(65) Bigeleisen, J., and Wolfsberg, M., *Advan. Chem. Phys.*, **1**, 15 (1958).

(66) Blackley, D. C., and Melville, H. W., *Makromol. Chem.*, **18**, 16 (1956).

(67) Blokh, G. A., and Mamaĭsur, O., *Zh. Obsch. Khim.*, **29**, 3580 (1959).

(68) Blokh, G. A., Golubkova, E. A., and Miklukhiv, G. P., *Dokl. Akad. Nauk SSSR*, **90**, 201 (1953).

(69) Bobalek, E. G., Bradford, J. R., Leutner, F., and Akiyama, R., *Anal. Chem.*, **28**, 906 (1956).

(70) Boghetich, L., Mortimer, G. A., and Daues, G. W., *J. Polymer Sci.*, **61**, 3 (1962).

(71) Bonner, J., Parker, M. W., and Montermoso, J. C., *Science*, **120**, 549 (1954).

(72) Bradbury, J. H., and Melville, H. W., *Proc. Roy. Soc.* (London), **A222**, 456 (1954).

(73) Breitenbach, J. W., Billek, G., Falthansl, G., and Weber, E., *Monatsh.*, **92**, 1100 (1961).

(74) Bresler, S. E., Zakharov, G. M., and Kirillov, S. V., *Visokomol. Soedineniya*, **3**, 1072 (1961).

(75) deBrouckére, L., van Leemput, R., and Stein, R., *Intern. J. Appl. Radiation Isotopes*, **9**, 154 (1960).

(76) Bueche, F., Cashin, W. M., and Debye, P., *J. Chem. Phys.*, **19**, 1242 (1951).

(77) Bulanovskaya, Z. S., Varashavskii, Ya. M., Karpov, V. L., and Petrov, I. Ya., *Dokl. Akad. Nauk. SSSR*, **138**, 146 (1961).

(78) Burlant, W., and Neerman, J., *J. Org. Chem.*, **26**, 3602 (1961).

(79) Burlant, W., Neerman, J., and Serment, V., *J. Polymer Sci.*, **58**, 491 (1962).

(80) Bywater, S., *Trans. Faraday Soc.*, **51**, 1267 (1955).

(81) Case, L. C., and Atlas, J. D., *J. Polymer Sci.*, **45**, 435 (1960).

(82) Catch, J. R., *Research*, **9**, 479 (1956).

(83) Chien, J. C. W., *J. Am. Chem. Soc.*, **81**, 86 (1959).

(84) Colclough, R. O., *J. Polymer Sci.*, **8**, 467 (1952).

(85) Dainton, F. S., and Sutherland, G. B. B. M., *J. Polymer Sci.*, **4**, 37 (1949).

(86) (a) Dainton, F. S., and Tomlinson, R. H., *J. Chem. Soc.*, 151 (1953); (b) Dainton, F. S., Tomlinson, R. H., and Batke, T. L., "Cationic Polymerization and Related Complexes," Plesch, P. H., Ed., W. Heffer and Sons, Cambridge, England, 1953, p. 80.

(87) Danusso, F., Pajaro, G., and Sianesi, D., *J. Polymer Sci.*, **22**, 179 (1956).

(88) Danusso, F., and Pajaro, G., *Atti accad. nazl. Lincei, Rend., Classe sci. fis., mat. nat.*, **22**, 48 (1957).

(89) Danusso, F., Pajaro, G., and Sianesi, D., *Chim. Ind.* (Milan), **41**, 1170 (1959).

(90) Danusso, F., Pajaro, G., and Sianesi, D., *Chim. Ind.* (Milan), **41**, 1176 (1959).

(91) Dogadkin, B. A., *J. Polymer Sci.*, **30**, 351 (1958), and many earlier references.

(92) Dole, M., and Cracco, F., *J. Am. Chem. Soc.*, **83**, 2584 (1961).

(93) Dutka, F., and Gál, D., *Intern. J. Appl. Radiation Isotopes*, **13**, 27 (1962).

(94) Feldman, C. F., and Perry, E., *J. Polymer Sci.*, **46**, 217 (1960).

(95) Firschung, F. H., and Rosen, I., *J. Polymer Sci.*, **36**, 305 (1959).

(96) Flory, P. J., "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(97) Frolova, M. I., Nevskiĭ, L. V., and Ryabov, A. V., *Vysokomolekul. Soedin.*, **6**, 877 (1961).

(98) Frye, A. H., and Horst, R. W., *J. Polymer Sci.*, **45**, 1 (1960).

(99) Funt, B. L., and Pasika, W., *Can. J. Chem.*, **38**, 1865 (1960).

(100) Funt, B. L., and Williams, F. D., *J. Polymer Sci.*, **46**, 139 (1960).

(101) Funt, B. L., and Williams, F. D., *J. Polymer Sci.*, **57**, 711 (1962).

(102) Gahnem, N. A., *Makromol. Chem.*, **36**, 109 (1960).

(103) Gleason, E. H., Miller, M. L., and Sheats, G. F., *J. Polymer Sci.*, **38**, 133 (1959).

(104) Glusker, D. L., Stiles, E., and Yoncoskie, B., *J. Polymer Sci.*, **49**, 297 (1961).

(105) Godsay, M. P., Harpell, G. A., and Russell, K. E., *J. Polymer Sci.*, **57**, 641 (1962).

(106) Golub, M. A., and Shipman, J. J., *Spectrochim. Acta*, **16**, 1165 (1960).

(107) Graham, R. K., Dunkelberger, D. L., and Cohn, E. S., *J. Polymer Sci.*, **42**, 501 (1960).

(108) Grudinina, M. M., and Aleksandrova, E. M., *Izv. Vysshikh Uchebn. Zavedeniĭ, Khim. i Khim. Tekhnol.*, **3**, 176 (1960).

(109) Hammond, G. S., Boozer, C. E., Hamilton, C. E., and Sen, J. N., *J. Am. Chem. Soc.*, **77**, 3238 (1955).

(110) Hammond, G. S., and Kopecky, K. R., *J. Polymer Sci.*, **60**, S54 (1962).

(111) Henglein, A., *Z. Naturforsch.*, **11**, 616 (1955).

(112) Henrici-Olivé, G., and Olivé, S., *J. Polymer Sci.*, **48**, 329 (1960).

(113) Henrici-Olivé, G., and Olivé, S., *Makromol. Chem.*, **48**, 237 (1961).

(114) Henrici-Olivé, G., and Olivé, S., *Makromol. Chem.*, **51**, 236 (1962).

(115) Henrici-Olivé, G., and Olivé, S., *Makromol. Chem.*, **58**, 188 (1962).

(116) Henrici-Olivé, G., Olivé, S., and Schultz, G. V., *J. Polymer Sci.*, **56**, 233 (1962).

(117) Hodnett, E. M., and Jensen, A. W., *J. Polymer Sci.*, **43**, 183 (1960).

(118) Hoffmann, E. G., and Hoberg, H., *Z. Elektrochem.*, **58**, 646 (1954).

(119) Huggins, M. L., Hermans, J. J., *et al.*, *J. Polymer Sci.*, **8**, 257 (1952).

(120) Huggins, M. L., Natta, G., Desreux, V., and Mark, H., *J. Polymer Sci.*, **56**, 153 (1962).

(121) Ingalls, R. B., and Wall, L. A., *J. Chem. Phys.*, **35**, 370 (1961).

(122) Johnson, D. H., and Tobolsky, A. V., *J. Am. Chem. Soc.*, **74**, 938 (1952).

(123) Johnson, J. R., *Record Chem. Progr.* (*Kresge-Hooker Sci. Lib.*), 137 (1950).

(124) Johnston, J. A., Racusen, D. W., and Bonner, J., *Proc. Natl. Acad. Sci. U.S.*, **40**, 1031 (1954).

(125) Jones, M. H., Melville, H. W., and Robertson, W. G. P., *Nature*, **174**, 78 (1954).

(126) Jones, M. H., Melville, H. W., and Robertson, W. G. P., *Simp. Intern. Chim. Macromol.* (Turin-Milan), 271 (1954).

(127) Keckwick, R. G. O., Archer, B. L., Barnard, D., Higgins, G. M. C., McSweeney, G. P., and Moore, C. G., *Nature*, **184**, 268 (1959).

(128) Kennedy, J. P., *J. Polymer Sci.*, **38**, 263 (1959).

(129) Kennedy, J. P., and Thomas, R. M., *J. Polymer Sci.*, **45**, 227 (1960).

(130) Kiprianova, L. A., and Rekasheva, A. F., *Vysokomolekul. Soedin.*, **3**, 1446 (1961).

(131) Kobayashi, M., *Bull. Chem. Soc. Japan*, **33**, 1416 (1960).

(132) Kobayashi, M., *Bull. Chem. Soc. Japan*, **34**, 560 (1961).

(133) Kobayashi, M., *Bull. Chem. Soc. Japan*, **34**, 1045 (1961).

(134) Kolthoff, I. M., O'Connor, P. R., and Hausen, J. L., *J. Polymer Sci.*, **15**, 459 (1955).

(135) Koton, M. M., Kiseleva, T. M., and Bessenov, M. I., *Zh. Fiz. Khim.*, **28**, 2137 (1954).

(136) Koton, M. M., Kiseleva, T. M., and Bessenov, M. I., *Dokl. Akad. Nauk SSSR*, **96**, 85 (1954).

(137) Krimm, S., Liang, C. Y., and Sutherland, G. B. B. M., *J. Polymer Sci.*, **22**, 227 (1956).

(138) Landler, I., *Rec. trav. chim.*, **68**, 992 (1949).

(139) Landler, I., and Magat, M., *Bull. soc. chim. Belges*, **57**, 381 (1948).

(140) Levin, P. I., Miller, V. B., Nevskiĭ, L. V., Neĭman, M. B., Kargin, V. A., and Rylov, E. E., *Tr. Khim. Khim. Tekhnol.*, **2**, 3 (1959).

(141) Liang, C. Y., Lytton, M. R., and Boone, C. J., *J. Polymer Sci.*, **44**, 549 (1960).

(142) Liang, C. Y., Lytton, M. R., and Boone, C. J., *J. Polymer Sci.*, **47**, 139 (1960).

(143) Liang, C. Y., Lytton, M. R., and Boone, C. J., *J. Polymer Sci.*, **54**, 523 (1961).

(144) Liang, C. Y., Pearson, F. G., and Marchessault, R. H., *Spectrochim. Acta*, **17**, 568 (1961).

(145) McNall, L. R., and Eby, L. T., *Anal. Chem.*, **29**, 951 (1957).

(146) Mayo, F. R., *J. Am. Chem. Soc.*, **65**, 2324 (1943).

(147) Mayo, F. R., and Gregg, R. A., *Discussions Faraday Soc.*, **2**, 328 (1947).

(148) Mayo, F. R., and Gregg, R. A., *J. Am. Chem. Soc.*, **70**, 2373 (1948).

(149) Mayo, F. R., and Gregg, R. A., *J. Am. Chem. Soc.*, **75**, 3530 (1953).

(150) Mayo, F. R., Gregg, R. A., and Matheson, M. S., *J. Am. Chem. Soc.*, **73**, 1691 (1951).

(151) Mayo, F. R., *J. Am. Chem. Soc.*, **75**, 6133 (1953).

(152) Melville, H. W., Peaker, F. W., and Vale, R. L., *Makromol. Chem.*, **28**, 140 (1958).

(153) Melville, H. W., and Sewell, P. R., *Makromol. Chem.*, **32**, 139 (1959).

(154) Merrett, F. M., *Trans. Faraday Soc.*, **50**, 759 (1954).

(155) Mochel, W. E., and Peterson, J. H., *J. Am. Chem. Soc.*, **71**, 1426 (1949).

(156) Mochel, W. E., Crandall, J. L., and Peterson, J. H., *J. Am. Chem. Soc.*, **77**, 494 (1955).

(157) Morthland, F. W., and Brown, W. G., *J. Am. Chem. Soc.*, **78**, 469 (1956).

(158) Morton, M., Cala, J. A., and Piirma, I., *J. Am. Chem. Soc.*, **78**, 5394 (1956).

(159) Murray, A., and Williams, D. Ll., "Organic Syntheses with Isotopes," Interscience Publishers, Inc., New York, N. Y., 1958, p. 2.

(160) Nagai, H., Watanabe, H., and Nishioka, A., *J. Polymer Sci.*, **62**, S95 (1962).

(161) Natta, G., Farina, M., and Peraldo, M., *Atti accad. nazl. Lincei, Rend., Classe sci. fis., mat. nat.*, **25**, 424 (1958).

(162) Natta, G., Pasquon, I., Giachetti, E., and Pajaro, G., *Chim. Ind.* (Milan), **40**, 267 (1958).

(163) Natta, G., Pasquon, I., Pajaro, G., and Giachetti, E., *Chim. Ind.* (Milan), **40**, 556 (1958).

(164) Natta, G., Pajaro, G., Pasquon, I., and Stellacci, V., *Atti accad. nazl. Lincei, Rend., Classe sci. fis., mat. nat.*, **24**, 479 (1958).

(165) Natta, G., and Pasquon, I., "Advances in Catalysis," Academic Press, New York, N. Y., 1959.

(166) Natta, G., Giachetti, E., Pasquon, I., and Pajaro, G., *Chim. Ind.* (Milan), **42**, 1091 (1960).

(167) Natta, G., Guiffrè, L., and Pasquon, I., *Chim. Ind.* (Milan), **43**, 871 (1961).

(168) Overberger, C. G., and Ang., F., *J. Am. Chem. Soc.*, **82**, 929 (1960).

(169) Pajaro, G., and Desio, V., *Gazz. Chim. Ital.*, **91**, 880 (1961).

(170) Park, G. S., *Proc. Radioisotope Conf., 2nd Oxford, Engl.*, **2**, 11 (1954).

(171) Park, R. B., and Bonner, J., *J. Biol. Chem.*, **233**, 340 (1958).

(172) Pasquon, I., *J. Polymer Sci.*, **60**, S47 (1962).

(173) Pedersen, C. J., *Ind. Eng. Chem.*, **48**, 1881 (1956).

(174) Pedersen, H. L., *Acta Chem. Scand.*, **16**, 870 (1962).

(175) Peraldo, M., and Farina, M., *Chim. Ind.* (Milan), **42**, 1349 (1960).

(176) Pfann, H. F., Salley, D. J., and Mark, H., *J. Am. Chem. Soc.*, **66**, 983 (1944).

(177) Point, J. J., *Radioisotopes Sci. Res. Proc. Intern. Conf., Paris, Sept., 1957*, **2**, 438 (1958).

(178) Pravednikov, A. N., and Shen-Kan, I., *J. Polymer Sci.*, **53**, 61 (1961).

(179) Razuvaev, G. A., Petukhov, G. G., and Dodonov, V. A., *Vysokomolekul. Soedin.*, **3**, 1549 (1961).

(180) Rekasheva, A. F., and Kiprianova, L. A., *Vysokomolekul. Soedin.*, **3**, 1448 (1961).

(181) Rodriguez, L., and Gabant, J., *J. Polymer Sci.*, **57**, 881 (1962).

(182) Russel, G. A., *Chem. Ind.* (London), 1483 (1956).

(183) Russel, G. A., *J. Am. Chem. Soc.*, **79**, 3871 (1957).

(184) Schultz, G. V., Henrici-Olivé, G., and Olivé, S., *Makromol. Chem.*, **31**, 88 (1959).

(185) Schultz, G. V., Henrici-Olivé, G., and Olivé, S., *Z. Physik. Chem.* (Frankfurt), **27**, 1 (1961).

(186) Semon, W. L., Craig, D., Fowler, R. B., Regenass, F. A., Tucker, H., Yanko, J. A., Shipman, J. J., and Belt, R. F., *Science*, **128**, 359 (1958).

(187) Shelton, J. R., and McDonel, E. T., *J. Polymer Sci.*, **32**, 75 (1958).

(188) Shelton, J. R., *J. Appl. Polymer Sci.*, **2**, 345 (1959).

(189) Shelton, J. R., McDonel, E. T., and Crano, J. C., *J. Polymer Sci.*, **42**, 289 (1960).

(190) Shipman, J. J., and Golub, M. A., *J. Polymer Sci.*, **58**, 1063 (1962).

(191) Smets, G., Roovers, J., and van Humbeek, W., *J. Appl. Polymer Sci.*, **5**, 149 (1961).

(192) Smith, W. V., and Campbell, H. N., *J. Chem. Phys.*, **15**, 338 (1947).

(193) Smith, W. V., *J. Am. Chem. Soc.*, **71**, 4077 (1949).

(194) Soboleva, I. G., Makletsova, N. V., and Medvedev, S. S., *Kolloidn. Zh.*, **19**, 619 (1957).

(195) Stockmayer, W. H., and Peebles, L. H., *J. Am. Chem. Soc.*, **75**, 2278 (1953).

(196) Stockmayer, W. H., Clarke, J. T., and Peebles, L. H., *J. Am. Chem. Soc.*, **82**, 4780 (1960).

(197) Swain, C. G., Stockmayer, W. H., and Clarke, J. T., *J. Am. Chem. Soc.*, **72**, 5426 (1950).

(198) Swain, C. G., Schaad, L. J., and Kresge, A. J., *J. Am. Chem. Soc.*, **80**, 5313 (1958).

(199) Tadokoro, H., Nishiyama, N., Nozakura, S., and Murahashi, S., *J. Polymer Sci.*, **36**, 553 (1959).

(200) Tadokoro, H., Nishiyama, N., Nozakura, S., and Murahashi, S., *Bull. Chem. Soc. Japan*, **34**, 381 (1961).

(201) Teas, H. J., and Bandurski, R. S., *J. Am. Chem. Soc.*, **78**, 3549 (1956).

(202) Traylor, T. G., and Bartlett, P. D., *Tetrahedron Letters*, **24**, 30 (1960).

(203) Trotman, J., and Szwarc, M., *Makromol. Chem.*, **37**, 38 (1960).

(204) Tsuda, Y., *Chem. High Polymers* (Japan), **17**, 366 (1960).

(205) Tsuda, Y., *J. Appl. Polymer Sci.*, **5**, 104 (1961).

(206) Varshavskii, Ya. M., Vasil'Ev, G. Ya., Karpov, V. L., Lazurkin, Yu. S., and Petrov., I. Ya., *Dokl. Akad. Nauk SSSR*, **118**, 315 (1958).

(207) Wall, L. A., and Brown, D. W., *J. Polymer Sci.*, **14**, 513 (1954).

(208) Wall, L. A., Brown, D. W., and Hart, V. E., *J. Polymer Sci.*, **15**, 157 (1955).

(209) Wall, L. A., and Brown, D. W., *J. Phys. Chem.*, **61**, 129 (1957).

(210) Walling, C., *J. Am. Chem. Soc.*, **70**, 2561 (1948).

(211) Walling, C., and Hodgon, R. B., *J. Am. Chem. Soc.*, **80**, 228 (1958).

(212) Wiley, R. H., and Sale, E. E., *J. Polymer Sci.*, **42**, 479 (1960).

(213) Wiley, R. H., and Sale, E. E., *J. Polymer Sci.*, **42**, 491 (1960).

(214) Wiley, R. H., and Davis, B., *J. Polymer Sci.*, **46**, 423 (1960); erratum, *J. Polymer Sci.*, **61**, S33 (1962).

(215) Wiley, R. H., and Davis, B., *J. Polymer Sci.*, **62**, S132 (1962).

(216) Wiley, R. H., and Davis, B., *J. Polymer Sci.*, **62**, S140 (1962).

(217) Yoshida, T., *Bull. Chem. Soc. Japan*, **23**, 209 (1950).