Reactivities and Nomenclature of Vinyl-Type Compounds *

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Contrary to SHAKESPEARE's Juliet the author believes that names do make a difference and that the specific ones which we use for chemical compounds have greater importance than is generally recognized. Whether we name a monomer as a vinyl compound or an allyl compound, as a vinyl ether or as a styrene derivative, can affect teaching, research and development of useful products. One of the purposes of this review is to apply research in polymerization reactivity and molecular structure to classifying the vinyl-type or ethylenic monomers containing $CH_2=C\langle$ groups into such classes as acrylic, styrene, vinyl, vinylidene allyl, and allylidene.

Too often in the past chemical reactivity and structure have not been given primary consideration in choosing nomenclature of monomers and polymers, either because of incomplete knowledge or because more pragmatic criteria have been given preference. As examples of misleading names in chemical literature, allyl compounds have been confused with vinyl and acrylic compounds. There are indeed some borderline compounds whose classifications are not obvious. Behavior of vinyl-type monomers in polymerization with different types of catalysts, in hydrolysis, in addition of active hydrogen compounds or halogens and with regard to isomerization are useful criteria when names are in doubt. Where alternate names are possible it seems best to adopt the one more consistent with chemical reactivity.

This review shows that most 1-alkenes are among those monomers which ought to be regarded as allyl compounds although contrary to common practice. Electron withdrawal vs. electron-donation by substituents can help to distinguish allyl from acrylic monomers. The recent success in preparing high polymers of controlled structure (stereopolymerizations) from 1-olefins by use of complex transition metal catalysts encourages their application to other allyl compounds. Monoallylidene compounds such as $CH_2=CHCH$ and $CH_2=C-CH_2$ show similarities to monoallyl compounds in chain transfer and in resistance to forming high polymers by free radical addition polymerization. Alkyl vinyl ethers also resemble monoallyl compounds somewhat in reactivity,

but are more readily polymerized using strong Lewis acid catalysts.

Vinyl-Type Compounds

Vinyl-type compounds can be defined as those containing the groups $CH_2=C\langle$, $CF_2=C\langle$ or $CHF=C\langle$ where the free bond can bear alkyl, alkoxyl, aryl, halogen and other groups. With few exceptions these compounds under suitable conditions have given homopolymers of high molecular weight (as distinguished from dimers, trimers, hexamers, etc.). In some literature the vinyl-type compounds have been called ethylenic or vinylidene compounds, which are logical names but have been less generally used.

Homopolymerizability extends somewhat beyond the compounds defined above, particularly where a small 2-substituent other than F is present or where the double bond is part of a ring. However, in most of these cases the homopolymers have rather low weight average molecular weights, e. g., below 10,000 or below the range generally useful directly as synthetic materials. Some of these have been known for a long time while others have been discovered only recently as more effective ionic methods of polymerization have been developed. Examples are indene, 2-methylstyrene, maleic anhydride and vinylene carbonate. Many of the 2- or beta-substituted compounds such as

$$NCCH=CHCN \quad and \quad ROOCCH=CHCOOR$$

which do not homopolymerize readily do, however, participate readily in suitable copolymerization. Large second substituents as in alpha-isobutyl methacrylate and 1,1-diphenyl ethylene impart steric hindrance both to homopolymerizations and copolymerizations.

The vinyl-type compounds which have been most studied and have been most widely used are the styrenes, acrylic, vinyl halide and vinyl ester monomers which readily give high polymers by peroxide or other free radical initiators on heating. These reactions as well as their photopolymerizations have been best interpreted in terms of chemical chain reactions[1] in which the grow-

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[1] W. NERNST, Z. Elektrochem. 24 (1919) 335; Chem. Abstr. 14 (1919) 38; cf. M. BODENSTEIN and H. S. TAYLOR, Z. angew. Chem. 28 (1915) III, 621; Chem. Abstr. 10 (1915) 2077.
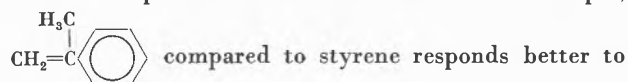
ing polymer end is a free radical. The monomers consist of the ethylene nucleus substituted by electron attracting and/or conjugated groups. The hydrogen atoms present in the ethylenic or vinyl group are relatively unreactive. Free oxygen, arylamines, quinones and phenols are inhibitors of polymerization. Note that a number of the conceivable vinyl-type monomers with strongly electron donating groups are unstable and have never been isolated. These include vinyl, vinylidene and isopropenyl alcohols, mercaptans and amines.

The vinyl halides $CH_2=CHX$ and vinyl esters $CH_2=CHOCOCH_3$ tend to give branched polymers by free radical polymerizations with chain transfer to polymer. Some polymers have been reported by special ionic methods but products of high molecular weight remain doubtful. Lewis acids can inhibit polymerization in many cases. A group of vinyl monomers including N-vinyl pyrrolidone and N-vinyl carbazole polymerize by both free radical and Lewis acid catalysts but are inhibited by alkali.

Acrylic monomers have strongly electron attracting multiple bond groups showing conjugation with the ethylenic double bond. These monomers, such as $CH_2=CHCOOH$, $CH_2=CHCOOR$ and $CH_2=CHCONH_2$, can polymerize rapidly by free radical methods, and the reactive tertiary hydrogen atoms in the polymers $-CH_2-CH-$ tend to give branched or crosslinked poly-
$$-\overset{|}{C}=O$$
mers by chain transfer. In methacrylic monomers such as $CH_2=C\overset{\diagup CH_3}{\diagdown COOH}$, $CH_2=C\overset{\diagup CH_3}{\diagdown COOR}$ and $CH_2=C\overset{\diagup CH_3}{\diagdown CONH_2}$ the electron donating property of the methyl group is overcome by the strong electron attraction and activation of the multiple bond group. Commercial polymers from acrylic monomers are made almost entirely by free radical polymerizations. However, at lower temperatures Lewis basic catalysts (electron donating) give acrylic polymers some of which have novel steric features. Lewis acids generally retard or inhibit polymerization of acrylics. Even acrylic compounds with considerable steric hindrance such as alpha-methylene glutaronitrile can copolymerize readily by free radical methods. Highly acidic acrylic monomers such as $CH_2=C\overset{\diagup CN}{\diagdown COOR}$ and $CH_2=C(CN)_2$ no longer homopolymerize by free radical initiators but respond best to weak Lewis bases such as water.

Styrene, 1,3-butadiene and ethylene are unusual in giving homopolymers of high molecular weight by all of the major methods of polymerization (free radical, cationic and anionic). In general the substitutions of electron donating or attracting groups into styrene an butadiene lead to changes in response to catalysts which would be expected from inductive effects. For example, $CH_2=\overset{\overset{H_3C}{|}}{C}\langle\text{⬡}\rangle$ compared to styrene responds better to Lewis acid catalysts and yields polymers less readily by free radical methods. Small electron donating groups such as R and CR in the ring of styrene make the ethylenic double bond more basic and promote cationic polymerizations. Conversely, strong electron attracting groups (meta directing) such as NO_2 tend to retard both cationic and free radical polymerizations.

Lewis basic monomers such as isobutylene, beta-pinene, vinyl ethers and vinylidene ethers do not homopolymerize by free radical or anionic methods but form homopolymers of high molecular weight by use of appropriate Lewis acid catalysts usually at low temperatures.

Allyl and Allylidene Compounds

Not all of the vinyl-type monomers defined by the generalized formulas above respond readily to conventional free radical, Lewis acid or Lewis base catalysts to give homopolymers of high molecular weight. In fact, a very large number of monofunction 1-olefinic hydrocarbons, allyl and allylidene compounds have resisted attempts to prepare linear high polymers until recently. The allyl-type double bonds are relatively unreactive because the substituents are relatively weakly electron donating and little or no conjugation or resonance is present. Typical compounds are the following:

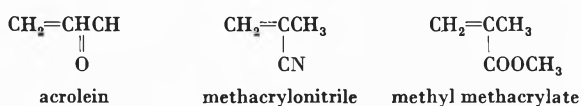| $CH_2=CHCH_3$	$CH_2=CHCH_2Cl$	$CH_2=CHCH(OCOCH_3)_2$
propylene	allyl chloride	allylidene diacetate
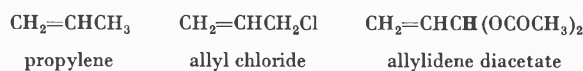
Chain transfer reactions with the underlined reactive allylic hydrogen atoms prevent the formation of polymers of high molecular weight by free radical methods. However, polyfunctional allyl compounds such as diallyl phthalates and triallyl esters do form high polymers by heating with peroxides. The lower 1-olefines like typical volatile allyl compounds have rather sharp or pungent odors. Ethylene which contains no allylic hydrogen atoms yields polymers of high molecular weight by free radical high pressure conditions. The other mono-1-olefines and some monoallyl compounds have responded only to transition metal and other complex Lewis acid catalysts to give high polymers. As in the case of alkyl vinyl ethers, some of these cationic polymerizations can be designed to give either stereoregular or amorphous polymers (stereopolymerizations). Most familiar of the complex transition metal catalysts are reaction products of aluminium alkyls or aluminium alkyl halides with titonium halides which were considered by ZIEGLER and NATTA to produce anionic polymerizations.

In contrast to vinyl and acrylic compounds, many different allyl compounds occur in nature. The name allyl comes from allium, Latin for garlic. Allyl disulfide and other allyl compounds are produced by garlic, onions and related plants. The reactivity and definition of allyl compounds show that typical 1-olefinic hydrocarbons

are in fact allyl compounds. The definition of allyl compounds given below is consistent with a recent review of the literature of allyl and related compounds[2].

Allyl compounds are those vinyl-type compounds having double bonds of low reactivity and where polymerizations are complicated by the presence of one or more reactive hydrogen atoms attached to a third carbon atom (alpha with respect to the double bond). Thus allyl and allylidene compounds may be represented as

$$CH_2{=}CH\underset{\diagup}{C}H_2 \text{ and } CH_2{=}CH\underset{\diagdown}{C}H,$$ but with exceptions noted

below. The underlined allylic hydrogen atoms are exceptionally reactive in chain transfer. The radicals produced by their attack by growing polymer radicals generally are not sufficiently reactive to propagate further polymerization[3]. Note that allylic halogen atoms $CH_2{=}CHCH_2Cl$ also may be highly reactive. Degradative chain transfer studied by BARTLETT and coworkers has received great emphasis in elucidating polymerization reactions of allyl compounds. The e values of -1.0 to $+.5$ and Q values below 0.1 of typical allyl compounds show low inductive effects and low resonance. This low reactivity of allyl double bonds must also receive adequate attention.

There are at least two types of exceptions to the general formulas above for allyl and allylidene compounds. When strong electron attracting groups are attached to the ethylenic group the reactivity is greater and the hydrogen atoms on a third carbon do not show allylic reactivity[4]. Thus the following behave as acrylic and not as allyl compounds:

$$CH_2{=}CHCH \atop \underset{O}{\|} \qquad CH_2{=}CCH_3 \atop \underset{CN}{|} \qquad CH_2{=}CCH_3 \atop \underset{COOCH_3}{|}$$

acrolein   methacrylonitrile   methyl methacrylate

Likewise methacrolein, methacrylic acid, methacrylamide, alpha-methylene glutaronitrile and itaconic anhydride do not behave as typical allyl compounds. The same considerations will apply when hydrogen atoms on a third carbon are associated with other polar groups on the second carbon such as $-NO_2$ and $-C R \atop \underset{O}{\|}$.

Another apparent exception to the application of the general formula for allyl compounds seems to occur when two electron donating groups are attached to the ethylenic nucleus as in isobutylene $CH_2{=}C(CH_3)_2$. Although isobutylene resembles allyl compounds in some respects, it polymerizes readily at low temperatures with strong Lewis acid catalysts. The lower reactivity of the methyl hydrogen atoms compared to secondary or tertiary hydrogen atoms also is a factor.

[2] MABEL D. REINER and C. E. SCHILDKNECHT, unpublished.
[3] P. D. BARTLETT and R. ALTSCHUL, *J. Amer. Chem. Soc.* 67 (1945) 812.
[4] C. E. SCHILDKNECHT, *Polymer Eng. & Sci.* 6 (1966) 240.

Allyl compounds bearing substituents on the second carbon have modified reactivities. Although these have been incompletely studied, electron donating groups as in methallyl compounds $CH_2{=}CCH_2 \atop \underset{CH_3}{|}$ and methylene dioxolanes

$$CH_2{=}C{-}CH_2 \atop \underset{O\diagdown \diagup O}{|\qquad|} \atop \underset{CH_2}{}$$ have lower e values, respond

better to acid catalysts and less readily to free radical catalysts. Chlorallyl compounds $CH_2{=}C{-}\underset{\diagup}{C}H_2 \atop \underset{Cl}{|}$ have higher Q values and are somewhat more reactive with peroxide catalysts.

Compounds without allylic hydrogen or chlorine atoms apparently do not behave as allyl compounds. $CH_2{=}CHCF_3$ polymerizes at high pressures with much lower ratios of transfer to propagation than in the case of propylene[5]. Surprisingly high softening polymers reported by irradiation of $CH_2{=}CHCCl_3$ were attributed to 1.3 polymerization with isomerization[6].

Radical-Chain Polymerizations of Acrylic, Styrene and Vinyl Monomers

These groups of monomers are best known because most of them polymerize by free radical chain reactions with heating or irradiation and many of their polymers have achieved commercial importance. Their behavior can be correlated in terms of three major qualities of the groups substiuted into ethylene: (a) inductive effects or polarity (electron attracting vs. electronating donating groups), (b) resonance or conjugation and (c) steric effects. Electron attracting and conjugated groups normally promote polymerization by radical initiation as well as by anionic methods (Lewis basic or electron donating catalysts). Electron donating groups promote polymerization by cationic methods (Lewis acid or electrophilic catalysts). It is interesting that most volatile acrylic and styrene monomers having pronounced conjugation and unsubstituted alpha-hydrogen atoms usually have strong odors, while vinyl esters, vinyl halides and methacrylic monomers have relatively mild odors.

Free radical initiated polymerizations with added peroxide or azo catalyst have been most employed industrially with these monomers. Vinyl ethers, like isobutylene, respond best to cationic polymerizations and resemble allyl compounds more than typical vinyl compounds.

Quantitative values for polarity and for reactivity attributed largely to resonance can be expressed respectively as e and Q values of ALFREY and PRICE for the

[5] L. A. WALL, private communication, 1966.
[6] Brit. 888,730 (Dow-Corning).

different monomers[7]. These are measured from radical copolymerizations in bulk or solution generally in the range of 50 to 100 °C to low conversion and analysis of the resulting copolymers. In general radicals easiest formed are believed to be least reactive, while the less reactive monomers give most reactive radicals. Styrene radicals and acrylonitrile monomer are relatively reactive. Thus in radical copolymerization the relative rate of addition to terminal styrene radicals of acrylonitrile ($r_1 = .52$) is much greater than the rate of fruitful reactions of acrylonitrile radicals with styrene monomer ($r_2 = .03$). The r_1 and r_2 values are reactivity ratios applying to radical copolymerizations as described for e and Q values.

Bulky, non-conjugated alpha-substituents in ethylenic compounds generally prevent formation of homopolymers of high molecular weight and copolymerizations may also occur reluctantly; for example, alpha-isopropyl acrylates and alpha-cyclohexyl acrylates[8].

The composition and structure of polymers and copolymers prepared by radical-chain reactions are relatively little affected by specific peroxide or azo catalysts or by types of radiation employed. This is in contrast to ionic polymerizations. However, lower temperatures in radical initiation of some monomers of the types $CH_2=CHY$ or $CH_2=CYZ$ tend to favor formation of more alternating or D L D L polymer structures (syndiotactic).

The relatively high e and Q values of acrylic monomers resulting from electron attracting and conjugated substituents are shown:

		e	Q
Acrylic acid	$CH_2=CHCOOH$	0.77	1.15
Ethyl acrylate	$CH_2=CHCOOC_2H_3$	0.22	0.52
Methacrylic acid	$CH_2=\overset{\overset{CH_3}{\vert}}{C}-COOH$	0.65	2.34
Methyl methacrylate	$CH_2=\overset{\overset{CH_3}{\vert}}{C}-COOCH_2$	0.40	0.74
Acrylamide	$CH_2=CHCONH_2$	1.30	1.18
Acrylonitrile	$CH_2=CHCN$	1.20	0.60
Methacrylonitrile	$CH_2=\overset{\overset{CH_3}{\vert}}{C}-CN$	0.81	1.12

In the methacrylic compounds the electron donating methyl group reduces the e values somewhat but the predominating influence is that of the electron attracting resonating group containing multiple bonds to carbon. In general acrylic monomers tend to polymerize rapidly even at comparatively low temperatures. The acrylic monomers (but not the methacrylic) tend to give

highly branched polymers unless regulators such as mercaptans are added. Lewis acids tend to retard radical polymerization of acrylic monomers.

Styrene is given values of $e = -0.80$ and $Q = 1.0$ arbitrarily as a reference monomer. Most styrene derivatives bear less electron attracting groups substituted into ethylene than the acrylics. However, reactivity as measured by Q is high as in the case of the acrylic monomers. Some typical values are given below:

	e	Q
o-methylstyrene	− 0.78	0.90
m-methylstyrene	− 0.72	0.91
p-methylstyrene	− 0.98	1.27
alpha-methylstyrene	− 1.27	0.98
m-divinyl benzene	− 1.77	3.35
p-cyanostyrene	− 0.21	1.86
p-chlorostyrene	− 0.33	1.28
p-nitrostyrene	+ 0.39	1.63

The reactivity of different styrene derivatives follows approximately the orientation effects of substituents in benzene substitution and sigma values in the Hammett equation[9]. Strongly meta directing and electron attracting groups such as in nitrostyrenes give high e values. The other styrene monomers here tend to copolymerize readily with acrylic monomers such as acrylonitrile giving alternating monomer units in the macromolecule chains. Such alternating copolymerizations between reactive monomers having opposite inductive effects often occur thermally without added free radical initiator. The freedom from catalyst residues can have practical advantages. These reactive monomers can be regarded as self-initiating. Note that such copolymerizations seem to have free radical, not ionic characteristics. The greater the tendency to alternation the lower is the product of the reactive ratios $r_1 \times r_2$.

Vinyl halides and vinyl esters are characterized by very low Q values (little conjugation or resonance possibilities). Ethylene has been reported to have similar values vinylidene chloride is more reactive.

		e	Q
Vinyl chloride	$CH_2=CHCl$	0.20	0.04
Vinylidene chloride	$CH_2=CCl_2$	0.36	0.22
Vinyl fluoride	$CH_2=CHF$	1.28	0.01
Ethylene	$CH_2=CH_2$	− 0.20	0.02
Vinyl acetate	$CH_2=CHOCOCH_3$	− 0.22	0.03
Vinyl n-butyrate	$CH_2=CHOCOC_4H_9$	− 0.26	0.04
Vinyl trifluoroacetate	$CH_2=CHOCOCF_3$	1.06	0.03

These monomers homopolymerize and copolymerize with each other by free radical methods but not do give high polymers readily by the older methods of cationic

[7] L. J. YOUNG, J. Polymer Sci. 54 (1961) 411 (900 monomers). T. ALFREY and L. J. YOUNG in Copolymerization, High Polymers, Vol. 18, editor: G. HAM, Interscience, 1964.

[8] K. CHIKANISHI and T. TSURUTA, Makromol. Chem. 81 (1965) 198.

[9] C. WALLING et al., J. Amer. Chem. Soc. 70 (1948) 1537; M. CHARTON, J. Org. Chem. 30 (1965) 557.

or anionic polymerization. With monomers of high e an Q values they can resist copolymerization even with high temperatures. For example, mixtures of vinyl acetate and styrene are self-inhibited under ordinary conditions. A number of these monomers undergo chain transfer readily with monomer and with polymer and tend to give branched polymers. In low reactivity these monomers approach typical behaviour of 1-olefins, vinyl ethers and monoallyl monomers.

A group of N-vinyl monomers has still lower e values, but they homopolymerize by selected free radical systems because of higher Q values:

	e	Q
2-Vinyl pyridine	-0.50	1.30
4-Vinyl pyridine	-0.20	0.82
N-Vinyl pyrrolidone	-1.14	0.14
N-Vinyl carbazole	-1.40	0.41
N-Vinyl phthalimide	-1.52	0.36

Some of these monomers respond also to cationic polymerization and bases act as inhibitors against polymerization.

The dienes are divinyl and diisopropenyl compounds showing high Q values and low e values. They polymerize very readily in heterogeneous systems such as emulsion free radical polymerization; also rather unpredictably in proliferous or popcorn polymerization upon active surfaces. They are often quite resistant to radical polymerization in homogeneous solutions or in bulk liquid.

	e	Q
1,3-butadiene or divinyl	-1.05	2.39
Isoprene or vinyl isopropenyl	-1.22	3.33
Chloroprene or 2-chloro-1,3-butadiene	-0.02	7.26
Hexafluoro-1,3-butadiene	0.47	0.93

A few monomers bearing strongly electron attractive groups do not homopolymerize readily by free radical initiation. The first two homopolymerize even with relatively weak Lewis basic initiators such as water and they polymerize readily with added basic comonomers such as vinyl ethers and N-vinyl compounds.

		e	Q
Methyl alpha-cyanoacrylate	$CH_2=C{<}^{CN}_{COOCH_3}$	2.10	High
Vinylidene cyanide	$CH_2=C(CN)_2$	2.58	20.13
Maleic anhydride	$CH=CH$ $O=C{-}O{-}C=O$	2.25	0.23
Maleonitrile	$CH=CH$ CN CN	2.32	0.42
Fumaronitrile	$CH=CH$ CN CN	1.96	0.80

In the cases of the cyanoacrylates and vinylidene cyanide strong Lewis acids are useful inhibitors against polymerization. The 1,2-disubstituted maleic and fumaric monomers do not give homopolymers of very high molecular weight but they copolymerize very readily with basic monomers.

The concept of acceleration of free radical polymerization and increase in polymer molecular weight resulting from high viscosity preventing termination of macroradicals (effect of Trommsdorff and Lagally) has continued to be useful and has been extended. The termination rate constant may be inversely proportional to solvent viscosity in some cases[10]. For stiff chains the effect may be less. The reviewer suggests that acceleration of polymerization of methyl methacrylate in poor solvents such as in lower alcools may involve inaccessibility of macroradical ends within clumped chain molecules. When a monomer is a poor solvent for its polymer, as in the case of acrylonitrile, bulk polymerizations become very rapid once initiated.

Telomerizations

Knowledge of vinyl-type polymerizations has been advanced through studies of chemical participation of saturated solvents and other added agents in free radical polymerizations. In reactions with inhibitors such as aromatic amines or nitro compounds, phenols and mercaptans, a growing macroradical is believed to abstract hydrogen terminating the chain and giving a resonance stabilized inhibitor radical incapable of propagating a new macromolecule. Reactive solvents and other telogens may give terminated polymers of low molecular weight (telomers) plus new radicals which may be capable of propagating new polymer chains. STAUDINGER and SCHWALBACH had observed that polymers of low molecular weight prepared in chloroform solution contained chemically bound chlorine[11]. HANFORD and JOYCE suggested the names telogen and telomer in systems giving products of low molecular weight, but the use of these terms has gradually been extended to terminated polymers of higher molecular weights. They found in the high pressure aqueous polymerization of ethylene using peroxide catalysts and added halogen compounds that carbon-halogen bonds were largely attacked giving liquid to waxy halogen-terminated telomers[12]. Ethylene and CCl_4 gave mixtures of a,a,a,ω-tetrachloroalkanes. Chloroform was unusual among halogen compounds in that hydrogen was attacked and the telomers contained terminal CCl_3 groups which on hydrolysis gave terminal carboxyl groups. Ethers and related compounds were particularly reactive in telomerization but with ethylene

[10] A.E.NICHOLSON and R.G.W.NORRISH, *Disc. Faraday Soc. 22* (1956) 104; R.D.BURKHART, *J. Polymer Sci. A 3* (1965) 883.
[11] H.STAUDINGER and A.SCHWALBACH, *Ann. Chem. 48* (1931) 8.
[12] R.M.JOYCE, W.E.HANFORD et al., *J. Amer. Chem. Soc. 70* (1948) 2529, *72* (1950) 2213; cf. U.S. 2,440,800 (DuPont), appl. 1942.

they did not give liquid products but wax-like materials of 20 or more monomer units[13]. Telomerizations have been used in preparation of commercial low molecular fluoropolymers but have been rather slow in reaching industrial importance. Recently telomerization of ethylene with trimethyl borate followed by methanolysis has been investigated for the synthesis of long-chain alcohols[14]. More interesting possibilities remain for exploration such as the synthesis of medium and high molecular weight polymers terminated by stable polar groups imparting surface activity, antistatic and stabilizing properties. The concept of telomers merges with that of chain transfer regulators of the mercaptan type which have long been used in commercial butadiene and acrylic polymerizations.

It is not surprising that polar and resonance factors are important in chain transfer as shown by values of chain transfer constants C defined by the formula $\frac{1}{DP} = \frac{C}{M} + \frac{1}{DPo}$ (where M is monomer concentration and DP is degree of polymerization or average number of monomer units per polymer molecule)[15]. With carbon tetrabromide at 60 °C chain transfer constants were reported as follows[16]: vinyl acetate > 39, styrene 2.2, methyl acrylate 0.41, methyl methacrylate 0.27. Thus relatively basic monomers including allyl compounds chain transfer most readily, while conjugated acidic monomers which give unreactive radicals do not abstract halogen or hydrogen readily. Tertiary hydrogen atoms such as in isopropyl compounds and acrylate ester polymers are more reactive in chain transfer than primary and secondary hydrogen atoms.

Ethylene with peroxide catalysts is about equally reactive with $CHCl_3$ and with CCl_4 as telogens, while vinyl acetate at 60 °C is about 60 times as reactive with CCl_4 as with $CHCl_3$[17]. Possibilities of preparing copolymers by multiple transfer seem to have been overlooked. This seems to occur when isopropyl vinyl ether, benzoyl peroxide and $CHCl_3$ or CCl_4 react at 50 to 60 °C to give crosslinked polymers[18]. With methylene chloride only traces of polymer are formed. These polyfunctional telomerization reactions show several characteristics of radical-cation polymerizations to be discussed later.

Ionic Polymerizations of Vinyl, Styrene and Acrylic Monomers

Early in this century ionic polymerizations such as sodium catalysis of dienes were studied before initiation by peroxides was generally known. Later special attention was given to ionic polymerization of those ethylenic compounds which did not respond to free radical polymerization to give products of high molecular weight. Polymerizations of Lewis basic or electron rich ethylenic monomers such as isobutylene, alkyl vinyl ethers and alpha-methylstyrene initiated by strong Lewis acids such as BF_3 and $AlCl_3$ are characterized by violence from ordinary temperatures. The development of controlled conditions at lower temperatures by OTTO and others was necessary for preparation of high polymers free of side products. It was suggested in the 1930's that these were chain-type reactions leading to chain polymers. However, the evidence of chain mechanisms in ionic polymerizations today is much less convincing than in the case of radical polymerizations.

Cationic and anionic polymerizations include a wider range of behavior than radical reactions. The inhibitors of radical polymerizations have little effect. Among substances which retard or prevent ionic polymerizations are those which destroy acids or basic catalysts, e.g., more than traces of water in cationic polymerizations. Low energies of activation, low heats of polymerization, speed of reaction and other characteristics of ionic polymerizations have been discussed[19], but recently very slow ionic polymerizations and other diverse types have been developed.

It has been generally supposed following ideas of WHITMORE that ionic polymerizations occur by growth of macro-ions (positive carbonium ions or negative carbanions). However, after many years proof is incomplete. Certainly the behavior of ethylenic monomers in ionic polymerization follows more closely the e values representing inductive electronic effects than the Q values. Perhaps ionic polymerizations would be better named polar polymerizations, remembering that they comprise diverse types, all different from free radical reactions.

Behavior in copolymerization is one of the best criteria of ionic or polar reactions. While in free radical initiated mixtures of two different monomers the polymeric products almost always contain units from both monomers, this is not true with ionic systems. Different monomers often require initiators of different Lewis acidities or basicities, so that one monomer homopolymerizes without participation of the second one present. Thus one alkyl vinyl ether such as isopropyl vinyl ether can homopolymerize in the presence of another less reactive vinyl ether.

However, ionic copolymerizations are possible under favorable conditions as in the preparation of butyl rubber from isobutylene and isoprene. Monomer copolymerization reactivity ratios are not generally useful in

[13] W. E. HANFORD and ROLAND, U.S. 2,402,137 (DuPont); M. D. PETERSON and A. G. WEBER, U.S. 2,395,292 (DuPont); C. S. MARVEL et al., J. Amer. Chem. Soc. 69 (1947) 52.

[14] W. T. HOUSE et al., Ind. Eng. Chem., Prod. Res. Dev. 5 (1966) 331.

[15] F. M. MAYO et al., J. Amer. Chem. Soc. 65 (1943) 2324, 70 (1948) 2373, 3689, 3740.

[16] N. FUHRMAN and R. B. MESROBIAN, J. Amer. Chem. Soc. 76 (1954) 3281.

[17] F. M. LEWIS and F. R. MAYO, J. Amer. Chem. Soc. 76 (1954) 457.

[18] F. GROSSER, U.S. 2,547,819 (General Aniline & Film Corp.) and C. E. SCHILDKNECHT, recent unpublished work.

[19] C. E. SCHILDKNECHT, Vinyl and Related Polymers, Wiley, 1952; C. E. SCHILDKNECHT, Polymer Processes, Interscience, 1956. P. H. PLESCH, The Chemistry of Cationic Polymerization, Macmillan, New York 1963.

different types of ionic systems. The composition of copolymers obtained from ionic systems depends more upon specific catalysts as well as solvents which influence acidity. In general there is less tendency for alternation of units in the copolymer molecules but more tendency to form blocks of successive identical units.

That in typical ionic polymerizations propagation as well as initiation is regulated by added catalysts is also demonstrated by the discovery of stereoregulation in ionic polymerizations of monomers of the type $CH_2=CHY$ and $CH_2=CYZ$. Many of these ionic polymerizations involve growth of polymer masses directly from heterogeneous catalyst systems. By contrast, in radical polymerizations initiators of limited soluble and direct growth of polymer masses have seldom been employed.

The first stereopolymerizations forming either stereoregular, crystallizable polymers or random, amorphous polymers by choice of catalysts and other conditions in cationic heterogeneous systems were observed from alkyl vinyl ethers[20], 1-olefins[21] and styrene[21]. The more stereoregular DDDD-polymers result from slow growth or proliferous polymerization upon relatively weak Lewis acid complexes such as boron fluoride etherates in the case of vinyl ethers, and reaction products of alkyl aluminum compounds and titanium halides in the case of 1-olefins and styrene. Lithium alkyls and certain other organometallic Lewis basic catalysts were found to yield stereoregular styrene, acrylic and methacrylic polymers, as well as cis-1,4-diene polymers. Generally more rapid and more homogeneous ionic polymerizations tend to give amorphous polymers. Of the activated transition metal compound catalysts, titanium favors stereoregular 1-olefin polymers while vanadium favors amorphous rubberlike polymers and copolymers. Both in the alkyl vinyl ethers[22] and the alkyl acrylates[23] stereoregular polymers form more readily from isobutyl monomers than from ethyl and higher n-alkyl compounds. Recently stereoregular polyvinyl ethyl ethers have been prepared by slow polymerizations with boron fluoride etherate, liquid propane and a large excess of fine solid carbon dioxide[24].

Ethylene, butadiene and styrene can be polymerized by all three methods of free radical, cationic and anion polymerization. Both transition metal and lithium complex catalysts can be used to prepare linear polyethylene, isotactic polystyrene and predominantly cis-1,4-polybutadiene. Stereoregulation as well as other evidence shows that catalysts in ionic systems can be more than initiators—they also may control propagation and polymer structure.

Most polymerizations initiated by high energy radiations at room temperature and above are of the free radical type. However, in recent years some radiation-promoted polymerizations at low temperatures and in particular solvents have been discovered to have characteristics of cationic polymerization, e.g., inhibition by water and amines. Positive ions seem to have sufficiently long duration for cationic polymerizations, especially in isobutylene, cyclopentadiene, alpha-methyl styrene, beta-pinene and in isobutyl vinyl ether[25]. Isobutylene has been polymerized ionically by use of ultraviolet light and an electric field said to eliminate need for an added gegen ion or heterogeneous surfaces[26]. The advantages of keeping the ions apart suggests a Trommsdorff-like effect in ionic polymerization.

Irradiation of maleic anhydride with aldehydes or ketones has been reported to initiate radical-cationic polymerization of isobutyl vinyl ether[27]. Radiation induced polymerization of styrene in an electric field at $-78\,^{\circ}C$ has been attributed to ionic polymerization[28].

Relative rates of polymerization of geometrical isomeric monomers are of interest. cis-Stilbene was reported to polymerize to oligomers faster than trans-stilbene at $-78\,^{\circ}C$ with titanium tetrachloride-trichloroacetic acid[29]. cis-Propenyl n-butyl ether was reported more reactive than the trans isomer in polymerization at $-78\,^{\circ}C$ with boron fluoride etherate catalyst[30]. However, the trans alkenyl vinyl ethers more readily stereopolymerized cationically to crystallizable polymers in Italian work[31]. The cis-hydrocarbon and long chain acid isomers ordinarily react faster than trans in additions of bromide, hydrogen, bisulfite, oxygen and mercuric acetate in methanol.

Cationic telomerization of butadiene with acetic acid was described[32]. Styrene and acetic acid using 0.5 M boron fluoride-acetic acid complex 20 hours at $25\,^{\circ}C$ gave 90% of telomers of the type $H(CH_2CH\Phi)_n\,OAc$ along with 10% of styrene dimer[33]. The liquid telomers consisted of $n=1$, 10%; $n=2$, 38%; $n=3$, 20% and $n>3$, 31%. The same workers telomerized styrene cationically with acetonitrile and with formaldehyde in acetic acid. Ethylene has been telomerized with aromatic hydrocarbons in presence of modified Ziegler type catalysts and halocycloalkanes[34].

[20] C.E.SCHILDKNECHT et al., Ind. Eng. Chem. 40 (1948) 2108, 41 (1949) 2981.

[21] G.NATTA et al., J. Amer. Chem. Soc. 77 (1955) 1708; cf. N. G. MERCKLING et al., French 1,135,808 (DuPont), appl. 1954.

[22] C.E.SCHILDKNECHT, Ind. Eng. Chem. 50 (1958) 107.

[23] M.L.MILLER et al., J. Amer. Chem. Soc. 80 (1958) 4115; J. Polymer Sci. 38 (1959) 63; Polymer 4 (1963) 75.

[24] G.A.HEAVNER and C.E.SCHILDKNECHT, unpublished work.

[25] S.H.PINNER et al., Chem. Ind. (London) 1957, 1274; M.MAGAT, Makromol. Chem. 35 (1960) 159; F.WILLIAMS et al. (review), Polymer Preprints, Amer. Chem. Soc. Meeting, N. Y. C., September 1966.

[26] E.W.SCHLAG and J.J.SPARAPANY, J. Amer. Chem. Soc. 86 (1964) 1875.

[27] H.YAMAOKA and K.TAKAKURA, J. Polymer Sci. B 4 (1966) 509.

[28] I.SAKURADI et al., Makromol. Chem. 97 (1966) 17.

[29] P.H.PLESCH and D.S.BROCKMAN, J. Chem. Soc. 1958, 3563.

[30] T.HIGASHIMURA et al., Kobunshi Kagaku 18 (1961) 561, Preprint Amer. Chem. Soc., Polymer Div., p. 409, September 1966.

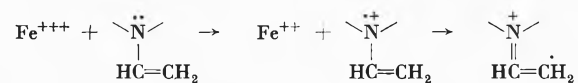[31] G.NATTA et al., Rend. Accad. Naz. Lincei (8) 28 (1960) 442.

[32] E.L.JENNER and R.S.SCHREIBER, J. Amer. Chem. Soc. 73 (1951) 4348.

[33] D.D.COFFMAN and E.L.JENNER, J. Amer. Chem. Soc. 76 (1954) 2685.

[34] D.V.FAVIS, U.S. 3,097,246 (Esso).

Monomers which either are very strongly electrophilic or nucleophilic can be polymerized by weakly basic or acidic substances. For example, methyl alpha-cyanoacrylate will polymerize exothermically from room temperatures on addition of diethyl ether or isobutyl vinyl ether. The characteristics of some of these reactions seem different from conventional cationic and anionic polymerizations and some have been called electron-transfer polymerizations. Of particular interest are polamerizations of basic monomers such as N-vinyl carbazole and of alkyl vinyl ethers by weak electron acceptors accompanied by the formation of deeply colored complexes. Thus N-vinyl carbazole treated with p-chloroanil, acetonitrile, tetracyanoethylene or allowed to stand in carbon tetrachloride solution slowly polymerizes from room temperatures[35]. The infrared spectrum of the polymer isolated from the colored solutions is similar to that of polymer prepared using boron fluoride-etherate as catalyst. Vinyl carbazole also was polymerized by metal ion oxidizing agents possibly initiated as follows[36]:

$$Fe^{+++} + \overset{\displaystyle ..}{\underset{\displaystyle HC=CH_2}{\diagdown N \diagup}} \rightarrow Fe^{++} + \overset{\displaystyle .+}{\underset{\displaystyle HC=CH_2}{\diagdown N \diagup}} \rightarrow \overset{\displaystyle +}{\underset{\displaystyle HC=CH_2}{\diagdown N \diagup}}$$

Dilute aqueous solutions of perchloric acid initiated exothermic polymerization of N-vinyl carbazole in orange-colored solutions[37]. Vinyl ethers and vinyl carbazole homopolymerize readily in liquid sulfur dioxide.

A striking example of oxidizing conditions participating in ionic polymerization is irradiation by ultraviolet light of a mixture of maleic anhydride and dioxane or by heating maleic anhydride-dioxane with benzoyl peroxide. The red-brown solution can initate violent homopolymerization of isobutyl vinyl ether at 50 °C[38]. Red-brown solutions accompany also the violent polymerization of isopropyl vinyl ether, benzoyl peroxide and carbon tetrachloride from 50 °C to give crosslinked polymers[39]. The colors suggest also those encountered in anionic polymerization of styrene, e.g., by sodium at 60 °C. A number of such ionic polymerization processes seem to be characterized by induction periods, deeply colored solutions and polymer products of rather low molecular weight. This is an interesting field not only for preparation of polymers but for study of electronic structures in relation to color. The names radical-cationic and radical-anionic polymerizations have been suggested.

By cationic systems copolymerization of some vinyl-type monomers has been observed with aldehydes and with compounds. For example, styrene and 1.3-dioxo-lane in toluene were reacted with BF_3 etherate catalyst to form block copolymers having rather long sequences of each monomer unit[40].

By certain cationic or anionic systems it has been possible to prepare homopolymers of moderately high molecular weight from certain beta- or 2-substituted ethylenic compounds. By acidic catalysts homopolymers have been prepared from indene, cumarone, acenaphthylene[41], 2-methoxystyrene[42].

Anionic conditions using alkali metal organic catalysts have given polymers from ethyl[43] and from t-butyl crotonate[44]. The latter produced stereoregular polymers when phenyl magnesium bromide acted for two hours at 27 °C. Tributyl phosphine at −15 °C promoted vinyl-type polymerization of crotonaldehyde along with some cyclization[45]. Products of number average molecular weight above 3,000 were obtained.

Other Reactions of Vinyl, Styrene and Acrylic Monomers

Surprisingly few detailed studies have been reported of the other reactions than polymerization of the numerous available monomers. Qualitative observations from the literature and experience of the reviewer are summarized here.

Electron donating alkyl and alkoxy groups substituted into ethylene promote rapid addition of bromine to double bonds. Electron attracting and conjugated groups as acrylic, methacrylic, maleic and fumaric compounds very greatly retard addition of bromine. Propylene adds hydrogen very much faster than ethylene under similar conditions over contact catalysts. Styrene, vinyl ethers and many ethylenic compounds are readily hydrogenated.

HCl generally adds only slowly to ethylenic compounds. HBr adds more rapidly and in the Markownikoff[46] way to many unsymmetrical olefinic hydrocarbons, as well as to chloro- and bromo-substituted olefins. BAUER observed reverse addition of hydrogen halides to vinyl halides in presence of oxidizing agents[47]. When the direction of addition of hydrogen halides to unsymmetrical alkenes and haloalkenes can be reversed by addition of peroxides or oxygen the mechanism is believed to change from ionic to free radical[48]. Reversed addition of HBr

[35] H. SCOTT et al., Tetrahedron Letters 14 (1963) 1073; J. Polymer Sci. B 2 (1964) 689; J. W. BREITENBACH and O. F. OLAJ, J. Polymer. Sci. B 2 (1964) 685; H. NOMORI, J. Polymer Sci. B 4 (1966) 261.
[36] C. H. WANG, Chem. Ind. (London) 1964, 751.
[37] O. F. SOLOMON et al., J. Polymer Sci. B 2 (1964) 311.
[38] H. YAMAOKA and K. TAKAKURA, J. Polymer Sci. B 4 (1964) 509.
[39] C. E. SCHILDKNECHT, unpublished work,

[40] D. J. LODER and W. F. GRESHAM, U.S. 2,394,862 (DuPont), appl. 1942; M. OKADA et al., Makromol. Chem. 94 (1966) 181.
[41] A. W. CAMPBELL et al., J. Amer. Chem. Soc. 58 (1936) 105.
[42] T. HIGASHIMURA et al., Polymer Preprint Amer. Chem. Soc. Meeting, N. Y. C., September 1966.
[43] O. C. BOCKMAN and C. SCHUERCH, Polymer Letters 1 (1963) 145.
[44] G. NATTA et al., U.S. 3,259,612 (Montecatini); M. L. MILLER and J. SKOGMAN, J. Polymer Sci. A 2 (1964) 4551; U.S. 3,274,168 (American Cyanamid).
[45] J. N. KORAL, J. Polymer Sci. 61 (1962) 537; U.S. 3,163,622 (American Cyanamid); Makromol. Chem. 62 (1963) 148.
[46] V. MARKOWNIKOFF, C. R. Acad. Sci. 81 (1875) 670.
[47] W. BAUER, Germ. 394,194 and U.S. 1,540,748 (Röhm & Haas); Chem. Abstr. 19 (1925) 2210; cf. Germ. 368,467; U.S. 1,414,852 (Röhm & Haas).
[48] F. R. MAYO and C. WALLING, Chem. Rev. 27 (1940) 351.

to allyl bromide and to diallyl without the presence of oxygen were favored by photochemical reaction[49].

Active hydrogen compounds generally add slowly and in the reverse way to ethylenic compounds bearing strong electron attracting groups as in the case of acrylic and methacrylic monomers. The alkali salts may be somewhat more reactive. Even substitution of halogen on or next to the double bond of an olefinic hydrocarbon retards addition reactions, but addition generally is still in the Markownikoff way. Small proportions of n-propyl iodide were obtained, however, from propylene and HI[50].

The addition of mercuric acetate from methanol solution to ethylene derivatives such as styrene, divinyl benzene, alkyl vinyl ethers, N-vinyl carbazole, allyl alcohol, allyl ethers and allyl esters occurs readily to give compounds of the type $CH_2\!-\!CH\!-\!R$ [51]. This reaction occurs

$$\underset{OCH_3 \quad HgAc}{\big|\qquad\big|}$$
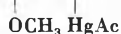
too slowly with acrylic, methacrylic, maleate and itaconate esters for analytical purposes.

POSNER, using thiophenol and benzyl mercaptan, discovered that mercaptans have a prevailing tendency to add in the reverse way to ethylenic double bonds[52]. Note that peroxide catalyzed free radical reactions are generally inhibited by high concentrations of mercaptans and such additions seem to be ionic in character. Mercaptans add only very slowly to monomers of low basicity such as maleic and fumaric acids[53]. Bisulfite salts generally add of olefins in the Posner way, but the products are often mixtures.

Epoxidation of olefinic hydrocarbons or of oleic acid with perbenzoic acid or peracetic acid are complete in a few hours, but crotonic acid and acrylic compounds react very slowly.

Olefinic monomers often hydrolyze or saponify more rapidly than their saturated analogs. Lower alkyl vinyl ethers hydrolyze to alcohol and acetaldehyde slowly in water and much faster in dilute mineral acid. Vinyl acetate hydrolyzes in dilute mineral acid or mercuric solutions and faster in alkaline solutions. Acrylic and methacrylic monomers are saponified by strong aqueous alkali.

Styrenes, vinyl ethers, acrylic and methacrylic monomers may react with oxygen in light with formation of hydroperoxides and other oxidation products. However, some monomers bearing hydroxyl, mercaptans or amine groups are self stabilized against such autoxidation. Small concentrations of added phenols, arylamines or sulfur compounds can of course retard oxidation as well as polymerization. Additions of soluble Lewis acids to methyl methacrylate and to some other acrylic monomers retard oxidation as well as polymerization[54].

Non-Vinyl Polymerizations of Vinyl-Type Compounds

The vinyl esters, vinyl halides, styrenes, and acrylic monomers generally react so readily by vinyl-type addition polymerizations that other possible types of polymerization reactions generally have been obscured. However, in recent years closer studies and explorations of unusual reaction conditions have revealed several other mechanisms by which macromolecules may form from ethylenic compounds, especially reactions involving migration of active hydrogen, isomerization polymerizations, cyclization and attack of other than vinyl multiple bonds when present.

Early examples of non-vinyl polymerizations were encountered more often with the allyl and related compounds, discussed later, whose double bonds have low reactivity in normal addition polymerization. These reactions become more significant with heating irradiation or addition of ionic catalysts and under particular conditions selected to retard vinyl-type addition polymerization, e.g., in presence of inhibitors of normal vinyl polymerization.

Hydrogen-migration or H-polymerizations may be regarded as related to chain transfer where an active hydrogen atom is displaced at each polymerization step. A single ethylenic monomer can supply both the active hydrogen and the double bond as in the H-polymerization of acrylamide to a polyamide discovered by BRESLOW and coworkers[55]

$$CH_2\!=\!CHCONH_2 \xrightarrow{\text{NaOR}} -\!-\!CH_2CH_2CONH\!-\!-$$

Sodium t-butylate catalyst could be added to a solution of acrylamide in dry pyridine containing an arylamine as inhibitor of vinyl polymerization. Polymers formed as a separate phase.

Much research remains in designing anionic conditions to obtain by H-polymerization products of really high molecular weight. «Copolymers» of mixed vinyl-type and H-type structure were indicated by polymerization of acrylamide in presence of peroxide and base[56]. The H-polymerization of acrylic and other monomers has received much attention from Japanese workers[57]. Methacrylamide and crotonamides respond more sluggishly. BRESLOW and coworkers showed that substituents in the acrylamide molecule decreased both the rate and the molecular weight of polymer. A substituent on the nitrogen showed the greatest effect, on the beta carbon next and on the alpha carbon least.

[49] W. E. VAUGHN et al., J. Org. Chem. 7 (1942) 477.
[50] A. MICHAEL and V. LEIGHTON, J. prakt. Chem. [2] 60 (1899) 445.
[51] R. W. MARTIN, Anal. Chem. 21 (1949) 922.
[52] T. POSNER, Ber. dtsch. chem. Ges. 38 (1905) 646.
[53] E. J. MORGAN and E. FRIEDMAN, Biochem. J. 32 (1938) 738.
[54] C. E. SCHILDKNECHT, unpublished work.

[55] D. S. BRESLOW, G. E. HULSE and A. S. MATLACK, J. Amer. Chem. Soc. 79 (1957) 3760.
[56] C. E. SCHILDKNECHT, H. KNUTSON and S. S. STIVALA, 126th Amer. Chem. Soc. Meeting, N. Y. C., September 1954; Ind. Eng. Chem. 50 (1958) 107.
[57] N. OGATA, J. Polymer Sci. 46 (1960) 271; Makromol. Chem. 40 (1960) 55; S. OKAMURA et al., Chem. High Polymers (Japan) 19 (1962) 323, 20 (1963) 364; H. TANI et al., Makromol. Chem. 76 (1964) 82.

These reactions are anionic (nucleophilic) but free radical initiated examples are also known, at least with allyl compounds. The addition of these active hydrogen compounds seems to occur predominantly in the Posner or Michael manner to give the less branched polymers.

YOKOTA and coworkers studied monomers containing amide hydrogens of different acidities[58]. Using sodium t-butoxide at 105 °C N-cycloheylacrylamide only gave a vinyl-type polymer while H-polymer structures predominated from N-benzyl, N-phenylethyl, N-*p*-anisyl, N-*p*-tolyl, N-phenyl and N-*m*-chlorophenyl acrylamides. Polymers of mixed vinyl and H-polymer structure confirmed by infrared were obtained by lithium butyl catalysis from *p*-vinyl benzamide[59]. Addition of lithium chloride suppressed the H-polymerization perhaps by reducing the basicity of the amide groups by complex formation.

H-type homopolymerizations have also been reported with vinyl sulfonamide[60], methyl vinyl ketone[61] H-migration polymerizations occur when divinyl, diacrylic or diallyl compounds react with diamines, diols, dithiols or other bifunctional compounds bearing reactive hydrogens.

$$CH_2=CH-A-CH=CH_2 + HBH \rightarrow --CH_2CH_2-A-CH_2CH_2B--$$
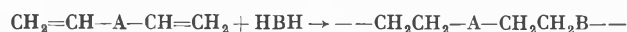
Examples include base catalyzed reactions of divinyl sulfone with polyfunctional hydrogen donors such as malonate esters, glycols and thioglycols discovered by SCHOENE[62], divinyl sulfone plus urea[63], reaction of non-conjugated dienes with dimercaptans by MARVEL and students[64], diacrylic monomers + diamines[65], diacrylates + diisopropylamine and H_2S[66].

When the compounds of functionality greater than two are used nucleophilic additions of active hydrogen compounds can give crosslinked products. Thus cellulose fibers can be crosslinked by divinyl sulfone for shrink proofing[67], a process discouraged by physiological properties of the sulfone. A triacrylyl triazine derivative reacted with H_2S in alkaline solution to give crosslinked polymers[68].

Another H-polymerization (also known as hydride shift or isomerization polymerization) occurring in cationic systems with olefinic hydrocarbons has attracted much recent interest. Isopropyl ethylene (or 3-methyl-1-butene) was discovered to give polymers of mixed structure by very low temperature polymerization using

Lewis acid catalysts such as $AlCl_3$ and $TiCl_4$[69] in contrast to the predominantly vinyl-type stereoregular polymers prepared by Ziegler type catalysts at elevated temperatures. KENNEDY presumed that the $3 \rightarrow 2$ hydride shift to the more stable carbonium ion precedes propagation. The substantially pure 1,3 isomeric polymer can only be obtained near -130 °C while the vinyl-type 1,2 polymer structure increases at higher temperatures. $AlCl_3$ gave more hydride-shift polymerization than boron fluoride.
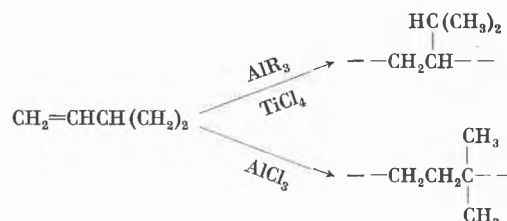

H-polymerization structures have been reported in polymers prepared from propylene, isobutylene and from styrene, but further confirmation is required. A 1,6 high polymer from styrene might have very interesting properties if it could be prepared.

The participation of cyclization in polymerization of ethylenic monomers was discovered with diallyl o-phthalate and has been most studied in diallyl compounds. Diacrylic monomers such as acrylic anhydride also can give soluble polymers containing rings[70] which apparently open upon hydrolyzing to acrylic acid polymers. Jones proposed the name cyclopolymerization.

Some cyclizations of preformed chains may occur, of course, such as in rapid polymerizations of acrylonitrile to colored polymers.

Opening of some $C\equiv N$ groups in acrylonitrile polymerizations and their participation of carbonyl double bonds in vinyl-type addition polymerizations under special conditions have been suspected.

Vinyl-type monomers may participate in condensation polymerizations such as the reactions of *p*-xylylene dichloride with styrene or methyl methacrylate to give heat resistant polymers[71]:
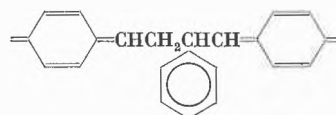
Radical Polymerizations of Allyl and Related Compounds

The monoallyl and monoallylidene compounds resemble alkyl vinyl ethers and non-conjugated olefinic hydrocarbons in that they do not form homopolymers of high

[58] K. YOKOTA, M. SHIMIZU, Y. YAMASHITA and Y. ISHII, *Makromol. Chem. 77* (1964) 1.

[59] T. ASAHARA and N. YODA, *Polymer Letters 4* (1966) 921.

[60] D. S. BRESLOW, G. E. HULSE and A. E. MATLACK, *J. Amer. Chem. Soc. 79* (1957) 3760.

[61] S. IWATSUKI, Y. YAMASHITA and Y. ISHII, *Polymer Letters 1* (1963) 545.

[62] D. L. SCHOENE, U.S. 2,493,364 and U.S. 2,505,366 (U.S. Rubber, 1950).

[63] J. W. SCHAPPEL, U.S. 2,623,035 (Amer. Viscose).

[64] C. S. MARVEL et al., *J. Amer. Chem. Soc. 73* (1951) 1037.

[65] G. E. HULSE, U.S. 2,759,913 (Hercules).

[66] J. G. ERICKSON, *J. Polymer Sci. A 1* (1966) 519.

[67] D. L. SCHOENE and V. S. CHAMBERS, U.S. 2,524,399 (1950).
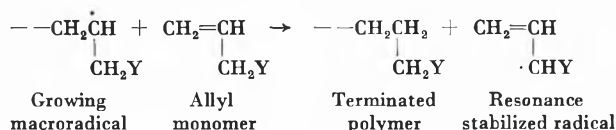
[68] R. WEGLER and A. BALLAUF, *Chem. Ber. 81* (1948) 530.

[69] W. R. EDWARDS and N. F. CHAMBERLAIN, Preprint *Amer. Chem. Soc., Coatings & Plastics Chemistry, September 1962*, p. 105; *J. Polymer Sci. A 1* (1963) 2299; J. P. KENNEDY et al., *Makromol. Chem. 53* (1962) 28, *64* (1963) 1; *J. Polymer Sci. A 2* (1964) 381, 2093.

[70] J. F. JONES (Goodrich), *J. Polymer Sci. 33* (1958) 7.

[71] P. J. CANTERINO and J. E. COOK, U.S. 3,193,538 (Phillips).

molecular weight on heating with radical catalysts at normal pressures and they retard radical polymerizations of most vinyl, styrene and acrylic-polymerizations. The presence of allylic hydrogen atoms on a third carbon $CH_2=CHCH_2X$ and $CH_2=CHCHXY$ prevents an electron attracting or resonating group from being attached directly to the ethylenic nucleus. Therefor the double bonds of allyl compounds have low activation and low reactivity. Typical monoallyl compounds such as allyl acetate on heating with peroxide catalysts slowly form low yields of oils or viscous liquid low polymers of *DP* up to about 20. The explanation of BARTLETT and coworkers has been generally accepted that reaction of radicals with allylic hydrogen atoms causes self termination (allylic degradative transfer or auto-inhibition)[72].

$$--CH_2\overset{\bullet}{C}H + CH_2=CH \rightarrow --CH_2CH_2 + CH_2=CH$$
$$\quad\quad | \qquad\qquad\quad | \qquad\qquad\qquad | \qquad\qquad\quad |$$
$$\quad\; CH_2Y \qquad\quad CH_2Y \qquad\quad\; CH_2Y \qquad\;\; \cdot CHY$$

| Growing macroradical | Allyl monomer | Terminated polymer | Resonance stabilized radical |

For each polymerization experiment there was a linear relation between peroxide consumed and allyl acetate low polymer formed. However, at high initial catalyst concentrations this ratio fell off. Degradative transfer was confirmed by faster rates and higher polymer molecular weights from deuterated allyl acetate. Alkyl vinyl ethers give only liquid low polymers in free radical homopolymerizations which may also result in part from degradative transfer[73].

Degradative chain transfer has been somewhat overemphasized with regard to allyl compounds in polymerization. Low reactivity of the allyl group from absence of strong resonance effects needs more consideration. Values of e and Q from radical copolymerization data show also the similarity of monoallyl compounds to 1-alkenes and to alkyl vinyl ethers[74].

By free radical initiation high polymers normally form from most of these monomers only by copolymerization with reactive Lewis acidic monomers such as maleic anhydride.

Early work gave even lower molecular weight polymers from allyl chloride and allyl alcohol by free radical systems than from allyl acetate. Recently amorphous, elastomeric solid polymers of somewhat higher molecular weight have been prepared from allyl chloride at pressures above 100,000 psi and using isopropyl percarbonate as initiator[75]. High pressures gave less transfer but no high polymers from allyl acetate[76].

Divinyl ether polymerizes on warming with peroxide catalysts to give brittle crosslinked polymers, while diallyl ether with benzoyl peroxide and ultraviolet gives soluble soft solid polymers[77]. The allyl monomers which have been used most successfully in commercial polymers have been the polyfunctional ones which can be formed in partially polymerized states followed by completion of polymerization or curing to thermoset structures in presence of peroxide initiators. Thus diallyl diglycol carbonate is used with little modification for cast optical plastics, while the diallyl phthalates, triallyl cyanurate and related monomers are more often used along with preformed unsaturated polyesters in fiber and filler reinforced thermoset articles. The relatively low reactivity of the allyl groups permits formation of syrupy prepolymers. Another advantage of low reactivity is control of copolymerizations when small proportions of polyfunctional allyl monomers are added as curing or crosslinking agents with other monomer or polymer mixtures. Typical allyl monomers show little tendency for thermal polymerization without added initiators. Some of them can be heated to surprisingly high temperatures with little reaction.

The following values of e and Q show the low reactivity of diallyl, non-conjugated dienes and divinyl ether monomers:

	e	Q
$CH_2=CH_2$	-0.20	0.02
$CH_2=CHCH_3$	-0.78	0.002
$CH_2=CH(CH_2)_2CH_3$	-0.63	0.07
$CH_2=C(CH_3)_2$	-0.96	0.03
$CH_2=CHOC_2H_5$	-1.17	0.03
$CH_2=CHO(CH_2)_3CH_3$	-1.20	0.09
$CH_2=CHOCH_2CH(CH_3)_2$	-1.77	0.02
$CH_2=CHOC(CH_3)_3$	-1.58	0.15
$CH_2=CHCH_2Cl$	$+0.11$	0.06
$CH_2=CHCH_2OH$	$+0.29$	0.05
$CH_2=CHCH_2OCOCH_3$	-1.13	0.03
$CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2Cl$	-0.91	0.12
$CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2OCOCH_3$	-1.33	0.04
$CH_2=\overset{\overset{Cl}{|}}{C}-CH_2OCOCH_3$	-1.12	0.53
$CH_2=\overset{\overset{Cl}{|}}{C}-CH_2Cl$	$+0.44$	0.27
$CH_2=\overset{\overset{Cl}{|}}{C}-CH_2OH$	$+0.56$	0.25

	e	Q
Diallyl-o-phthalate	$+0.36$	$.04$
Diallyl melamine	-0.95	$.02$
Diallyl phenyl phosphonate	-0.07	$.05$
Diallyl phenyl phosphonate	-0.07	$.05$
Diallyl n-butyl phosphonate	-0.07	$.05$
Dimethallyl oxalate	-0.15	$.04$
Divinyl ether	-1.28	$.04$
Vinyl cyclohexene	-1.64	$.06$

[72] P.D.BARTLETT and R.ALTSCHUL, *J. Amer. Chem. Soc.* 67 (1945) 812; P.D. *Bartlett* and F.O.TATE, *ibid.* 75 (1953) 91.
[73] C.E.SCHILDKNECHT, *Polymer Eng. & Sci.* 6/3 (1966) 240.

[74] L.J.YOUNG in *Polymer Handbook*, editors: J.BRANDRUP and E.H. IMMERGUT, Interscience, 1966; cf. *J. Polymer Sci.* 54 (1961) 444.
[75] F.P.REDING *et al.*, U.S. 3,245,969 (Carbide).
[76] C.WALLING and J.PELLON, *J. Amer. Chem. Soc.* 79 (1957) 4782.
[77] C.E.SCHILDKNECHT, unpublished work.

A typical styrene or methacrylate ester monomer requires 20 p.p.m. of phenolic type inhibitor and a dimethacrylate much more inhibitor in order to prevent polymerization on storage for a year at room temperature. Diallyl esters without added inhibitor often do not polymerize appreciably on storage for a year under air. In some circumstances the relatively slow rates of polymerization of allyl monomers to catalysts has technical advantages and rates can be accelerated by adding some acrylic or methacrylic monomer.

Free radical copolymerization and regulation with minor proportions of monoallyl compounds have promise for preparing soluble polymers with controlled branching.

Polyfunctional allyl comonomers have great promise in minor proportions with vinyl-type polymers and monomer-polymer systems for introducing high radical concentrations at relatively high temperatures, e.g., for crosslinking. Even substantially saturated polymers can be crosslinked by addition of di- or triallyl esters followed by irradiation or heating with high temperature peroxides[78]. Polyfunction styrene and acrylic monomers are too reactive at lower temperatures for such applications and for monomer storage.

Methallyl compounds $CH_2=C-CH_2Y$ have been much
$|$
CH_3
less investigated than allyl compounds. One reason is the ready isomerization of methallyl alcohol to isobutyraldehyde in presence of mineral acids. As would be expected from the electron donating qualities of the methyl group, methallyl compounds seem to polymerize less readily than corresponding allyl compounds in free radical systems. The lower e values of methallyl compounds compared to corresponding allyl compounds should make them respond better in cationic polymerization. Exploratory work by the reviewer gives some evidence of this. Compounds of the type $-CH=CHCH_3$ do not polymerize readily by conventional radical methods. Crotyl and cinnamyl esters are less reactive in polymerization than allyl esters[79].
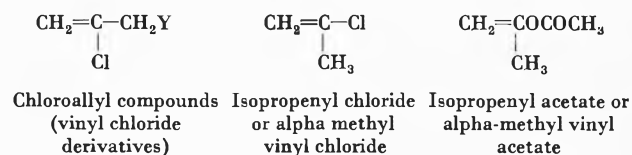
The so-called air drying polymerization of certain unsaturated hydrocarbons, long chain esters and ethers containing peroxidizable allylic hydrogen atoms seems to involve different radical processes from homogeneous conventional radical initiated polymerizations. The thickening and solidification of linseed oil, one of the very oldest polymerization processes used by man, remains incompletely understood. Such unsaturated liquids which form skins of polymer in contact with air, especially in the presence of traces of transition compounds (driers such as cobalt naphthenate), generally will not respond to heating with added radical initiators out of contact with air. For air oxidative polymerization to occur readily a molecule seems to require at least two non-conjugated double bonds associated with hydrocarbon or ether groups as in drying oils, sorbitol tetraallyl ether, polyallyl ethers of starch and certain diallylidene cyclic acetal esters which in patents have been named vinyl dioxolane esters[80].

Allyl alkyl ethers and methyl linoleate, for example, do not show air drying polymerization. Many possibilities for faster curing air-polymerizing unsaturated prepolymers remain to be explored.

Molecular oxygen retards polymerization of allyl esters such as diallyl diglycol carbonate, diallyl phthalates, diallyl adipate and triallyl cyanurate, but the effect seems less than in the case of typical acrylic and methacrylic compounds. Dissolved high polymers, as in syrups, reduce the inhibiting effects of air but surfaces unprotected from oxygen will remain soft and tacky in most cases. Certain polyfunctional allyl ethers have been added to vinyl-type monomer systems for the purpose of overcoming inhibition by air, especially in coatings. From a number of crosslinked cast polymers prepared by the reviewer from different polyfunctional allyl compounds by photopolymerization with benzoyl peroxide in beakers under air, the average thickness of the top soft layers was less than encountered with methacrylic esters.

Among borderline compounds are several which seem to polymerize more readily with free radical catalysts than do typical monoallyl compounds, but homopolymers of high molecular weight have not yet been confirmed:

$CH_2=C-CH_2Y$	$CH_2=C-Cl$	$CH_2=COCOCH_3$
$\|$	$\|$	$\|$
Cl	CH_3	CH_3
Chloroallyl compounds (vinyl chloride derivatives)	Isopropenyl chloride or alpha methyl vinyl chloride	Isopropenyl acetate or alpha-methyl vinyl acetate

In radical copolymerizations with vinyl halides, styrenes and acrylic monomers the allyl compounds show very low reactivity and they can be used as inhibitors or regulators. In attempted copolymerizations with allyl or diallyl compounds, products close to homopolymer composition may result in some cases. Special procedures may be required in order to prepare chemically homogeneous copolymers (interpolymers).

In contrast to the above, certain compounds of high molecular weight bearing hydroperoxidizable allylic hydrogen atoms can graft copolymerize readily with styrenes and acrylic monomers. An example seems to be the graft copolymerizations of shellac and derivatives dispersed in aqueous medium[81] where the shellac ammonium salt may function both as initiator and dispersing agent. Scientific aspects of graft copolymeriza-

[78] S.H.PINNER, Nature 182 (1959) 1108.
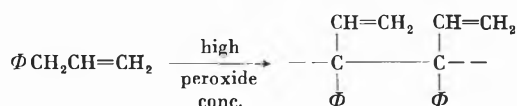[79] F.STRAIN, U.S. 2,397,631 (PPG = Pittsburgh Plate Glass Co.).

[80] C.K.IKEDA, U.S. 3,010,918; U.S. 3,010,923–4 (DuPont).
[81] R. J. FREY and M. H. ROTH, U.S. 2,961,420 (Monsanto); H. SCHMALZ and E.H.HOFFMAN. Germ. 1,151,381 (Resart); cf. U.S. 3,061,564 (Röhm&Haas).

tions with purified shellacs and drying oils merit closer attention.

Besides degradative chain transfers another type of reaction can consume free radicals and retard crosslinking in diallyl and polyallyl monomers, namely, cyclization. SIMPSON found evidence of partial cyclization in diallyl orthophthalate polymerization[82], and later work has supported cyclization in other radical polymerizations such as diallyl and triallyl quaternary ammonium halides[83], divinyl formal[84] allyl vinyl sulfonate[85]. When the two ethylenic groups have different reactivities as in allyl acrylate the degree of cyclization may be 58%[86], somewhat lower than predictions of BUTLER and RAYMOND[87]. Cyclizations in chain propagation may occur more generally in ionic polymerization discussed below.

Attempts have been made to prepare polymers by polyrecombination from allyl aromatic compounds encouraged by the stability of allylic radicals:

$$\varPhi CH_2CH=CH_2 \xrightarrow[\substack{peroxide \\ conc.}]{high} --\overset{\overset{\displaystyle CH=CH_2}{|}}{\underset{\underset{\displaystyle \varPhi}{|}}{C}}--\overset{\overset{\displaystyle CH=CH_2}{|}}{\underset{\underset{\displaystyle \varPhi}{|}}{C}}--$$

For example, SOSIN treated p-allyl anisole, the p-methoxy compound, at 200 °C under nitrogen by adding t-butyl peroxide portionwise[88]. Crosslinked and oligomer fractions of uncertain structure were obtained.

Ionic Polymerizations of Allyl Compounds

Until recently few homopolymers of high molecular weight had been prepared by either free radical or ionic polymerizations of monoallyl compounds. Strong Lewis acid catalysts react as electron donors with many allyl compounds with evolution of heat and formation of low molecular discolored polymers and/or "Lewis complexes". Recently, however, special heterogeneous conditions using diluents with weakly acidic electron attracting catalysts, such as boron fluoride etherates or Ziegler-type transition metal catalysts, have given high polymers from monoallyl compounds some of which show stereoregularity. This work confirms the similarity of such allyl compounds to alkyl vinyl ethers and to 1-olefins.

NATTA, MAZZANTI and coworkers obtained stereoregular high melting polymers from monoallyl silane using Ziegler-type catalysts[89] and CAMPBELL and HAVEN prepared stereoregular allylbenzene polymers[90].

Polymers from allyl alcohol and monoallyl esters showing stereoregularity were prepared using boron fluoride etherate by GOODMAN and MATHER in laboratories of ICI[91]. These products presumably have vinyl-type structure and they give crystalline X-ray patterns. Recently solid polymers of allyl chloride have been grown upon activated aluminium metal[92]. Dimethallyl gave solid polymers using BF$_3$ etherate and other electrophilic catalysts[93].

Little success has been reported in anionic polymerization of allyl compounds by Lewis basic catalysts in accordance with unpublished experiments of the reviewer.

Relatively little detailed research has been reported upon ionic copolymerizations except for a few systems of industrial interest. One of the latter is the terpolymerization of ethylene, propylene and non-conjugated dienes such as diallyl. The stereopolymerization of ethylene and propylene to amorphous elastomers of high molecular weight using vanadium halides or oxyhalides activated by organoaluminum compounds was disclosed by NATTA, MAZZANTI and coworkers in 1957[94]. Among the terpolymer EPT rubbers quickly made available in the U.S. some have used a little diallyl or 1,5-hexadiene to promote curing. Later 1,4-hexadiene or allyl propenyl was found more suitable.

Recently allyl halides have been copolymerized with 1-olefins using BF$_3$ or AlCl$_3$ in alkyl chloride solvent[95]. Allyl chloride in alkyl chloride could first be reacted with Lewis acid catalyst to give a deeply colored solution. This was added to a solution of alkene in ethyl chloride at low temperatures to form copolymers of high molecular weight.

Polymerizations of Allyl Compounds by Non-Vinyl Mechanisms

Allyl compounds have provided numerous examples of H-polymerization to products of low or intermediate molecular weight. The ready addition of mercaptans to olefins had been demonstrated by POSNER and NICOLET[96]. It was found difficult to suppress the Posner type addition in reaction of allyl lauryl sulfide with lauryl mercaptan, but additions of sulfur favored Markownikoff addition[97]. In early research HOFMANN had observed gradually rising boiling temperatures in the distillation of allyl mercaptan. Polymerization of allyl mercaptan and related ethylenic compounds on heating was

[82] W. SIMPSON, T. HOLT and R. J. ZETIL, J. Polymer Sci. 10 (1953) 489.
[83] J. B. BUTLER and R. J. ANGELO, J. Amer. Chem. Soc. 79 (1957) 3128.
[84] Y. MINOURA and M. MITOH, J. Polymer Sci. A 3 (1965) 2149.
[85] E. J. GOETHALS, Polymer Letters 4 (1966) 691.
[86] R. C. SCHULZ et al., Makromol. Chem. 46 (1961) 281.
[87] G. B. BUTLER and M. A. RAYMOND, J. Polymer Sci. A 3 (1965) 3413.
[88] S. L. SOSIN et al., J. Polymer Sci. USSR 6 (1965) 1352; cf. A. KLAGES, Ber. dtsch. chem. Ges. 32 (1899) 1437.
[89] G. NATTA et al, Chim. e Ind. (Milan) 40 (1958) 813; Chem. Abstr. 53 (1958) 6673.
[90] T. W. CAMPBELL and A. C. HAVEN, J. Appl. Polymer Sci. 1 (1959) 73.

[91] I. GOODMAN and J. MATHER, Brit. 854,207 (ICI); Chem. Abstr. 55 (1961) 11920.
[92] M. OKUYAMA and H. HIRATA, Kolloid-Z. 212 (1966) 162–5.
[93] C. E. SCHILDKNECHT, E. HAGMANN and R. F. WILLIAMS, unpublished work.
[94] G. NATTA, G. MAZZANTI et al., Chim. e Ind. (Milan) 39 (1957) 733, 743, 825; J. Polymer Sci. 51 (1961) 411.
[95] E. A. HUNTER and C. L. ALDRIDGE, U. S. 3,299,020 (Esso).
[96] T. POSNER and NICOLET, Ber. dtsch. chem. Ges. 38 (1905) 646.
[97] S. O. JONES and E. E. REID, J. Amer. Chem. Soc. 60 (1938) 2452.

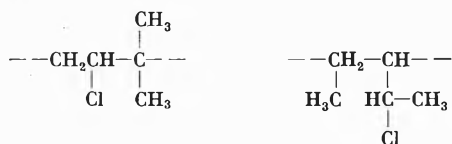attributed by von Braun and Murjahn to the reaction of SH groups with the double bond[98]:

$$CH_2=CHCH_2SH \rightarrow --CH_2CH_2CH_2S--$$
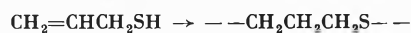
Treatment of allyl mercaptan with sodium ethoxide followed by CCl_4 gave brown color and polymer[99]. Such polymerizations of allyl mercaptan may occur by free radical or anionic mechanisms, but the unique odor of the monomer has discouraged research.

Marvel and his students succeeded in making high polymers by free radical emulsion H-polymerization of diallyl with dimercaptans and reported interesting characteristics of these reactions[100].

Diallyl as well as diallyl ether have been heated or irradiated with phenyl phosphine to give linear polyphosphines[101]. Diallyl ether and phenyl phosphine heated 90 hrs. at 70 °C with benzoyl peroxide formed a tough elastomer.

Similar to hydride shift type or H-polymerization discussed above is the intramolecular chloride shift polymerization of the allyl compound 3-chloro-3-methyl-1-butene $H_2C=CHCClCH_3$ recently discovered[102]. $AlCl_3$ was
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad CH_3$$
used as catalyst in liquid ethyl chloride at -130 to -30 °C giving soft amorphous polymers having about equal proportions of 1,3 and 1,2 strutures:

$$--CH_2CH-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-- \quad\quad\quad --CH_2-\overset{}{\underset{\underset{\underset{\displaystyle Cl}{|}}{HC-CH_3}}{\underset{|}{CH}}}--$$
$$\quad\quad\quad |$$
$$\quad\quad Cl$$

Polymerization of allyl benzene using BF_3 or $AlCl_3$ gave polymers having benzene in the main chain judging from infrared, NMR and oxidation studies[103]. In CS_2 at 30° with $AlBr_3$ catalyst allyl benzene gave polymer of structure
$$\quad\quad\quad\quad\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$$
$$--CHCH_2\langle\bigcirc\rangle-- \text{ having } DP \text{ of about } 32\,[104].$$

Intramolecular cyclization in some free radical polymerizations of diallyl compounds to soluble polymers have been noted above. Recently cyclization has been found to contribute to certain ionic polymerizations of allyl compounds. Among these compounds are non-conjugated diolefinic hydrocarbons using Ziegler catalysts[105], 4-vinyl cyclohexene by Ziegler catalyst[106], 2-

[98] J. von Braun and R. Murjahn, *Ber. dtsch. chem. Ges.* 59 B (1926) 1207.

[99] H. J. Backer and P. L. Stedehouder, *Rec. Trav. Chim. Pays-Bas* 52 (1933) 453.

[100] C. S. Marvel et al., *J. Amer. Chem. Soc.* 70 (1948) 993 to 75 (1953) 6318.

[101] A. Y. Garner, U.S. 3,010,946 (Monsanto); cf. U.S. 2,671,080.

[102] J. P. Kennedy et al., *Makromol. Chem.* 93 (1966) 191.

[103] S. Murahashi et al., *Chem. High Polymers* (Tokyo) 23 (1966) 253, 354.

[104] E. B. Davidson, *J. Polymer Sci. B* 4 (1966) 175.

[105] C. S. Marvel and J. K. Stille, *J. Amer. Chem. Soc.* 80 (1958) 1740; and H. S. Makowski et al., *J. Polymer Sci. 2 A* (1964) 1549.

[106] G. B. Butler and M. L. Miles, *J. Polymer Sci. A 3* (1965) 1609.

allyl-1-methylene cyclohexane by BF_3 in methylene chloride at -70 °C[107].

Other Reactions of Allyl Compounds

Since allyl compounds in general polymerize less readily than other vinyl-type monomers their other reactions become more important during polymerization, and in many cases the side reactions contribute to polymer structure. Chain transfer and cyclization reactions have been discussed already. Allyl oxygen and sulfur compounds have unshared electrons which can promote electronic shifts in presence of catalysts.

The literature until 1948 on reactions of many allyl compounds has been reviewed[108].

In contrast to non-existent vinyl alcohol and isopropenyl alcohol, allyl alcohol and methallyl alcohol can be purified and stored. However, allyl alcohol can isomerize to propionaldehyde. Methallyl alcohol isomerizes quite rapidly even in dilute mineral acid solutions:

$$CH_2=\overset{\overset{\displaystyle }{}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2OH \xrightarrow{H^+} (CH_3)_2CHCHO$$
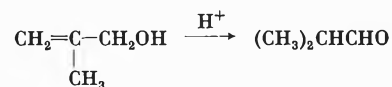
This reaction can prevent preparation of methallyl esters by Fischer esterification with strong acid catalysts. The slightly delayed severe sting in the nose from vapors of allyl alcohol seems to result from oxidation to acrolein in the tissues[109]:

$$2\,CH_2=CHCH_2OH + O_2 \rightarrow 2\,CH_2=CHCHO + 2\,H_2O$$
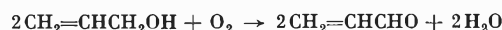
Propenyl compounds $CH_3CH=CHY$ are more stable to oxidation than related allyl compounds.

Allylic rearrangements may occur readily where a substituent moves from one end to the other of the resonating allyl group

$$CH_2=CH\dot{C}H_2 \leftrightarrow \dot{C}H_3CH=CH_2 \text{ or } CH_2\cdots CH\cdots CH_2$$
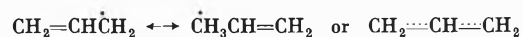
For example, either one of the following pure bromides (obtained from butadiene + HBr) on standing isomerizes to the equilibrium mixture indicated:

$$\begin{array}{cc} CH_2=CHCHBrCH_3 & BrCH_2CH=CHCH_3 \\ 15\% & 85\% \end{array}$$

The corresponding chlorine compounds, however, do not isomerize readily in this way. The peroxide ascaridole was observed to catalyze this type of isomerization. The isomerization of $CH_3CH=CH-CH_2Cl$ and $CH_2=CHCH_2CH_2Cl$ to an equilibrium mixture is ca-

[107] G. B. Butler and M. L. Miles, *Polymer Eng. & Sci.* 6 (1966) 72.

[108] *Allyl Chloride and Other Allyl Halides*, Shell Chemical Co., New York/San Francisco 1949.

[109] C. E. Schildknecht and G. E. Carvell, 1965.

talyzed by ferric chloride indicating an ionic reaction. Changes in double bond positions may be called allylic shifts whether true allyl compounds are involved or not.

Allyl ethers can isomerize slowly to propenyl ethers at 150 to 175 °C in presence of Lewis basic catalysts[110]. Thus with potassium *t*-butoxide an hour gave 35% isomerization of triallyl pentaerythritol.

In the Claisen rearrangement an allyl group moves from an ether linkage to become attached normally at the adjacent position on an aromatic ring[111]. Thus allyl phenyl ether on heating without catalyst gives *o*-allyl phenol. Allyl ethers of enols such as O-allyl acetoacetate esters also can rearrange to C-allyl compounds. Allyl thioaryl ethers also can give Claisen type rearrangements[112], but amine catalysts generally are necessary. Allyl vinyl ether and allyl isopropenyl ether can rearrange to allyl acetaldehyde and allyl acetone respectively[113].

Allyl phenole on heating with concentrated alkali can isomerize to propenyl phenols but this reaction seldom occure under conditions of Claisen rearrangements.

Allyl bromide adds HBr in the Markownikoff way, but presence of peroxides or oxygen promotes the reverse or Posner addition[114].

$$CH_2{=}CHCH_2BR + HBr \nearrow CH_3CHBrCH_2Br$$
$$\searrow CH_2BrCH_2CH_2Br$$
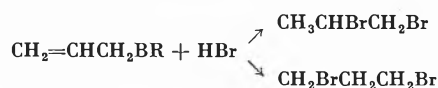
HCl adds only very slowly and neither HCl or HI give pronounced peroxide catalyzed reversals. The addition of HCl is an ionic reaction which is catalyzed by Lewis acids including iodine. The Posner type addition apparently has a free radical mechanism. Allyl chloride with HBr gives some peroxide-catalyzed reversal. Allyl mercaptans and apparently allyl alcohols tend to undergo additions in the Posner manner. Diallyl ether and H_2S react under ultraviolet light to give linear polymers of molecular weight 200 to 1000 (Posner addition)[115]:

$$CH_2{=}CHCH_2OCH_2CH{=}CH_2 + H_2S \xrightarrow{UV}$$
$$-\,-CH_2CH_2CH_2OCH_2CH_2CHS-\,-$$
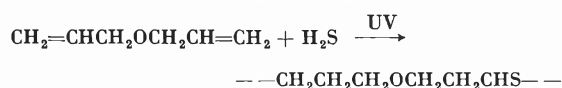
Like alkenes and vinyl ethers the allyl compounds all add bromine fairly rapidly (in contrast to acrylic and maleic compounds). SIGGIA found that bromine adds faster to allyl esters in water or methanol than in acetic acid or CCl_4 (when the compounds are miscible)[116].

Substituents on the third carbon alpha to the double bond by inductive effects can influence rates of addition[117]. Thus under similar conditions the following in carbon tetrachloride solution decolorized bromine solution almost instantly at room temperature in diffused light: allyl alcohol, diallyl amine, cyclohexene, 2-methyl-1-pentene, allyl ethylene glycol, allylurea and safrole. The following required from 0.5 to 10 minutes for decolorization: allyl acetate, allyl propionate, allyl caproate, diallyl adipate, allyl bromide, allyl cyanide, diallyl maleate. The following required more than 10 minutes: diallyl fumarate, diallyl-*o*-phthalate, diallyl-*m*-phthalate.

Allyl monomers differ greatly in rates of photochemical oxidation under air. Allyl alcohols, mercaptans and amines are self-stabilized against free radical oxidation. Small additions of numerous allyl compounds have been found to inhibit or retard radical oxidations and polymerizations[118], but the relations of these activities to self-oxidation and resonance stabilization of radical species remain to be clarified.

Polyfunctional Vinyl-Type Compounds. With the exception of conjugated dienes used in rubber synthesis, only a few of these have reached large scale production, but a number have growing applications in new fields of copolymer technology. Divinyl benzene isomers, among the first readily available crosslinking agents, are unstable in storage, generally give brittle copolymers and do not provide double bond of different reactivity. Monomers such as dimethacrylates of tri- or tetra-ethylene glycol show better stability as monomers and in copolymers. They also provide more flexible crosslinks and less brittle copolymer products. In general polyfunctional allyl and allyl-vinyl monomers have most promise because of better latitude in controlling crosslinking along with selection of peroxide initiators. Such monomers as allyl methacrylate, diallyl maleate, diallyl fumarate, diallyl phthalates and triallyl cyanurate in 1 to 5% concentration can be employed to crosslink not only comonomers and partial polymers but also finished saturated polymers. Suitable heating with peroxides or other radical-forming compounds and/or radiation with radiation sensitizers are adapted to the particular crosslinking monomers. Among the fields of application are dental plastics, finishes, synthetic rubbers and their latices, electrical insulations, fiber reinforced plastics, adhesives, flocculating agents, semi-permeable membranes, optical plastics.

Polyfunctional allyl monomers such as the three isomeric diallyl phthalates, diallyl glycol carbonate, triallyl isocyanurate and diallyl adipate, can be brought to formable partial polymer stages before curing in useful shapes. In general the polyfunctional styrene, acrylic and vinyl ester monomers polymerize too rapidly to arrest the reactions at such partially polymerized forms

[110] T. J. PROSSER, U.S. 3,168,575 (Hercules).
[111] L. CLAISEN, *Ber. dtsch. chem. Ges. 45 B* (1912) 3157; D. S. TARBELL, *Chem. Rev. 27* (1940) 497.
[112] C. D. HURD and GREENGARD, *J. Amer. Chem. Soc. 52* (1930) 3356.
[113] C. D. HURD and L. R. POLLACK, *J. Amer. Chem. Soc. 60* (1938) 1905.
[114] M. S. KHARASCH and F. R. MAYO, *J. Amer. Chem. Soc. 55* (1933) 2468, *60* (1938) 3097.
[115] W. E. VAUGHN and F. F. RUST, U.S. 2,522,589 (Shell); *J. Org. Chem. 7* (1942) 472.
[116] S. SIGGIA et al., *Anal. Chem. 35* (1963) 362.
[117] C. E. SCHILDKNECHT and D. J. WALBORN, unpublished work.
[118] G. F. D'ALELIO, U.S. 2,339,058 (General Electric).

suitable for storage or shipment. The prepolymerizable polyfunctional allyl esters have made possible new techniques and superior properties especially in thermosetting moldings and fiber reinforced thermoset cast forms.

It is interesting that one polyfunctional allyl monomer, allyl cinnamate, was polymerized thermally and photochemically long ago[119]. Soluble prepolymer was isolated and found to react only slowly with bromine. The finished crosslinked polymers were brittle but were considered as amber substitutes. Allyl cinnamalacetate[120] and allyl sorbate are examples of trifunctional monomers.

Diallyl and triallyl ester monomers first attracted attention in high energy radiation crosslinking of polymers in England by PINNER and others[121]. These monomers have advantages of storage stability without inhibitors, short propagation chain length and high chain transfer efficiency. With 25 parts or more of diallyl sebacate or triallyl cyanurate per 100 polyvinyl chloride "attenuated network" flexible products were obtained. The polyvinyl chloride apparently is not crosslinked directly but is attached to the plasticizing network of polyallyl ester. Even polymers such as methyl methacrylate polymer, which normally degrade on irradiation, are converted to insoluble networks by polyfunctional allyl monomers. Development of such multicomponent crosslinked polymer systems by heating with radical initiators is in progress. The polyallyl monomers can provide controllable high concentrations of free radicals at sufficiently high temperatures that saturated polymer chains can be attacked for formation of crosslinks. At the same time some of the unreacted non-volatile allyl monomers can act as stabilizers against oxidative degradation and discoloration.

Other recent developments in polyfunctional ethylenic monomers include water dispersible polyfunctional monomers such as allyl vinyl sulfonate[122] of interest for crosslinking semi-permeable hydrophilic membranes, stereoregular polymers from allyl acrylate[123] and from allyl methacrylate[124].

Related to polyfunctional monomers are polymers containing attached free ethylenic groups which can be reactive in crosslinking or for synthesis of graft copolymers. Drying oils, soluble diene copolymer rubbers, diallyl phthalate prepolymers and unsaturated polyester resins are examples of such commercial polymers. Patent literature shows numerous examples of partially unsaturated prepolymers which proved disappointing especially because of low reactivity in crosslinking. For example, vinyl allyl ether can be cationically polymerized through the vinyl group[125]. The soluble prepolymers only crosslink very slowly with catalysts in air. Polyvinyl acetate has been heated with allyl bromide and NaOH in ketone solution in order to prepare a polyvinyl allyl ether[126].

Polymerization of allene using organometallic catalysts gave polymers of complex structure with some side methylene groups. Polymerization of 1,5-divinyl ethylene oxide through the epoxy groups gave polymers with side vinyl groups[127]. Allyl-containing epoxy resins have been prepared[128].

A number of condensation polymers bearing free allyl groups have been evaluated. Allyl melamine resins cure only slowly in films[129]. Allyl-terminated polyurethane rubbers have been prepared[130]. Allyl phenols have been reacted with formaldehyde to give allyl-substituted phenolic resins[131], and phenol-formaldehyde resins have been allylated but these have had limited success[132]. Allyl phenols have been used for preparation of allyl-substituted phenylene oxide polymers[133].

Unsaturated epoxy compounds have been polymerized to give unsaturated ether polymers. Thus allyl glycidyl ether with alkyl aluminum catalyst in ether gave predominantly polymerization through the epoxy group forming amorphous elastomers[134]. Homopolymers of 1,4-pentadiene monoepoxide gave ether polymers bearing side allyl groups[135]. Allylation of shellac by allyl alcohol has been described[136].

The industrial trend in crosslinking in elastomers is toward heating substantially saturated polymers with high temperature peroxides and polyfunctional allyl monomers and particularly in curing of coatings to the use of other than ethylenic addition reactions. Thus copolymers of N-methylol acrylamide, or copolymers of acrylamide treated with formaldehyde and alcohols to give methylol ether groups, may then be cured in films by condensation reactions. Copolymers of 2-hydroxethyl methacrylate may be cured by esterification cross links or by reaction with formaldehyde condensate resins. Acrylic copolymers containing epoxy or hydroxyl groups along with methacrylic acid groups can be cured by heating through formation of ester crosslinks. Small additions of salts or inorganic acids may accelerate cure.

[119] C. LIEBERMANN and M. KARDOS, Ber. dtsch. chem. Ges. 46 (1912) 1065; cf. A. KRONSTEIN, Ber. dtsch. chem. Ges. 46 (1913) 1812.
[120] F. F. BLICKE, J. Amer. Chem. Soc. 17 (1923) 1562.
[121] S. H. PINNER et al., Plastics (London) 25 (1960) 35; Nature 184 (1959) 1303; J. Appl. Polymer Sci. 3 (1960) 338.
[122] E. J. GOETHALS, J. Polymer Sci. B 4 (1966) 691.
[123] M. DONATI and M. FARINO, Makromol. Chem. 60 (1963) 233.
[124] D. M. WILES and S. BROWNSTEIN, J. Polymer Sci. B 3 (1965) 951.

[125] R. PAUL et al., Bull. Soc. Chim. France 1–2 (1950) 121; Brit. 659,288 (Rhône-Poulenc).
[126] D. K. ALPERN and W. KIMEL, Paint, Varnish & Plastics Div., Amer. Chem. Soc. Meeting, April 1947.
[127] E. L. STOGRYN and A. J. PASSANNANTE, U. S. 3,261,819 and U. S. 3,261,848 (Esso).
[128] R. M. CHRISTENSON and W. C. BEAN, U. S. 2,910,455 (PPG).
[129] P. ZUPPINGER and G. WIDMER, U. S. 2,885,382 (Ciba).
[130] G. X. R. BOUSSU et al., U. S. 3,219,633 (Michelin).
[131] H. YOSHIOKA and M. KAWANO, Japan 3743 (1958); Chem. Abstr. 53 (1958) 5704.
[132] N. G. GAYLORD, U. S. 3,291,770 (Interchemical).
[133] C. J. KURIAN and C. C. PRICE, J. Polymer. Sci. 49 (1961) 267; A. S. HAY, French 1,322,152 (General Electric): Chem. Abstr. 60 (1961) 685.
[134] E. J. VANDENBERG, U. S. 3,065,213 (Hercules).
[135] E. L. STOGRYN and A. J. PASSANNANTE, U. S. 3,261,874 (Esso).
[136] S. V. PUNTAMBEKAR and T. K. VENKATACHALAM, Indian J. Technol. 1/6 (1963) 231–3.