ALLYL POLYMERIZATIONS

R. C. LAIBLE

Textile, Clothing, and Footwear Division, U. S. Army Quartermaster Research and Engineering Center, Natick, Massachusetts

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CONTENTS

I. INTRODUCTION

Allyl-type polymerizations have received much less emphasis than the corresponding vinyl polymerizations; this is because the former compounds polymerize with difficulty to give products of low molecular weight. To explain the interest of the Textile, Clothing, and Footwear Division of the Quartermaster Research and Engineering Laboratories in such work, it is necessary to review briefly the development of flameproofing agents, with special emphasis on military requirements.

During World War II the Quartermaster Corps initiated a project at Columbia University to study the factors involved in flame retardancy in order to prepare better flame retardants for textiles. The flame-retardant-treated end item was intended for use in the clothing of tank crews for protection against flame hazards. All the treatments then available suffered from some deficiency, such as lack of permanence, excessive loss of tear strength, or unsatisfactory flame-retardant properties.

The esterification of cellulose with mixtures of phosphoric acid and urea appeared to be the most promising approach to the problem, and accordingly received emphasis at Columbia University.

The development of a brominated triallyl phosphate polymer by Dr. George Walter of the Glenn L. Martin Company in 1949–50 considerably altered this emphasis. This treatment imparted satisfactory flame and glow resistance to fabrics; methods of improving the hand and tear strength of the treated fabric were worked out in the Quartermaster Research and Engineering Laboratories.

As a result of the interest stimulated by this compound, chain-transfer products of triallyl phosphate were developed which possessed some advantages over the parent compound. One of these products, the so-called bromoform adduct developed by The Department of Agriculture, could be applied to fabric as an oil-in-water emulsion with conventional finishing equipment.

Present after the polymerization of triallyl phosphate was residual unsaturation, which served two purposes. The first was for the addition of bromine to decrease the flammability of the volatile degradation products; the second was that even after bromination and application to cloth, additional polymerization and cross-linking could take place, making the treatment permanent to laundering. Owing to the anticipated high cost of this product, the Quartermaster Corps sponsored research on the development of other compounds which might cost less and be easier to apply. Many of the new flame retardants which were developed involved allyl polymerization in some form. These developments are discussed briefly in this paper.

From the difficulties experienced by various laboratories working on these allyl polymers, it soon became apparent that, to make further progress in the field of allyl polymerization, it would be necessary to review the available literature in this field. In the Appendix more than one hundred allyl monomers are listed. The polymerization of some of these monomers has been unsuccessful; however, even these listings may be helpful to workers attempting to select suitable monomers for flame-retardant preparations or for other uses.

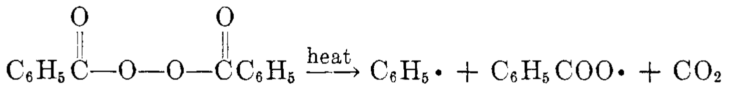
II. GENERAL POLYMERIZATION THEORY

A. Processes

Polymerizations, and in fact all chain reactions, involve three constituent processes: chain initiation, chain propagation, chain termination. A fourth process, chain transfer, will also be discussed in detail because of its importance to polymerizations in general and allyl polymerizations in particular.

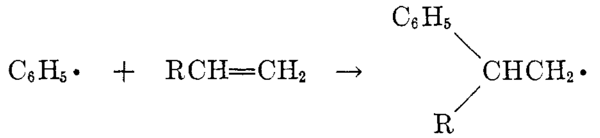
The initiation reaction may be thermal, photochemical, or catalytic. In the plant production of polymers, catalytic initiation is usually employed, as the time to complete the reaction and the average molecular weight of the polymer may be more easily controlled by this method.

The catalysts can be divided into the Friedel–Crafts type, which causes polymerization by increasing the polarity of the monomer double bond, and the peroxide type. The latter type includes the organic peroxides and the inorganic per salts, both of which decompose to give free radicals which initiate growing chains of a free-radical nature. For benzoyl peroxide this decomposition is believed to proceed according to the following equation:

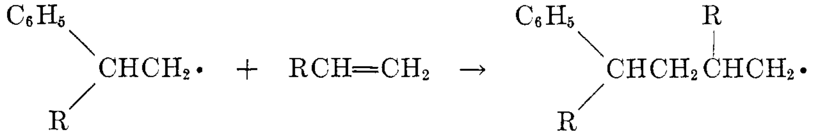


$$C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}—O—O—\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5 \xrightarrow{\text{heat}} C_6H_5\cdot + C_6H_5COO\cdot + CO_2 \qquad (1)$$

One of the radicals produced then adds to the monomer double bond to give a larger radical, and the propagation reaction has started.



(2)

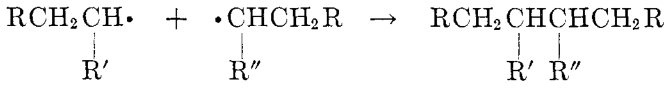


(3)

The propagation reaction is straightforward and requires no discussion.

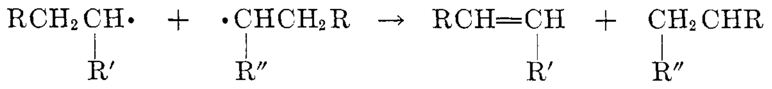
The termination of the growing chains is much more complex, as there are many possible paths depending on the nature of the growing polymer, the monomer, and the solvent present. The usual termination reactions are coupling and disproportionation, as shown below:

Coupling:



$$RCH_2\underset{\underset{\displaystyle R'}{|}}{CH}\cdot + \cdot\underset{\underset{\displaystyle R''}{|}}{CH}CH_2R \rightarrow RCH_2\underset{\underset{\displaystyle R'}{|}}{CH}\underset{\underset{\displaystyle R''}{|}}{CH}CH_2R \qquad (4)$$

Disproportionation:



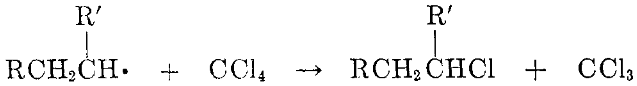
$$RCH_2\underset{\underset{\displaystyle R'}{|}}{CH}\cdot + \cdot\underset{\underset{\displaystyle R''}{|}}{CH}CH_2R \rightarrow RCH{=}\underset{\underset{\displaystyle R'}{|}}{CH} + CH_2\underset{\underset{\displaystyle R''}{|}}{CHR} \qquad (5)$$

Both of the reactions shown above result in the destruction of two growing chains for each interaction.

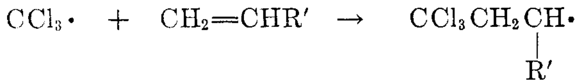
Other so-called termination and propagation reactions are really chain-transfer reactions. For instance, in solvent polymerizations the growing radical may react with the solvent rather than with another monomer molecule. This could be called a termination reaction, since the growing chain is terminated. However, the solvent fragment then becomes a free radical and has a certain probability of starting a new chain.

Where carbon tetrachloride is the solvent the reaction proceeds as follows:

Chain transfer with solvent:



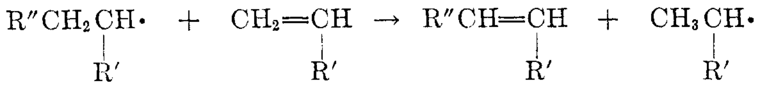
$$\mathrm{RCH_2\overset{R'}{\overset{|}{C}}H\cdot \; + \; CCl_4 \; \rightarrow \; RCH_2\overset{R'}{\overset{|}{C}}HCl \; + \; CCl_3\cdot} \tag{6}$$



$$\mathrm{CCl_3\cdot \; + \; CH_2{=}CHR' \; \rightarrow \; CCl_3CH_2\underset{R'}{\underset{|}{C}}H\cdot} \tag{7}$$

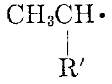
Equation 6 corresponds to termination, and equation 7 is a propagation reaction. The presence of a solvent such as carbon tetrachloride tends to shorten the chain length (lower the molecular weight) but does not terminate the chain reaction. If the solvent radical produced were very inactive or stabilized by resonance, the chain reaction itself would be terminated, as would the individual chains.

Another type of chain transfer which can occur is that with monomer molecules. Instead of the monomer molecule adding to the growing active chain, a hydrogen atom is abstracted from or transferred to the monomer molecule. This terminates the growing chain and produces an active monomer molecule. This reaction would lower the molecular weight but would not terminate the chain reaction unless the monomer molecule produced an exceedingly stable free radical.



$$\mathrm{R''CH_2\underset{R'}{\underset{|}{C}}H\cdot \; + \; CH_2{=}\underset{R'}{\underset{|}{C}}H \; \rightarrow \; R''CH{=}\underset{R'}{\underset{|}{C}}H \; + \; CH_3\underset{R'}{\underset{|}{C}}H\cdot} \tag{8}$$

In equation 8 a possible chain-transfer reaction is shown which would end a chain, but the radical produced,

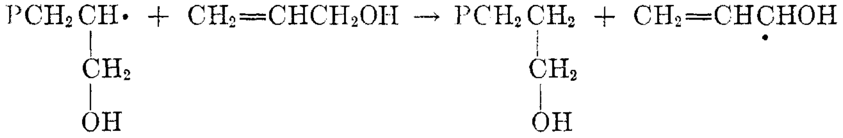


$$\mathrm{CH_3\underset{R'}{\underset{|}{C}}H\cdot}$$

would be able to initiate a new chain unless R′ were some group contributing considerable resonance stabilization to the free radical.

B. Importance of chain transfer

This chain transfer with monomer molecules is not too important in most polymerizations, e.g., vinyl polymerizations. However, this is the greatest difference between allyl polymerizations and other types of polymerizations. Chain transfer between an active growing chain and an allyl monomer can not only lead to termination of this growing chain but can also terminate the chain reaction. This chain transfer of the monomer with the growing polymer chain is shown in equation 9 with allyl alcohol as the monomer example.



$$PCH_2\underset{\substack{|\\ CH_2\\ |\\ OH}}{C}H\cdot + CH_2{=}CHCH_2OH \rightarrow PCH_2\underset{\substack{|\\ CH_2\\ |\\ OH}}{C}H_2 + CH_2{=}CH\underset{\bullet}{C}HOH \quad (9)$$

The monomer radical produced is stabilized by resonance and is consequently less active.

$$CH_2{=}CH\underset{\bullet}{C}HOH \leftrightarrow \cdot CH_2CH{=}CHOH \quad (10)$$

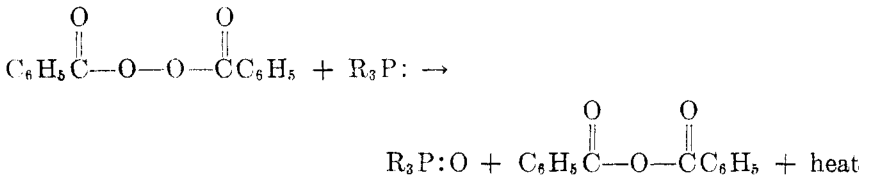
The allyl radical produced has less tendency to initiate a new polymer chain; therefore, this chain transfer will be essentially a termination reaction. This is called "degradative chain transfer" and is the major reason for the low-molecular-weight products obtained in the polymerization of allyl-type monomers. Chain transfer with monomers is more important in allyl polymerizations because of this ability of the allyl radical to stabilize itself by resonance, which makes the abstraction of a hydrogen atom easier. Because of this fact even small amounts of allyl alcohol inhibit or retard the polymerization of other monomers.

III. INITIATION OF ALLYL POLYMERIZATIONS

Large amounts of initiators are required for allyl polymerizations because the growing chains are terminated by "degradative chain transfer" after only a few monomer units have been added (36, 364). The methods of initiation used have included heat, light, irradiation, peroxides, hydroperoxides, perborates, persulfates, and oxygen. Allyl monomers do not respond as readily to heat and light as other monomers, so catalysts are preferred (216).

A. Benzoyl peroxide

For bulk and solution polymerizations, benzoyl peroxide has been the catalyst most frequently used. However, in the case of certain classes of monomers, the addition of benzoyl peroxide has caused a temperature rise but no polymerization. This phenomenon is probably due to some sort of compound formation between the benzoyl peroxide and the unshared electrons on a nitrogen or phosphorus atom. The reaction probably proceeds according to the following equation:



$$C_6H_5\overset{\substack{O\\ \|}}{C}{-}O{-}O{-}\overset{\substack{O\\ \|}}{C}C_6H_5 + R_3P{:} \rightarrow R_3P{:}O + C_6H_5\overset{\substack{O\\ \|}}{C}{-}O{-}\overset{\substack{O\\ \|}}{C}C_6H_5 + \text{heat} \quad (11)$$

B. Other free-radical-producing catalysts

Nozaki and Bartlett found that amines such as aniline and triethylamine accelerate the decomposition of benzoyl peroxide to such an extent that the resulting reaction can be considered explosive (281). Esteve and Laible found that triallyl phosphite would not polymerize in the presence of benzoyl peroxide, but that a sharp temperature rise occurred immediately after adding the catalyst. In reactions such as this a change of catalysts from benzoyl peroxide to tertiary butyl peroxide often allows the polymerization to proceed normally. Diallylmelamine was also polymerized in this manner (208).

No discussion of catalysts useful in the polymerization of allyl esters would be complete without some mention of the development of the peroxycarbonates by Strain. These compounds possess the advantage of decomposing at a lower temperature than benzoyl peroxide, but extreme caution is necessary to avoid explosions due to the instability of these catalysts (371).

Catalysts such as the hyponitrites also decompose at a much lower temperature than benzoyl peroxide and have been found to be effective in the polymerization of methyl methacrylate (227). Their effectiveness in the polymerization of allyl compounds is not known and should be investigated.

Azobis(isobutyronitrile) has recently been used as an initiator for the study of allyl polymerizations in order to avoid the kinetic complications of benzoyl peroxide, which undergoes induced decomposition (137).

C. Friedel–Crafts catalysts

Very few instances have been recorded where a catalyst of the Friedel–Crafts type was recommended for the polymerization of allyl compounds. Butler used a boron trifluoride–diethyl ether complex to initiate the polymerization of allyl ethers of allyl-substituted phenols. The use of this catalyst was necessary because phenols, possible by-products upon heating, inhibit polymerizations by peroxide. The allyl side chains were left untouched, and only the allyl ether groups were polymerized (66).

D. Mechanism of peroxide decomposition

The mechanism of the decomposition of peroxide has been discussed in Section II,A and illustrated by equation 1.

The decomposition of benzoyl peroxide in the bulk polymerization of allyl esters follows almost first-order kinetics with the rate constant increasing with initial peroxide concentration (153). In allyl alcohol the initial decomposition of benzoyl peroxide is a very rapid first-order reaction, but some or all of the products act as inhibitors and their accumulation slows down the reaction (152).

The potassium persulfate used as a catalyst for the emulsion polymerization of allyl acetate was also found to decompose with first-order kinetics over the entire range of concentrations used (39).

The polymerization of allyl acetate has been studied by Bartlett and Altschul in some detail. Chlorobenzoyl peroxide was used to initiate the polymerization so that the reactions could be followed more easily by analysis for chlorine. Most of the polymer molecules contain fragments of the peroxide, showing that the radicals produced by decomposition of peroxide actually add to a monomer molecule initiating the polymerization. About one-fifth of the polymer chains were initiated by some other radical. These other radicals must have been produced by chain transfer of peroxide fragments with solvent, monomer, or initiator (35).

IV. INHIBITION AND ACCELERATION

In general, allyl polymerizations have been found to be inhibited somewhat by copper, lead, and sulfur compounds as well as by atmospheric oxygen (366). Lynn, in his review of allyl plastics, mentions the use of copper as a polymerization catalyst under certain conditions and as an inhibitor under other conditions (216). In the polymerization of triallyl phosphate, copper completely stopped the polymerization (132).

Bartlett and Hammond attempted to develop quantitative expressions for the inhibitory activities of certain quinones in the peroxide-induced polymerization of allyl acetate (37). They also studied the inhibitory effects of various nitro compounds on the benzoyl peroxide-initiated polymerization of allyl acetate and calculated the instantaneous kinetic chain length from the rates of disappearance of monomer and peroxide. It was found that trinitrobenzene was the most active inhibitor studied, stopping 5.9 chains per mole. It was suggested that the radical attacks the nitro group. The primary products of the inhibition reactions are apparently retarders themselves, since the slopes of the curves of monomer plotted against peroxide consumption are still smaller than uninhibited runs even after the inhibitor is destroyed (172).

Allyl alcohol apparently has little tendency to polymerize; in fact, it slows up or inhibits the polymerization of other monomers. For example, allyl alcohol was shown to inhibit the polymerization of butadiene; therefore, one must prepare such a copolymer indirectly (229). Along the same line, Griffin, Esteve, and Laible found that a small percentage of added allyl alcohol (4 per cent) greatly inhibited the polymerization of triallyl phosphate, so that double the quantity of peroxide initiator was required to complete the polymerization (167). Others have used allyl alcohol to repress early gelation in the polymerization of allyl monomers and other unsaturated compounds (381, 383). The polymerizations are then easier to control and result in higher yields of polymers (414).

Nozaki and Bartlett found that oxygen retarded the decomposition of benzoyl peroxide (281). Many other authors have found that oxygen either accelerated or inhibited a particular polymerization (50). The anomaly of acceleration and inhibition by oxygen is due to the fact that allyl, vinyl, and vinylidene monomers form peroxides with oxygen and these peroxides can act as polymerization catalysts. Inhibition occurs because in many cases peroxide formation is preferred to polymerization (34).

Esteve and Laible found that the polymerization of triallyl phosphate was significantly faster in air than in nitrogen (130). In this case there may have been inhibition initially due to the reaction between free radicals and oxygen to produce peroxides. Later in the polymerization the peroxides decomposed, yielding active radicals and causing a resultant acceleration of the reaction.

Methacrylamide has been used to speed up the polymerization of polyallyl esters of polybasic carboxylic acids (e.g., diallyl oxalate) and thus to reduce color formation (199).

Pfann found methacrylic acid useful in the polymerization of methallyl alcohol, while Degering of the Quartermaster Research and Engineering Command frequently uses methacrylic acid to lower the dosage necessary to polymerize monomers by irradiation (120, 297).

Allyl polymerization is a chain reaction and the danger of explosions can be present both during the polymerization of the monomer and during its isolation. Before distilling triallyl phosphate it was necessary to wash the monomer carefully with sodium carbonate solution to remove the acid esters and to add sodium hydroxide pellets and hydroquinone to inhibit polymerization during distillation (125, 167).

Aromatic sulfonic acids accelerate the rate of cure of mixtures of allyl compounds such as diallylsilicone and diallyl silicate with unsaturated alkyd resins (174). Cerium salts have a similar effect on the thermosetting of some allyl polyesters (87).

Alkalis, such as sodium hydroxide or trimethylammonium hydroxide, completely inhibit the polymerization of polyallyl ethers of carbohydrates (277).

V. KINETICS

Considerable experimental work is necessary to determine the kinetics of any polymerization. The measurements include the total yield of polymer, the degree of polymerization (molecular weight), and the distribution curve as function of time, temperature, and concentration. In addition, logical assumptions must be made regarding the elementary reactions involved, in order to write down the differential rate equations representing the various steps in the polymerization. In simplest form these steps are: initiation, propagation, and termination. Integration of these equations then leads to expressions which can be compared directly with the experimental results, proving or disproving the validity of the original assumptions (223).

A. Total yield

The yield of polymer obtained under various conditions is easy to determine; the usual method involves the precipitation of aliquot portions of the polymer solution at various stages in the polymerization. Other methods of following the polymer formation include measurement of refractive index, viscosity, density, volume contraction, and bromination (111). Some of these methods are not suitable for the polyfunctional allyl polymerizations discussed in this report. For instance, bromination would not determine the amount of monomer left, because there would be pendant allyl groups in the polymer which could absorb bromine, and cross-linking would complicate the situation further.

B. Degree of polymerization

The degree of polymerization or molecular weight is more difficult to determine. Viscosity gives only relative values, and it is still necessary to determine the molecular weight by an absolute method in order to translate the viscosities to molecular weight. Most allyl polymers are of low molecular weight and a cryoscopic method of determining the degree of polymerization (D.P.) is preferred. Gaylord and Eirich dissolved their allyl polymers in 15–20 ml. of benzene, froze the solution, and determined the melting curve. Extrapolation of these readings to a break in the curve gave the freezing-point depression and thus the molecular weight (154). The available molecular-weight information on allyl polymers is quite meager and can be summarized in the following tabulation:

Monomer	Molecular Weight	Conditions	Reference
Allyl acetate	1300	Bulk polymerization; benzoyl peroxide	(35)
	1300	Emulsion polymerization; potassium persulfate	(233)
Allyl 1,1-d_2 acetate	3100	Bulk polymerization; benzoyl peroxide	(40)
Allyl alcohol	300	Hydrogen peroxide catalyst	(284)
Allyl benzoate	1500	Bulk polymerization at 80°C.; peroxide	(332)
Allyloxy-1,2-propanediol	1020	Bulk polymerization at 190°C.	(116)
Diallyl phthalate	3900	Bulk polymerization; benzoyl peroxide	(164)

If the polyfunctional allyl monomers possessing flame-retardant properties such as triallyl phosphate are polymerized to a degree comparable to allyl acetate (D.P. approximately equal to 13), molecular weights of about 3000 would be expected. That these polymers appear to possess higher molecular weights may be due strictly to cross-linking. Yield and per cent unsaturation are known for these polymers, and determination of the molecular weights would allow one to predict with considerable accuracy the extent of this cross-linking.

C. Allyl acetate

Allyl acetate has been the subject of extensive kinetic studies. It has been found that, in any given polymerization, the amount of monomer polymerized is a linear function of the concentration of peroxide decomposed (dM/dP = constant). The constancy of dM/dP is attributable to "degradative chain transfer" and results in the rate of polymerization being dependent upon the first power of the peroxide concentration (40, 154). This is in conflict with vinyl polymerizations, where the rate of polymerization is always proportional to the square root of the peroxide concentration. Bartlett and Tate have shown that the hydrogen atoms attached to the carbon atom alpha to the double bond are responsible for this chain transfer. It was possible to increase the rate of polymerization and the molecular weight obtained by a large factor, using a deuterium-substituted allyl acetate which would slow down this transfer reaction. Deuterium is transferred only one-third as fast as ordinary hydrogen, and the molecular weight was increased by a factor of 2.4 (40).

Recent work at Columbia University has shown that the use of high pressures may be a method of inhibiting "degradative chain transfer" in allyl polymerizations. Under a pressure of 8500 kg./cm.^{2} allyl acetate polymerizes like a typical vinyl monomer, but the molecular weight is only slightly affected by pressure (295a).

D. Other allyl monomers

The subject of the constancy of dM/dP has been reviewed by Sakaruda and Takahashi, who presented a whole kinetic scheme based upon the importance of degradative chain transfer in all allyl polymerizations (332). A recent article by Gaylord is concerned with this subject of dM/dP and its relationship to degradative chain transfer. It is pointed out that the fact that dM/dP is constant does not require the occurrence of degradative chain transfer as the exclusive chain-termination reaction. For allyl acetate most of the chain transfer is degradative (75 per cent), but with other allyl monomers such as allyl chloroacetate, allyl laurate, and allyl benzoate, which exhibit a constant dM/dP, degradative chain transfer is a much smaller proportion of the total transfer reactions (150, 332).

In the case of triallyl phosphate the degree of polymerization has not been determined, but the rate of polymerization appears to be proportional to the square root of the peroxide concentration and the first power of the monomer concentration (130, 209).

VI. DETERMINATION OF RESIDUAL UNSATURATION IN THE POLYMERS

A. Purpose

The determination of the unsaturation remaining after a polyfunctional allyl polymerization has two main objectives. The first is that this information, combined with approximate molecular-weight determinations, can furnish a measure of the extent of cross-linking which has taken place. The extent of cross-linking affects the solubility of the polymer, the viscosity of the resulting solutions, and the permanence of the treatment when applied to textiles. The second objective is that if allyl double bonds can be differentiated from other double bonds, one can determine the extent of the polymerization which proceeds through allyl bonds where other types of unsaturation are present.

B. Allyl acrylate

With allyl acrylate, the overall unsaturation and the allyl unsaturation have been determined. For the determination of the allyl unsaturation, a weighed amount of polymer was dissolved in a mixture of carbon tetrachloride and acetic acid, and then bromine-bromate solution was added. The solution was left in the dark for 1 hr.; then sulfuric acid and potassium iodide solutions were added. The separated iodine was titrated with sodium thiosulfate solution, and the allyl unsaturation was calculated. The overall unsaturation is determined similarly, but sodium chloride solution is used instead of potassium iodide. In the case of allyl acrylate the difference between the overall unsaturation and the allyl unsaturation gives the percentage of acrylic unsaturation remaining (156).

VII. PREDICTION OF POLYMERIZABILITY

A. Factors involved

Some of the factors influencing the polymerizability of allyl compounds are common to other addition polymerizations also. Toy and Cooper found that steric hindrance, the electrical character of the substituent group, and the presence or absence of inhibiting groups were very important in determining when a given allyl compound would polymerize (402). Their test of polymerizability involved heating 5 g. of each monomer for 18 hr. at 87–88°C. in the presence of 3 per cent benzoyl peroxide. It was known from previous work that dimethallyl and diallyl aryl phosphonates would polymerize into hard glassy solids under these conditions.

B. Classes of polymerizability

From the results of this test the dimethallyl and diallyl aryl and alkyl phosphonates under study could be divided into three classes as follows: (*1*) those polymerized to hard glassy solids (see table 1); (*2*) those polymerized to flexible solids or to gels (see table 2); (*3*) those polymerized so little that they are fluid after the polymerization test (see table 3).

TABLE 1

Monomers polymerized to hard glassy solids

Diallyl phosphite, $H\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$	Diallyl benzylphosphonate,* $C_6H_5CH_2\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$
Diallyl benzenephosphonate, $C_6H_5\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$	Diallyl phenylphosphonate, $C_6H_5O\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$
Diallyl isobutenylphosphonate,* $(CH_3)_2C=CH\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$	

* Also methallyl analogs.

TABLE 2

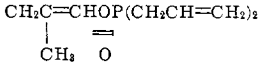
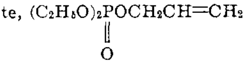
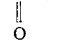
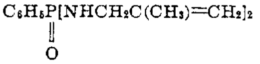
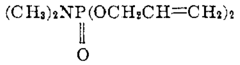
Monomers polymerized to flexible solids or gels

Diallyl cyclohexylphosphonate,* $C_6H_{11}\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$	Diallyl *n*-propylphosphonate, $C_3H_7\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$
Diallyl methylphosphonate, $CH_3\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$	Diallyl *n*-butylphosphonate,* $C_4H_9\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$
Diallyl ethylphosphonate, $C_2H_5\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$	Diallyl isobutylphosphonate, $i\text{-}C_4H_9\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$
Diallyl isopropylphosphonate, $(CH_3)_2CH\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$	Diallyl styrylphosphonate,* $C_6H_5CH=CH\underset{\underset{O}{\|}}{P}(OCH_2CH=CH_2)_2$

* Also dimethallyl analogs.

TABLE 3

Monomers unpolymerized or liquid after test

Diallyl isoöctenylphosphonate,  $\underset{\underset{CH_3}{\vert}}{CH_2C}{=}CH\underset{\underset{O}{\Vert}}{OP}(CH_2CH{=}CH_2)_2$	Diethylallyl phosphate,  $(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}OCH_2CH{=}CH_2$
Diallyl phenylthiophosphonate,  $C_6H_5\underset{\underset{S}{\Vert}}{P}(OCH_2CH{=}CH_2)_2$	Diethyl *N*,*N*-diallylphosphoramidate,  $(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}N(CH_2CH{=}CH_2)_2$
N,*N*′-Dimethallyl phenylphosphonamidate,  $C_6H_5\underset{\underset{O}{\Vert}}{P}[NHCH_2C(CH_3){=}CH_2]_2$	Diallyl *N*,*N*-dimethylphosphoramidate,  $(CH_3)_2N\underset{\underset{O}{\Vert}}{P}(OCH_2CH{=}CH_2)_2$

C. Conclusions

The authors conclude from the results shown that the amido grouping has an inhibiting effect on the polymerization. They found on further investigation that diallyl dimethylamido phosphonate not only did not polymerize but even retarded the polymerization of other diallyl phosphonates. On the other hand, diallyl dimethylamido phosphonates did not inhibit vinyl polymerizations such as that of methyl methacrylate (402).

Another conclusion reached was that the dimethallyl esters polymerized faster than the corresponding diallyl esters. This difference was quite marked with the monomers which were difficult to polymerize, but in most cases the diallyl phosphonate was placed in the same class as the analogous dimethallyl compounds. The authors explain the lack of polymerization of diethyl allyl phosphate by the fact that only one allyl group is present, as in allyl acetate which also gives products of very low molecular weight (402).

Bartlett has obtained considerable evidence for the type of chain transfer occurring in the case of allyl acetate. He found that a deuterium-substituted allyl acetate, $CH_2{=}CHCD_2OCOCH_3$, had a rate of polymerization two or three times as great as that for allyl acetate. The average molecular weight obtained was increased by a similar factor. It is known that deuterium is transferred only one-third as fast as ordinary hydrogen. These results seem to confirm Bartlett's previous conclusion that the transfer of hydrogen from the allylic position of allyl acetate to the chain-carrying free radical is the principal chain-termination step and is the reason for the low-molecular-weight products obtained (40).

In the polymerization of allyl chloride, the low-molecular-weight products formed may be due to the termination steps involving abstraction of a hydrogen atom or of a chlorine atom. The resultant radicals, $CH_2{=}CH\underset{\bullet}{C}HCl$ or $CH_2{=}CHCH_2\bullet$, would be considerably stabilized by resonance (151). This may account for the fact that, although allyl chloride, vinyl acetate, and vinyl chloride possess about the same reactivity with free radicals, allyl chloride exhibits a far lower overall rate of polymerization than the others (19).

This degradative chain transfer is an important reaction of allyl alcohol.

This is the reason that the polymerization of triallyl phosphate requires more catalyst when allyl alcohol is present than it does alone (167).

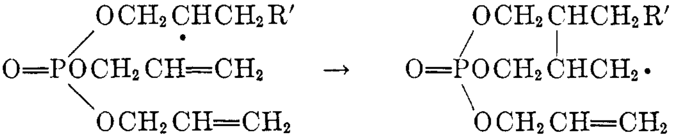
VIII. GELATION

The point at which gelation occurs in a polymerization is very important from both practical and theoretical points of view. Some chemists feel that the extent of reaction or conversion at the gel point has a fixed value for each particular set of monomers (79). One can then use the time required to reach the gel point as an indication of the reactivity of the monomer as compared to other monomers.

On the other hand, if the per cent conversion at the gel point could be increased, practical advantages would result. If recycling is impossible, the greater yield results in less waste and lower cost of the polymer. In cases where recycling is possible, fewer polymerizations are necessary to attain the same amount of product.

In the case of allyl methacrylate, mercaptans are used to delay gelation until a greater conversion to polymer has occurred. This polymerization takes place mainly through the methacrylate groups, but some allyl groups are included, leading to long branches, cross-linking, and subsequently early gelation. The mercaptans inhibit the polymerization of the allyl double bonds more than that of the methacrylate groups, and gelation is delayed (89, 90).

The factors involved in the gelation of diallyl phthalate have been quite thoroughly studied by English scientists. The "incestuous" tendency for two double bonds in the same diallyl monomer to enter the same polymerization chain delays the gel point (164, 178, 356). A similar phenomenon may take place in the polymerization of triallyl phosphate. A lower concentration of monomer to solvent was found to delay gelation. However, the residual unsaturation after polymerization was considerably less than when a greater concentration of monomer to solvent was used. More important from the author's point of view was the fact that the resultant retention when applied to cloth was also less, as fewer double bonds were available for further polymerization on the cloth. The advantage gained—greater yield—was not worth the price. Apparently, intramolecular polymerization is more important in dilute solution, as illustrated by the following equation (130).



$$\begin{array}{lcl} \quad\; OCH_2\underset{\bullet}{C}HCH_2R' & & \quad\; OCH_2CHCH_2R' \\ \;/ & & \;/ \qquad\quad | \\ O{=}POCH_2CH{=}CH_2 & \rightarrow & O{=}POCH_2CHCH_2\cdot \\ \;\backslash & & \;\backslash \\ \quad\; OCH_2CH{=}CH_2 & & \quad\; OCH_2CH{=}CH_2 \end{array}$$

The R′ in these formulas represents the polymer chain formed at the time when this intramolecular polymerization took place.

This type of polymerization results in decreased unsaturation without increasing the molecular weight and should be avoided when durable polymers are desired for use in the functional finishes field. This same explanation may account in part for the lack of durability of some other polymeric flame retardants.

IX. CHAIN TRANSFER

A. Theoretical considerations

The equation

$$\frac{1}{P_n} = \frac{1}{P_0} + \frac{C_s(S)}{(M)}$$

is a very useful one for determining the relative amount of chain transfer occurring between different solvents and a radical chain. The term P_n represents the actual degree of polymerization, P_0 represents the degree of polymerization obtained for the polymer when no solvent was present, S/M is the ratio of the solvent to monomer concentration, and C_s is the chain-transfer constant. Many chain-transfer constants have been determined for the polymerization of styrene in the presence of different solvents.

B. Practical applications

Similar studies have been conducted using allylic monomers, but the above equation is less valid in these cases. The equation assumes that chain transfer with monomer or initiator is very minor in the polymerization under study. In the case of allyl monomers, chain transfer with the monomer is very important and cannot be neglected. Qualitatively, however, it has been shown that halogenated compounds are very good chain-transfer agents. Practical use has been made of this fact in preparing flame-retardant polymer solutions, as shown in later paragraphs.

Lewis and Mayo recently reviewed the factors important in producing a chain-transfer product from a solvent and an allylic monomer. They found that, to obtain good yields of low-molecular-weight products from a solvent and a monomer, the transfer constant of the solvent should be near or greater than unity. This condition is met most easily when one component is an electron donor in the transition state and the other an electron acceptor. In the case of allylic monomers, very reactive solvents and strong polar effects are needed to reduce termination by degradative chain transfer with monomer and thus increase the likelihood of termination by chain transfer with solvent (212).

Allyl compounds have been copolymerized with trichloroalkenes, while diallyl maleate and diallyl fumarate have been polymerized in the presence of bromomethane to produce more flame-resistant resins (142, 388). Chain transfer should be a major reaction in both cases.

Even the degradative chain transfer characteristic of allyl monomers can serve a useful purpose. Small amounts of allyl halides are used to increase pregelation reaction times and the yields of soluble polymers in more reactive polymerizations (343, 384).

X. COPOLYMERIZATION THEORY

A. Chemical composition

Alfrey and Mark investigated a method of predicting the chemical composition of copolymers based on the equation

$$\frac{b}{a} = \alpha \frac{B}{A} \frac{\beta \mathrm{B} + \mathrm{A}}{\alpha \mathrm{B} + \mathrm{A}}$$

where b/a = molar ratio of monomer units in copolymers; B and A = molar concentrations of monomers (starting materials); α = ratio of respective rate constants for the addition of monomers B and A to type A radicals; and β = ratio of respective rate constants for addition of monomers B and A to type B radicals. Reliable experimental α and β values were reported for the system styrene–methyl methacrylate. These values were not affected by the presence of small proportions of impurities, by the amount of peroxide-type catalyst used, or by the addition of small amounts of hydroquinone in the absence of oxygen (22).

The system styrene–allyl chloride was next studied by Alfrey. From an experimental determination of the composition of the copolymers produced using different ratios of starting materials and the use of the equation mentioned above, the value of 0.032 was assigned to both α and β. The significance of the α value 0.032 is that allyl chloride monomer adds to a styrene free radical only about 0.032 times as fast as styrene monomer does. The small β value (0.032) means that allyl chloride monomer also adds to the allyl chloride free radical much more slowly than styrene adds to this same radical (21).

These same α and β values calculated for the styrene–allyl chloride system were applied to the polymerization of allyl acrylate by Ginden and Medvedev. The polymerization of allyl acrylate can be considered as a copolymerization where the two components are the "allyl" and the "acrylic" bonds of the monomer, present in a 1:1 ratio. The calculated share of the allyl bonds used in the polymerization is 3.2 per cent as shown below:

$$\frac{b}{a} = \alpha \frac{B}{A} \frac{\beta \mathrm{B} + \mathrm{A}}{\alpha \mathrm{B} + \mathrm{A}} = 0.032 \frac{(1)\ 1.032}{(1)\ 1.032} = 0.032$$

This value checks fairly well with that found experimentally, showing that most of the polymerization proceeds through the acrylic bonds. Further heating could convert the polymer to a cross-linked resin through the residual allyl groups (156).

B. Reaction rates

Nozaki attempted to arrange monomers qualitatively according to the relative rates at which they react with free radicals in a given copolymerization. It should be possible to apply the order to other reference radicals.

As can be seen from table 4, allyl chloride would be a minor part of any copolymer resulting from its polymerization with monomers such as acrylonitrile or styrene (280).

TABLE 4

Relative reactivity of monomers

Monomer	Relative Rate of Reaction	Monomer	Relative Rate of Reaction
Styrene	54	Vinyl chloride	4.6
Methyl methacrylate	48	Allyl chloride	2.0
Acrylonitrile	20	Vinyl acetate	1.5

C. Practical applications

Copolymers of allyl-type monomers with other unsaturated compounds sometimes possess better properties than either homopolymer. For instance, Celanese Corporation of America possesses a patent on the copolymerization of allyl esters of saturated acids with esters of saturated alcohols and unsaturated acids. They claim that the copolymers are much stronger and tougher than the polymers of the individual components (185).

Small amounts of allyl compounds such as diallyl maleate have been copolymerized with monomers like styrene to produce copolymers which are insoluble in some of the usual solvents for polystyrene (24).

A small amount of diallyl ether (2 to 4 per cent) when copolymerized with vinyl chloride gave a copolymer with a decomposition point of 199°C., as contrasted with 146°C. for the pure polyvinyl chloride polymer. A mixed catalyst of benzoyl peroxide and boron trifluoride was used for this polymerization (214). A small amount of diallyl benzenephosphonate copolymerized with vinyl acetate produces an infusible, insoluble, transparent solid, whereas the polymer of vinyl acetate alone is thermoplastic, softening at 35°C. (400). The copolymerization of allyl acetate with maleic anhydride proceeds 200 times as rapidly as the polymerization of either component alone (38).

Numerous patents have been obtained on the preparation of copolymers of acrylonitrile with allyl monomers to give sheets, films, or fibers possessing some measure of flame resistance (23, 95).

Other allyl polymerizations using a single monomer are essentially copolymerizations. Allyl methacrylate has two double bonds with different polymerization characteristics. Lowering the temperature at which this polymerization is conducted increases the conversion before gelation. This is probably due to the selective polymerization of the methacrylate double bond at the expense of the allyl (89). Another example is found in the copolymerization of vinyl *n*-propyl ketone with vinyl allyl ketone. The vinyl groups are first polymerized, after which more vigorous treatment will result in the cross-linking of the chains through the less readily polymerized allyl groups (66, 310). These two-stage polymerizations mentioned above have many useful applications.

XI. PHOSPHORUS POLYMERS AND COPOLYMERS USED IN FLAMEPROOFING

A. Brominated polytriallyl phosphate

George Walter of Glenn L. Martin Corporation developed and patented a process for the preparation of a brominated polytriallyl phosphate. This was the first step towards the preparation of a permanent flameproofing compound of the allyl phosphorus type (418, 419).

Since this brominated polytriallyl phosphate showed promise for flameproofing Army uniforms, considerable work was conducted on this subject under Quartermaster Corps auspices. The preparation of triallyl phosphate, the polymerization of this monomer, and its subsequent bromination were all investigated thoroughly in order to improve the products (167, 232).

This polymerization work was quite extensive and may serve as the source of considerable information on the polymerization of allyl-type compounds. Triallyl phosphate prepared by the Glenn L. Martin process was found to polymerize with much more difficulty than the triallyl phosphate prepared by the Whitehill and Barker process (167, 426). This inhibition was found to be due to the presence of allyl alcohol in the former material; therefore the effect of allyl alcohol on the polymerization of triallyl phosphate was investigated thoroughly. Up to 8 per cent allyl alcohol was found to increase the conversion before gelation in the polymerization of triallyl phosphate. Other work on the polymerization resulted in determination of the activation energy, the effect of oxygen on the rate of polymerization, and the order with respect to monomer and peroxide. This work is discussed under the appropriate sections of this report. The biggest discrepancy between this allyl polymerization and other allyl polymerizations appears to be the effect of oxygen. Esteve and Laible found that the polymerization of triallyl phosphate in air was faster than in a nitrogen atmosphere, while Bartlett and Altschul found that oxygen retarded the polymerization of allyl acetate and the decomposition of benzoyl peroxide (35, 132).

Brominated triallyl phosphate imparts good flame-retardant properties when applied to cloth or paper but suffers from two deficiencies. First, it is expensive to make because of the many steps involved in its manufacture. Second, it is applied from a solvent solution, making the finishing operation more difficult. Two different establishments working on triallyl phosphate attempted to develop related compounds which would possess advantages over the parent compound. The first attempt involved the preparation, polymerization, and bromination of triallyl phosphite. The product was easier to prepare and imparted good flame-retardant properties when applied to cloth. However, the effect was not permanent owing to hydrolysis of the polymer by the laundering process (208).

B. Chain-transfer products

Greater success was obtained by taking advantage of the well-known ability of halogenated materials to undergo chain transfer in polymerization reactions. Workers at the University of Rhode Island concentrated their efforts on the preparation of solvent chain-transfer products. When triallyl phosphate was polymerized in the presence of chloroform, a product resulted which contained 2 to 3 per cent chlorine. The polymerization was conducted under reflux, so the temperature was easier to control and no subsequent bromination step was necessary. The product imparted good flame-retardant properties to cloth but was somewhat inferior to the brominated triallyl phosphate treatment (232). A second product was prepared by polymerizing triallyl phosphate in the presence of tris(2,3-dibromopropyl) phosphate. The chain-transfer product resulting was comparable in flame-retardant properties to brominated triallyl phosphate (131).

The greatest success was obtained by the Southern Regional Research Laboratory, where triallyl phosphate was emulsion-polymerized using bromoform as a chain-transfer agent. Potassium persulfate was the catalyst for this polymerization, polyvinyl alcohol was used as the emulsifying agent, and sodium bicarbonate was used for control of acidity (146). The resulting product imparted good flame-retardant properties to cloth. This solution can be applied to cloth using standard procedures of textile processing, but it still suffers from the disadvantage of dependence on the availability of triallyl phosphate (147). When other halomethanes such as carbon tetrachloride, carbon tetrabromide, or trichlorobromomethane were used as chain-transfer agents, poor results were obtained. The molar ratio of bromoform to triallyl phosphate is quite critical. If too much bromoform is used, the polymeric molecular weight is too low and only soluble polymer is formed. Too little bromoform produces mostly insoluble polymer and a poor emulsion. The pH of the emulsion during and after polymerization is also quite critical and should be maintained between 7.5 and 8.5. The amount of sodium bicarbonate needed to maintain neutrality varies according to the quality of the triallyl phosphate used. The satisfactory emulsions contained particles approximately 1 micron in diameter (308).

An emulsion polymer similar to the triallyl phosphate–bromoform product can be prepared by utilizing an allyl ester of phosphonitrilate polymer, bromoform, polyvinyl alcohol, sodium carbonate, potassium persulfate, and water. This product is comparable in performance to the better flame retardants (169).

C. Other allyl phosphorus compounds

Victor Chemical Works has in past years developed several allyl phosphorus polymers under their own research program and also under Quartermaster auspices. These compounds included β-diallyloxyphosphonopropionitrile, diallyl chloromethanephosphonate, and diallyl β-carboxymethyl propanephosphonate; they possess distinct advantages over the flameproofing compounds previously mentioned. The most important advantage is that diallyl phosphite, a commercially available material, is the starting material for two of these monomers (413). The second advantage is that the compounds need only be polymerized, as no subsequent bromination step is necessary. Benzoyl peroxide is the catalyst used for polymerizing these compounds. In general, the polymerizations are similar to that of triallyl phosphate, which has been discussed previously (411, 413). The disadvantage found for some of these compounds has been the erratic behavior when used on textiles. The permanence of the treatment to laundering has been satisfactory in some cases and poor in others.

In the plastics field allyl esters of the acids of phosphorus have been copolymerized with styrene, methyl methacrylate, vinyl acetate, and acrylonitrile to give resins with improved flame resistance, wear resistance, transparency, thermal stability, and relative inertness to chemical reagents (60, 155, 191, 192, 387, 399).

D. Allyl aryl phosphonates

Other allyl phosphorus polymers developed by Victor Chemical Works previously included numerous allyl aryl phosphonates. The nature of the organic radical attached directly to the phosphorus atom determines the polymerizability of the monomer (400). All the methallyl and allyl aryl phosphonates are capable of polymerization into hard, clear, infusible and insoluble resins with flame-retardant properties (396). Diallyl benzenephosphonate can be copolymerized with vinyl acetate, methyl methacrylate, and other monomers to produce flame-resistant resins (400). A. D. F. Toy of Victor Chemical Works patented the polymerization of diallyl and dimethallyl esters of chlorobenzene-, toluene-, or chlorotoluenephosphonates in the presence of an organic peroxide at 70–90°C. A gel is formed and further heating at 90–120°C. gives a solid product. The polymers produced can be used in fabric laminates. The polymers mentioned should impart some flame resistance to the laminates, but, in general, one would think it would be preferable to avoid such a large percentage of carbon and hydrogen fuel as the aryl group provides. However, Toy and Cooper investigated the flame resistance of various allyl phosphorus polymers and found the following relationships (402):

Polymer	Flame Resistance	Phosphorus Content
		per cent
Diallyl benzenephosphonate	Good	13.0
Diallyl methylphosphonate	Good	17.6
Diallyl isobutylphosphonate	Fair	14.4
Triallyl phosphate	Poor	14.2
Diallyl phosphite	Very poor	19.1

Toy and Cooper conclude that the stability of the phosphorus polymer may be more important than the percentage of phosphorus present to the resulting flame resistance of the material (402). Diallyl benzenephosphonate is used as a cross-linking agent for converting thermoplastic resins to thermosetting copolymers. If 20 to 30 per cent of this monomer is used, the resulting copolymer is self-extinguishing.

The poor flame resistance of triallyl phosphate shown in this table is somewhat unexpected in view of the good flame-retardant properties imparted to textiles by brominated triallyl phosphate. This anomaly must be due to the action of the bromine, which not only limits the flammability of the volatile decomposition products but also alters the stability of the phosphorus polymer.

XII. FUTURE OF ALLYL POLYMERS

Allyl polymers and copolymers have been proposed for use as plasticizers, interlayers for safety glass, adhesives, lubricants, coatings for optical elements, and substitutes for glass windows in aircraft (91, 103, 135, 187, 288). In addition, allyl monomers are incorporated in copolymer compositions to impart flame resistance and to act as cross-linking agents. Diallyl benzenephosphonate is one example of a compound which serves these two purposes in the plastics industry. Small amounts of this material convert monomers normally yielding thermoplastic resins to thermosetting resins, while larger amounts (20 to 30 per cent) impart self-extinguishing properties to the resultant copolymers.

The future expansion of the use of allyl polymers is assured because of the great variety of monomers available. Many more different allyl monomers can be prepared than vinyl monomers because of the availability of allyl alcohol and the nonexistence of vinyl alcohol (183). The inherent disadvantage of allyl monomers is the extremely low molecular weight of the products obtained by their polymerization. This disadvantage is minimized by using polyfunctional allyl monomers so that sufficient cross-linking takes place to give the resultant polymers the solubility and hardness characteristic of materials of much higher molecular weight (224). For example, copolymers of triallyl cyanurate and diethylene glycol bisallyl carbonate have been suggested for use as aircraft glazing materials because of their strength, transparency, and lack of heat distortion at 200°C. (365). Many of the polymers of allyl carbonates have been recommended for use where scratch resistance and transparency are important (219, 250).

The ability of allyl phosphorus polymers to impart flame resistance to cellulosic textiles has been shown. The idea of preparing fibers with increased flame resistance from allyl polymers alone is intriguing but it is very unlikely, owing to the short chain lengths obtained. However, there is increased evidence that allyl monomers will be used in copolymer compositions suitable for the preparation of fibers with added resistance to flame or improved dyeability (61, 69, 70, 302).

In the plastics industry, materials such as triallyl citrate and diallyl ether will be used as cross-linking agents to increase the melting point and hardness of vinyl polymers (214). Recent work on the preparation of high-molecular-weight copolymers of acrylonitrile and allyl alcohol shows the possible potential of dye-sensitized photopolymerization as a method of increasing the molecular weights and utility of the copolymers of allyl monomers normally yielding low-molecular-weight polymers and copolymers (289).

XIII. SUMMARY

Considerably more theoretical and applied research will be necessary before allyl polymers can be utilized in the most advantageous manner.

In a field such as textile finishing, applied research is needed to relate the chemical and physical properties of the polymers to their performance on a fabric. The penetration and permanence of such a treatment can be affected by the molecular weight and residual unsaturation, and it is important to know the allowable latitude in these properties. Unexpected deficiencies in permanence or flexibility can then be attributed to either changes in the polymer properties or changes in the finishing operation, as the case may be.

Research is necessary to determine the reasons for the low molecular weights characteristic of allyl polymers and to find methods of increasing these molecular weights. Other catalysts such as the hyponitrites and the peroxydicarbonates could be used to lower the temperature of polymerization with a possible accompanying increase in molecular weight.

The development of a simple method of obtaining the molecular weight of polymers in this intermediate region (1,000 to 10,000) would considerably aid the theoretical and applied research. Conversion and concentration will have to be kept low to minimize cross-linking in order to determine these molecular weights.

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XV. APPENDIX

TABLE 5

Data on the polymerization of allyl monomers

Monomer	Catalyst	Polymerization Conditions	Results	References
Alkyl allyl carbonates	Benzoyl peroxide	5 days at 65°C.; bulk polymerization	Flexible polymer	(7)
Allyl acetate	Benzoyl peroxide (6%)	13 hr. at 80°C.; bulk polymerization	Soft transparent polymer; molecular weight = 1300	(35)
Allyl acetate	Potassium persulfate	70°C.; emulsion polymerization	Soft polymer; molecular weight = 1300	(233)
Allyl acetate (copolymer)	Potassium persulfate	60–100°C; emulsion polymerization	Latex of vinyl acetate–allyl acetate copolymer	(319)
Allyl acetate (copolymer)	Acetyl peroxide	13 hr. at 93–107°C.	Copolymer obtained with vinyl acetate soluble in common organic solvents	(226)
Allyl acetoacetate	Ultraviolet light	Water solution	Gel	(188)
Allyl acylamides (copolymers)	Potassium persulfate	8 hr. at 50–55°C.; emulsion polymerization	High-melting copolymer with acrylonitrile which can be made into yarns and sheets	(71)
Allyl acrylate	Benzoyl peroxide	Room temperature; bulk polymerization	Transparent, insoluble, cross-linked resins	(156, 307)
Allyl alcohol	Organic peroxide	50–100°C.; bulk or solution polymerization	Viscous liquid	(284)
Allyl alcohol	Hydrogen peroxide (2%)	116 hr. at 100°C.	Viscous liquid polymer; molecular weight = 300	(14)
Allyl alcohol (copolymer)	Benzoyl peroxide	16 hr. at 100°C.; water solution	A white powder formed by copolymerization with acrylonitrile	(206)
Allyl allyloxyacetate (copolymer)	Benzoyl peroxide	45–115°C.; conditions vary, depending on other monomer	Cross-links copolymer compositions	(109)
Allylamine carbonates	Benzoyl peroxide	10–100 hr. at 20–100°C.	Clear glass-like resins; also used as cross-linking agents for copolymerizations	(159)
Allylbenzene	Boron trifluoride	Bulk polymerization	Polymer formed	(223)
Allyl benzoate	Dichlorobenzoyl peroxide	80°C.; mass polymerization	Polymer with a degree of polymerization of about 9	(335)
Allyl caprylate	Organic peroxide	100–250°C.; bulk polymerization	Liquid polymer used as a lubricant	(136)
Allyl carbamate	Benzoyl peroxide (5%)	60 hr. at 60°C.	Thermoplastic polymer	(161)
Allyl (*N*-allyl)carbamate	Benzoyl peroxide (5%)	120 hr. at 55°C.	Failed to polymerize	(161)
Allyl (*N*-allyloxy)carbamate	Benzoyl peroxide (5%)	120 hr. at 55°C.	Failed to polymerize	(161)
Allyl (*N*-carballyloxy)-carbamate	Benzoyl peroxide (3%)	5 hr. at 65°C.	Hard, glass-like polymer	(161)
Allyl *N*-cyanocarbamate	Tertiary butyl peroxide (2%)	8 hr. at 165°C.	Failed to polymerize	(161)
Allyl *N*-isopropenylcarbamate	Benzoyl peroxide (2.5%)	48 hr. at 55°C.	Hard, glass-like polymer	(161)
Allyl carbonates (aromatic esters)	Benzoyl peroxide (5%)	60–90°C.; solution polymerization	Polymers; characteristics not given	(429)
Allyl chloride	(1) Oxidizing agent or oxygen (2) HF	Two-step polymerization	Viscous polymer, useful as a lubricant	(78)
Allyl chloride	Benzoyl peroxide	80°C.; mass polymerization	Polymer, with a degree of polymerization of 8.6	(332)
Allyl chloride	Sunlight	3 months exposure	30–40% yield of polymer	(223)
Allyl chloroformate	Ethyl percarbonate	30–60°C.	Resins which are useful as coatings, adhesives, etc.	(295)

TABLE 5—*Continued*

Monomer	Catalyst	Polymerization Conditions	Results	References
Allyl cyanide	Benzoyl peroxide (5%)	20 hr. at 75–115°C.; nitrogen atmosphere	Does not polymerize	(243)
Allyl cyanide (copolymer)	Benzoyl peroxide	18 hr. at 60°C.; emulsion, bulk, or solvent polymerization	Hard tough resin formed with acrylonitrile; softening point 220°C.	(69)
Allyldimethylamine (copolymer)	Azodiisobutyronitrile (2%)	80°C.; solvent polymerization	Copolymer obtained with vinyl acetate	(226)
Allyl esters of aromatic allyl carbonates	Benzoyl peroxide (5%)	60–80°C.; inert solvent	Polymers with various properties	(237, 429, 430)
Allyl ethers of carbohydrates	Oxygen, 7.5 l./hr.	80–120°C.; bulk polymerization	Gel	(433)
Allyl ethyl ether	Dichlorobenzoyl peroxide	80°C.; mass polymerization	Polymer, with a degree of polymerization of 4	(332)
Allyl halides	(1) Benzoyl peroxide (2) Hydrofluoric acid (3) Heat	Three-step polymerization; final treatment is to heat to 300°C.	Polymers which possess resistance to acids and hydrocarbons	(77)
Allyl laurate	Benzoyl peroxide	Bulk polymerization	Brown, viscous, liquid polymer	(119, 339)
Allyl linoleate	Tertiary butyl peroxide	24 hr. at 130°C.; bulk polymerization	21% yield of polymer of low molecular weight	(175)
Allyl methacrylate	Benzoyl peroxide	Not given	Mainly polymerized through methacrylate groups	(90, 327)
Allyl naphthenates	Tertiary butyl peroxide	140–210°C.	Polymer, with degree of polymerization of 5 to 10	(4)
Allyl starch	Cobalt naphthenate	Not given	Shellac- or enamel-like polymer	(82, 277, 313)
Allyl starch (copolymer)	Cumene hydroperoxide	100°C.; solution polymerization	Copolymer with styrene useful as a film; resistant to boiling water	(432)
Allyl stearate	Benzoyl peroxide	20 hr. at 80°C.	53% yield of polymer; characteristics not given	(175)
Allyl trifluoroethyl ether (copolymer)	Benzoyl peroxide	40 hr. at 75°C.	Copolymerized with diethyl fumarate or maleic anhydride	(64)
Bis(β-bromoallyl) allyl phosphate	Benzoyl peroxide	6 hr. at 100°C.	Slight increase in viscosity, but decomposition overshadows polymerization	(130)
Dialkyl allylphosphonates (copolymers)	Hydrogen peroxide	5 hr. at 60°C.; water solution	Copolymerized with acrylonitrile to give flame-resistant products such as fibers, films, or coatings	(95)
Diallyl adipate	Benzoyl peroxide	100°C.; bulk polymerization	Polymer; only electrical characteristics given	(198)
Diallyl benzenephosphonate	Benzoyl peroxide (3%)	18 hr. at 88°C.; bulk polymerization	A hard, glassy, solid polymer	(402)
Diallyl benzoylphosphonate	Benzoyl peroxide (3%)	18 hr. at 88°C.; bulk polymerization	A hard, glassy, solid polymer	(402)
Diallyl *n*-butyl phosphate	Benzoyl peroxide (2%)	2 hr. at 110°C.	Taffy-like polymer	(208)
Diallyl carbonate (copolymers)	Benzoyl peroxide	5 days at 65°C.	Hard, acid-resistant copolymers with other diallyl esters such as diallyl adipate	(6)
Diallyl chlorobenzenephosphonate	Organic peroxide	70–90°C.; bulk polymerization	Gel, which can be converted to solid by heating at 90–120°C.	(397)
Diallyl chloromethanephosphonate	Benzoyl peroxide	Polymerized in solution of dichloroethyl ether	Thermosetting molding powder	(403)
Diallyl chloromethanephosphonate	Benzoyl peroxide (3%)	12 hr. at 85°C.; bulk polymerization	Clear hard resin with flame-retardant properties	(403)
Diallyl chloromethanephosphonate (copolymer)	Benzoyl peroxide	85°C.	Copolymerization with diallyl phthalate gives hard yellow solid	(403)

TABLE 5—*Continued*

Monomer	Catalyst	Polymerization Conditions	Results	References
Diallyl cyanoethanephosphonate	Benzoyl peroxide	4–7 hr. at 85°C.; solution polymerization	Polymer can be precipitated from solution with toluene to give powder	(232, 411)
Diallyl cyclohexanephosphonate	Benzoyl peroxide	4 hr. at 70–115°C.; bulk polymerization	Solid polymer	(80)
Diallyl 2,3-dibromopropyl phosphate	Benzoyl peroxide	110°C.; solution polymerization	Decomposition, rather than polymerization	(128)
Diallyl 2,3-dibromopropyl phosphate (copolymer)	Benzoyl peroxide	100°C.; solution polymerization	Copolymer in 44% yield; probably a chain-transfer product rather than a copolymer	(128)
Diallyl dicarbamates	Benzoyl peroxide	80–150°C.; bulk polymerization	Hard, infusible, crystal-clear polymers	(213)
Diallyl dimethylamido phosphate	Benzoyl peroxide	18 hr. at 87°C.; bulk polymerization	Does not polymerize	(402)
Diallyl 3,5-dimethylphthalate	Benzoyl peroxide (6%)	200 hr. at 50–90°C.	Light yellow liquid which bakes to a hard clear film	(242)
Diallyl ester of chlorendic acid	Benzoyl peroxide	Not given	Polymer, with flame-retardant properties claimed	(409)
Diallyl ethylphosphonate	Benzoyl peroxide	18 hr. at 87°C.; bulk polymerization	Flexible solid polymer	(402)
Diallyl fumarate (copolymer)	Benzoyl peroxide	9 hr. at 60°C.; bulk polymerization	Resins obtained by copolymerization with allyl chloride	(207)
Diallyl fumarate (copolymers)	Benzoyl peroxide	64 hr. at 95°C.	Copolymers formed with chlorine-containing allyl monomers; some fire-resistant properties	(207)
Diallyl isobutenylphosphonate	Benzoyl peroxide (3%)	18 hr. at 88°C.; bulk polymerization	Polymerized to hard, glassy solid	(402)
Diallyl isobutenylphosphonate (copolymer)	Benzoyl peroxide	70–80°C.	Copolymer obtained with methyl methacrylate	(398)
Diallyl maleate (copolymers)	Tertiary butyl hydrogen peroxide	30 hr. at reflux	Soluble fusible products obtained by copolymerizing with allyl or methallyl alcohol	(382)
Diallyl melamine (copolymer)	Ditertiary butyl peroxide	30 min. at 135°C. in xylene solution	Copolymer formed with triallyl phosphate	(130)
Diallyl phenylphosphonate	Benzoyl peroxide	18 hr. at 88°C.; bulk polymerization	Polymerized to hard, glassy solid	(402)
Diallyl phenylphosphonate (copolymers)	Benzoyl peroxide (2%)	24 hr. at 70°C.; 24 hr. at 90°C.	Copolymer obtained with esters such as diallyl oxalate; copolymers are insoluble, infusible, and somewhat flame-resistant	(399)
Diallyl phenylthiophosphonate	Benzoyl peroxide	18 hr. at 88°C.; bulk polymerization	Does not polymerize	(402)
Diallyl phosphite	Benzoyl peroxide	18 hr. at 88°C.; bulk polymerization	Hard, glassy polymer	(402)
Diallyl phthalate	Benzoyl peroxide (3%)	65 min. at 85°C.	Polymer; molecular weight = 3900	(356)
Diallyl sebacinate	Benzoyl peroxide	100°C.; bulk polymerization	Solid polymer	(198)
Diallyl tetrachlorophthalate (copolymer)	Benzoyl peroxide	Not given	Copolymerized with alkyl maleates to give infusible, flame-resistant resins	(279)
Diethyl allyl phosphate	Benzoyl peroxide	18 hr. at 88°C.; bulk polymerization	Does not polymerize	(402)
Diethyl *N*,*N*-diallylamidophosphonate	Benzoyl peroxide	18 hr. at 88°C.; bulk polymerization	Does not polymerize	(402)
Di-*n*-butyl allyl phosphonate (copolymer)	Hydrogen peroxide	5 hr. at 60°C.; water solution	Fine white copolymer with acrylonitrile which can be spun into fibers	(95)
Ethylene bis(2-chloroallyl carbonate)	None	Attempted distillation at 22 mm. pressure	Polymer; properties not given	(246, 248)

TABLE 5—*Continued*

Monomer	Catalyst	Polymerization Conditions	Results	References
Methallyl chloride	Boron trifluoride	−50°C.	Properties not given; polymer suitable for impregnating wood	(1)
Methallyl chloride	Benzoyl peroxide	8 days at 75°C.; bulk polymerization	Polymer, which is mostly a soft resinous dimer	(45)
Methallyl chloride (copolymer)	Benzoyl peroxide	87 hr. at 45°C.	Copolymer obtained with vinyl chloride; useful as interlayer for safety glass	(239)
Methallyl ethers of carbohydrates	Benzoyl peroxide (15%)	97°C.	Gel	(275)
Methallyl ethers of carbohydrates	Benzoyl peroxide (5%)	97°C.	Negligible polymerization occurs	(275)
Pyrogallol tris(allyl carbonate)	Organic peroxide	Not given	Polymer	(246)
Tetraallyl esters of thiophosphonic acid	Tertiary butyl peroxide (2%)	115°C.; bulk polymerization	Polymerized to hard opaque solid	(173)
Tetraallylpentaerythritol	Oxygen	12 hr. at 100°C	Resin, which is nearly insoluble in acetone	(277)
Tetraallylsilane	Benzoyl peroxide (1%)	8 days at 100°C.; bulk or solvent polymerization	Clear, hard polymer	(200)
Tetraallylsilane	Benzoyl peroxide	Heated for several hours	Does not polymerize to a solid	(220)
Tetraallylsilane (copolymer)	Benzoyl peroxide	70°C.	Copolymers obtained with methyl methacrylate when silane limited to 40% or less of copolymer mixture	(220)
Tetraallylsilane (copolymer)	Benzoyl peroxide	70°C.	Copolymer obtained with glycol esters of unsaturated acids	(203)
Tetramethallyl stannate (copolymer)	Not given	Not given	White enamel-like copolymer obtained with methyl methacrylate	(316)
Tetramethallyl titanate	None	Heat	Does not polymerize upon heating	(316)
Tetramethallyl titanate (copolymer)	None	Room temperature	Colored infusible copolymer with vinyl acetate	(316)
Triallyl aconitate	Benzoyl peroxide	Polymerized in ampuls at 66–100°C.	Glassy infusible solid	(321)
Triallyl aluminate	None necessary	8 hr. at 210°C.; bulk polymerization	Stiff gel	(316)
Triallyl aluminate (copolymer)	None necessary	3 days at 65°C.; bulk polymerization	Hard, brittle, colorless copolymer obtained with methyl methacrylate which is much less soluble than polymethyl methylacrylate	(316)
Triallyl borate	Benzoyl peroxide (1%)	100 hr. at 100°C.; bulk polymerization	Did not polymerize completely	(321)
Triallyl borate	Air	Polymerized by bubbling air through monomer at 130°C.	Gel, which was hydrolyzed to form polyallyl alcohol	(33)
Triallyl citrate	Benzoyl peroxide	Bulk polymerization	Hard, brittle, thermosetting polymers	(25)
Triallyl cyanurate	Benzoyl peroxide	Not given	Polymerizes readily; polymer used in glass cloth laminates	(99, 118)
Triallyl phosphate	Benzoyl peroxide	60 min. at 100°C.; solution	White polymer which can be powdered; flame-retardant properties	(167)
Triallyl phosphate–chloroform chain-transfer product	Benzoyl peroxide	70 min. at 85°C.; solution in chloroform	White powder, somewhat tacky; imparts flame-retardant properties to fabric; contains 1-2% chlorine	(132)

TABLE 5—*Continued*

Monomer	Catalyst	Polymerization Conditions	Results	References
Triallyl phosphate-bromoform chain-transfer product	Potassium persulfate	90 min. at 80°C.; emulsion	Latex obtained which confers flame retardancy to cloth	(146, 147)
Triallyl phosphate (copolymer)	Benzoyl peroxide	2 days at 40°C. and 10 days at 65°C.	Copolymer obtained with vinyl acetate which is flame-resistant	(179)
Triallyl phosphite	Benzoyl peroxide	100°C.; solution polymerization	Sudden increase in temperature but no apparent polymerization occurs	(208)
Triallyl phosphite	Tertiary butyl peroxide	90 min. at 150°C.; solution polymerization	Taffy-like polymer; 60% conversion	(208)
Triethylene glycol bis-(methallyl)carbonate	None used	Attempted distillation at 2 mm. pressure	Polymer unintentionally formed	(246)
Trimethallyl aluminate	None needed	8 hr. at 210°C.; bulk polymerization	Stiff gel obtained	(316)
Trimethallyl aluminate (copolymer)	None needed	2 days at 65°C.; 1 day at 100°C.	Hard, brittle copolymer obtained with methyl methacrylate	(316)
Trimethallylglycerol	Oxygen	15 hr. at 97°C.	Insoluble resin	(275)
Vinyl allyl ether	Boron trifluoride	60°C.	Viscous product; allyl groups unpolymerized	(141)
Vinyl allyl ketone	Boron trifluoride	Not given	Copolymerized with vinyl *n*-propyl ketone; allyl groups untouched	(94, 310)