Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymerization of Aliphatic Aldehydes (*1*)

O. Vogl[a]
[a] CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE

To cite this Article Vogl, O.(1967) 'Polymerization of Aliphatic Aldehydes (*1*)', Journal of Macromolecular Science, Part A, 1: 2, 243 — 266
To link to this Article: DOI: 10.1080/10601326708053969
URL: http://dx.doi.org/10.1080/10601326708053969

J. MACROMOL. SCI. (CHEM.), A1(2), 243–266 (1967)

Polymerization of Aliphatic Aldehydes (*1*)

O. VOGL
CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE

Synopsis

Polyacetals of higher aliphatic aldehydes have been prepared as amorphous, elastomeric polymers and as crystalline, isotactic polymers. They are prepared by solution polymerization or bulk polymerization with appropriate cationic and anionic initiators at low temperature. The polyaldehydes obtained are thermally unstable and must be end-capped.

Aliphatic aldehydes with such functional groups as alkoxy, cyano, vinyl, and epoxy that do not interfere with the polymerizations have also been polymerized. Glutaraldehyde and succinaldehyde have been cyclopolymerized to polyacetals consisting almost completely of pyrane and tetrahydrofuran rings. Copolymerization of higher aldehydes with other aldehydes, such as *n*-butyraldehyde with isobutyraldehyde or acetaldehyde with formaldehyde, have been described. Copolymers with comonomers other than aldehydes, namely with isocyanates, have recently been reported.

The polymerization of the higher aliphatic aldehydes has many characteristics and problems in common with formaldehyde polymerization. The most notable difference is the lower thermal stability of the higher-aldehyde polymers. This difference is attributable to the electron-releasing tendency of the alkyl group on the carbonyl carbon of the higher aldehydes. This causes the carbonyl carbon to have a relatively higher electron density (less positive), and consequently the polarization of the carbonyl group is less pronounced than it is in the case of formaldehyde. This difference in the degree of polarization is reflected in the carbonyl stretching frequency of the aldehydes (2,3). Formaldehyde has a carbonyl frequency of 1755 cm^{-1}, as compared with 1740 cm^{-1} for higher aldehydes in the gas phase.

In terms of polymerizability this means that, although formaldehyde can be polymerized with weak nucleophiles or electrophiles, it takes strong acids and bases to polymerize higher aliphatic aldehydes (2,3).

Aliphatic aldehydes, much more than formaldehyde, are subject to the effect of ceiling temperature (4). The best value for the ceiling temperature (T_C) of formaldehyde is about 120°C. For *n*-butyraldehyde the T_C has been determined to be −16°C. The T_C is related to the heat of polymerization by the following equation:

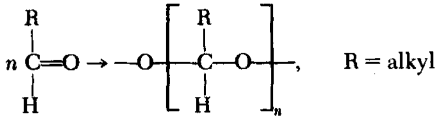
$$T_C = \frac{\Delta H_{\mathrm{polym}}}{\Delta S_{\mathrm{polym}}}$$

The entropy of polymerization for most polymerizations is quite constant at 25 to 30 eu/°C. Consequently, T_C is mainly influenced by the enthalpy ($\Delta H_{\mathrm{polym}}$) of polymerization. In the case of acetaldehyde $\Delta H_{\mathrm{polym}}$ has been estimated from the combustion data of paraldehyde to be 7 kcal/mole (2). This value of T_C does not decrease very much with the increase of the side chain; the T_C of *n*-butyraldehyde polymerization is substantially the same as the T_C of acetaldehyde.

Now that the thermodynamic data on aldehyde polymerization are known and, particularly, that the T_C of aliphatic aldehyde polymers is known to be below room temperature, it is not surprising that these polymers have not been isolated until a few years ago (5).

Recent breakthroughs in aldehyde polymerizations have created wide interest among polymer chemists. Several laboratories are now working on the different aspects of aldehyde polymerization, stereoregularity of aldehyde polymerization, optically active aldehyde polymers, copolymerization, cyclopolymerization, and the structure of these polymers.

The first higher-aldehyde polymers were prepared by subjecting *n*-butyraldehyde, isobutyraldehyde, and *n*-valeraldehyde to high pressures. Conant et al. (6–8) and Novak and Whalley (9) found that these aldehydes were transformed at 1000 atm into viscous oils and waxy solids, which depolymerized to monomer at room temperature within a few hours:



$$n\,\underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}}{=}\mathrm{O} \rightarrow -\mathrm{O}\left[\underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}}-\mathrm{O}\right]_n-, \qquad \mathrm{R} = \text{alkyl}$$

Several years later Letort (*10*) and Travers (*11*) found, independently, that a rubbery elastomer was produced when acetaldehyde was frozen and then allowed to melt. It was initially thought that this "crystallization polymerization" was a special kind of polymerization. It is now apparent (*12*) that the "crystallization polymerization" of acetaldehyde is one example of cationic polymerization. It is still useful for the production of pure polyacetaldehyde of very high molecular weight.

Staudinger (*13*) suggested that this polyacetaldehyde was a polyacetal. This was later confirmed by an infrared study (*14*); see Fig. 1. Polyacetaldehyde was found to revert readily back to monomer even at room temperature. X-ray studies showed polyacetaldehyde to be amorphous (*15*).

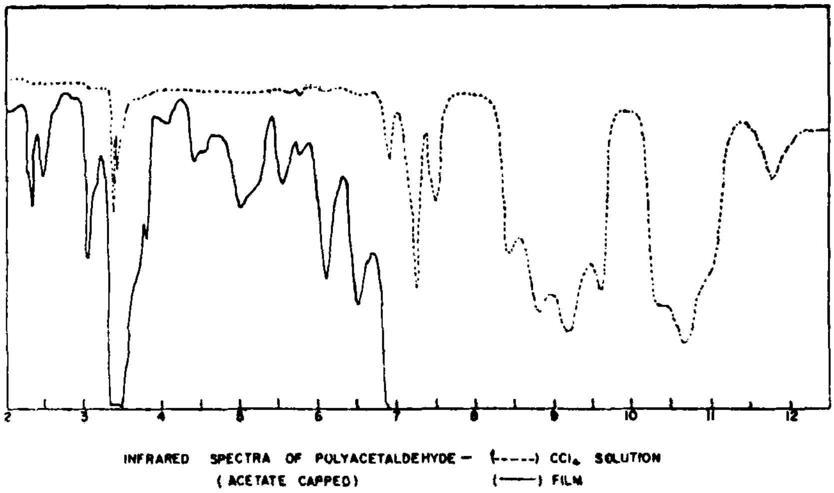


FIG. 1. Infrared spectra of polyacetaldehyde (acetate-capped): (---) CCl_4 solution; (—) film.

The mechanism of the acetaldehyde polymerization was initially thought to be a radical polymerization (*16*) that was fortuitously aided by the crystalline state of the monomer (*17*). The melting of the crystalline acetaldehyde was thought be responsible for the polymerization. It has now been established that this acetaldehyde polymerization is cationic and that acetaldehyde can be polymerized not only in the crystalline state but in the liquid state or in solution (*18*).

As a consequence of Natta's concept of stereoregularity (*19*) in polymers, based on his investigations of polypropylene, it was recognized that aldehydes should also be capable of producing stereoregular polymers (*20*). Studies of aldehyde polymerizations have led to the preparation of isotactic polyaldehydes (*20–23*). It was also found that the common elastomeric polyacetaldehyde (*18*) was "atactic." Its tacticity was determined independently by two laboratories (*24,25*). In recent reviews (*26,27*) it was found convenient to discuss polymers of higher aliphatic aldehydes on the basis of their structure and properties. They were classified into elastomeric, atactic, and isotactic polyaldehydes. This time the discussion of higher-aldehyde polymerization will be divided on the basis of the mechanism of polymer formation into cationic polymerization and anionic polymerization of higher aldehydes. Overlapping cannot be avoided in either classification.

CATIONIC POLYMERIZATION

Several years ago a generalization was made in the classification of higher-aldehyde polymerization (*5*). It was postulated that cationic initiation should give "atactic" polymer and that anionic polymerizations should give isotactic polyaldehydes. Additional studies of higher-aldehyde polymerization (*18*) have shown that this rule is still valid as a guide line, but some exceptions have been found. The determination of the structure of the atactic acetaldehyde polymer has also added to the understanding of the polymer formation. Acetaldehyde is the most important higher aldehyde, and its polymerization the most extensively studied.

If acetaldehyde is treated at room temperature with a strong acid such as sulfuric acid, a highly exothermic reaction sets in with the formation of the trimer, paraldehyde. This is an equilibrium reaction, and the equilibrium consists at room temperature of 88% paraldehyde and 12% acetaldehyde (*28*). If the initial reaction temperature is −10 to −30°C, in addition to the trimer the tetramer metaldehyde is formed in amounts of 5 to 10%. At −40°C and below polyacetaldehyde can be formed. Careful control of the temperature is essential, and no local temperature rise must take place; otherwise, trimerization cannot be avoided. At lower polymerization temperatures, −80 to −120°C, only the polymer is formed.

The effective reaction temperature can be controlled by various simple techniques: (a) activity of the initiator, (b) dielectric constant of the solvent, (c) concentration of monomer, and (d) initial temperature. A selection of the appropriate reaction variables controls the kind of product and the molecular weight of the polymer obtained. For example, BF_3 initiation gives paraldehyde even at −80°C, if ether is used as solvent, but a high yield of high-molecular-weight polyacetaldehyde is obtained with BF_3 in ethylene as solvent (b.p., −104°C). HCl, on the other hand, a much less active initiator, gives polyacetaldehyde of moderate molecular weight even in ether at−78°C. A list of moderately active, typical cationic initiators that give polyacetaldehyde in ether are given in Table 1.

TABLE 1

Acetaldehyde Polymerization with Cationic Initiators[a]

Initiator	Monomer concn., w-%	Results
CF_3COOH,CCl_3COOH, HCl,HNO_3, H_3PO_4, $AsCl_3$,AsF_3,SbF_3,$AlCl_3$, $ZnCl_2$,$ZrCl_4$	0.1–0.5	>75% polymer
H_2SO_4,BF_3,$SnCl_4$, $TiCl_4$,$SbCl_3$,$FeCl_3$, PCl_3	0.05–0.2	Paraldehyde

[a] Solvent, ether; initial reaction temperature, −65°C; reaction time, 5 hr.

During the years a number of initiators have been reported for acetaldehyde polymerization and have been identified as cationic initiators (*22*).

γ-Alumina (*29*), silica (*30–32*), and a number of metal oxides (*30*) are good initiators for the acetaldehyde polymerization. They are particularly effective when acetaldehyde is condensed onto these solid initiators from the gas phase, and polyacetaldehyde of very high molecular weight is produced. When liquid acetaldehyde is used, very poor yields of polyacetaldehyde are obtained. It was suggested that electron-deficient lattice defects provided the actual cationic initiators. This is reasonable since very accurate calcination conditions had to be followed to give efficient initiators (Table 2).

TABLE 2

Polymerization of Acetaldehyde by Alumina (*30*)
(acetaldehyde 15 ml; alumina 5 g)

Alumina					
Origin	Calcination temp., °C	Water content, %	Polymerization[a] time, hr	Conversion, %	Inherent viscosity $[\eta]^b$
A[c]	200	20.3	43	0	—
A	400	3.6	43	49	7.1
A	600	1.4	43	55	7.2
A	800	0.5	43	91	5.4
A	1000	0.2	43	76	6.6
A	1150	0.0	43	8	0.03
B[d]	—[e]	13.5	65	23	3.9
B	600	1.6	65	66	2.4
B	1000	0.2	43	57	4.3

[a] Polymerization temperature, −70°C.
[b] In 2-butanone at 27°C.
[c] Prepared by hydrolysis of aluminum isopropoxide.
[d] Commercial alumina (8 to 14 mesh).
[e] Commercial alumina used without calcination.

The efficiency of some of these initiators could be improved by the addition of certain acids, which by themselves are initiators of acetaldehyde polymerization. For example, γ-alumina or silica initiation is enhanced by the addition of HCl, BF_3, or CF_3COOH (*27*).

TABLE 3

Acetaldehyde Polymerization in the Presence
of Cationically Activated Initiator Mixtures (*32*)
(silica gel modified with various organic polymers)[a]

Additive	Yield, %	Solution viscosity $[\eta]$
Polyoxymethylene	53	9.7
Polypropylene	61	8.9
Polyvinyl chloride	68	5.6
Polyoxymethylene[b]	42	3.4

[a] Weight ratio of silica gel to polymers is 1:2.5; polymerization temperature, −70°; polymerization time, 15 hr. Activated with 0.5 cm^3 of BF_3 (gas).
[b] With alumina.

Additional improvement of acetaldehyde polymerization was reported when γ-alumina and BF_3 were combined with some polymers, notably polyformaldehyde (*32*); see Table 3.

All these initiator combinations gave polyacetaldehyde of very high molecular weight. This is important, because other solid initiators, which are discussed below, gave polymer of very low molecular weight ($MW=10^4$)

TABLE 4

Polymerization of Acetaldehyde with Various Metal Sulfates[a] (*33*)

Metal salt	Calcination[b] temp.,[c] °C	Conversion,[d] %
$ZnSO_4 \cdot 7H_2O$	100	7.9
$NiSO_4 \cdot 7H_2O$	350	18.3
$MnSO_4 \cdot 7H_2O$	100	1.4
$MgSO_4 \cdot 7H_2O$	230	1.3
$CuSO_4 \cdot 5H_2O$	230	64.9
$FeSO_4 \cdot 7H_2O$	230	68.0
$CuSO_4 \cdot 2H_2O$	230	0.9
$Na_2SO_4 \cdot 10H_2O$	Up to 350	0

[a] Initiator 1%, temperature −78°, time 20 hr.
[b] Calcination was carried out for 4 hr.
[c] The calcination temperature giving the higher yield of polymers is reported.
[d] The DP of these polymers ranged from 300 to 800.

Japanese workers have reported that certain neutral sulfates are effective initiators of the acetaldehyde polymerization (*33*). $CuSO_4$ and $NiSO_4$ were particularly useful; in these cases careful calcination of the solid initiator was important (Table 4). Better polymer yields were obtained with inorganic sulfates, which contain excess sulfuric acid (*34*); see Table 5. This indicated clearly the cationic nature of these acetaldehyde polymerizations. The solid, insoluble initiators seem to allow the controlled formation of the polymer rather than the trimerization to paraldehyde. When the same amount of sulfuric acid was used for the solution polymerization of acetaldehyde, only paraldehyde was obtained.

Several forms of phosphoric acid and acid phosphate have also been reported to be effective initiators of acetaldehyde polymerization (*35*). Trialkyl phosphines also initiate acetaldehyde to give the elastomeric polymer (*36*).

TABLE 5
Polymerization of Acetaldehyde with Various Metal Sulfate-Sulfuric Acid Complexes (34)
(initiator 0.5%; temp. −78°; time, 20 hr)

Metal salt	Composition of the complex (metal sulfate-*m* $H_2SO_4 \cdot n\ H_2O$) *m*	*n*	Conversion, %	DP
$CuSO_4$	0.003	0.20	65.7	1750
$SnSO_4$	0.20	0.30	61.4	600
$MgSO_4$	0.66	1.58	66.7	685
$ZnSO_4$	0.05	1.16	63.2	5040
$Al_2(SO_4)_3$	0.81	2.17	75.1	1780
$Fe_2(SO_4)_3$	0.39	1.48	67.9	720
$SnSO_4$	0.34	0.90	46.7	430
$MnSO_4$	0.55	1.02	32.8	580
$NiSO_4$	0.03	1.12	6.4	620

A special class of compounds that are "amphoteric" initiators are organoaluminum compounds (38,39). The nature of their initiation is not certain but can be deduced from the type of polyaldehyde formed. Trialkylaluminum was reacted with acetaldehyde at −78°C (37) (Fig. 2), and the polymerization was allowed to proceed. A typical "atactic" polyacetaldehyde was produced. In a separate experiment a molar amount of acetaldehyde was allowed to react with trialkylaluminum at room temperature,

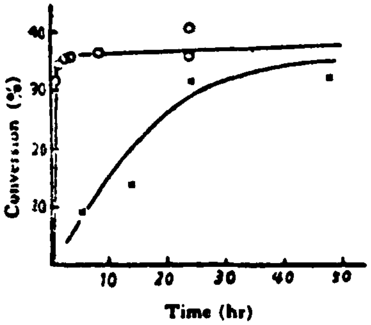


FIG. 2. Rate of acetaldehyde polymerization with $AlEt_3$ as initiator at two different mixing temperatures (37): O, catalyst addition at 20°C; ×, catalyst addition at −78°C. Charge, *n*-hexane 30 cm^3; acetaldehyde, 0.227 mole; $AlEt_3$, 0.00439 mole (37).

and this mixture was cooled to −78°C. A substantial amount of the crystalline polymer was formed. The former polymerization appears to be cationic; the latter, anionic or, as Furukawa called it (*40*), coordinative anionic.

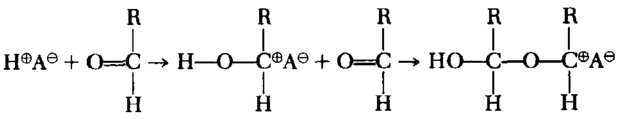
Furukawa et al. (*41,42*) have recently shown that dialkylaluminum chloride polymerizes acetaldehyde in a typical cationic way.

The polyacetaldehyde discussed thus far has been the "atactic" elastomeric polymer. If BF_3–etherate is used as initiator in ethylene as solvent and is allowed to crystallize from solution (*18*) prior to the addition of acetaldehyde, a small amount of crystalline, insoluble polyacetaldehyde is formed in addition to the "atactic" polymer. Crystalline polyacetaldehyde was later reported in polymerizations of acetaldehyde with CF_3COOH-treated γ-alumina as initiator.

Stereoregularity in cationic aldehyde polymerization plays a rather unimportant role in acetaldehyde polymerization (*18*). If the side chain becomes more bulky, as in the case of *n*-butyraldehyde, the portion of stereoregular isotactic polymer becomes substantial, as demonstrated in the polymerization of *n*-butyraldehyde with $SnBr_4$ as initiator. Nearly 25% of the total polymer was crystalline, and even the extractable polymer was partially crystalline.

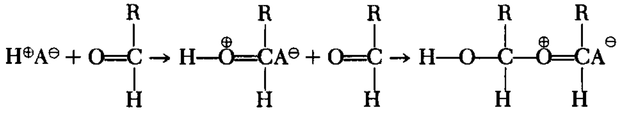
MECHANISM OF CATIONIC ALDEHYDE POLYMERIZATIONS

Several mechanisms of cationic aldehyde polymerization have been proposed in the last few years (*18*). The polymerization of aldehydes with Lewis acids is still not well worked out but is based on analogies. Aldehyde polymerization with protic acids appears to be simpler and is assumed to proceed as indicated



$$H^{\oplus}A^{\ominus} + O{=}\overset{\displaystyle R}{\underset{\displaystyle H}{C}} \rightarrow H{-}O{-}\overset{\displaystyle R}{\underset{\displaystyle H}{C}}{}^{\oplus}A^{\ominus} + O{=}\overset{\displaystyle R}{\underset{\displaystyle H}{C}} \rightarrow HO{-}\overset{\displaystyle R}{\underset{\displaystyle H}{C}}{-}O{-}\overset{\displaystyle R}{\underset{\displaystyle H}{C}}{}^{\oplus}A^{\ominus} \qquad (1)$$

in Eq. (1). Initiation consists of electrophilic attack of the proton on the carbonyl oxygen of monomeric acetaldehyde. Propagation proceeds by continuation of electrophilic attack of a carbonium ion on the carbonyl oxygen of monomeric aldehyde to form a new carbonium ion, which is capable of further growth. This mechanism does not seem to take into account the latest results in oxide polymerization, particularly tetrahydrofuran polymerization. Consequently, a modified mechanism, which parallels the tetrahydrofuran mechanism, is proposed for the aldehyde polymerization [Eq. (2)].



$$H^{\oplus}A^{\ominus} + O{=}\overset{R}{\underset{H}{C}} \rightarrow H{-}\overset{\oplus}{O}{=}\overset{R}{\underset{H}{C}}A^{\ominus} + O{=}\overset{R}{\underset{H}{C}} \rightarrow H{-}O{-}\overset{R}{\underset{H}{C}}{-}\overset{\oplus}{O}{=}\overset{R}{\underset{H}{C}}A^{\ominus} \qquad (2)$$

An oxonium, not a carbonium, ion is the carrier of the positive charge of growing cationic charge. The propagation occurs by nucleophylic attack of the carbonyl oxygen of the aldehyde monomer on the electrophilic terminal carbon next to the oxonium ion. This propagation forms a new oxonium ion, which can again be attacked on the terminal carbon atom by the nucleophilic part of the aldehyde molecule.

ANIONIC POLYMERIZATIONS

Anionic polymerization also produces polymers of higher aldehydes if the polymerization is carried out at low temperatures (*5*) (Table 6). As was indicated before, relatively strong bases are needed for this polymerization. For example, alkali metal alkoxides, soluble hydrides, such as lithium aluminum hydride, organometal compounds, such as butyllithium, and Grignard compounds (Table 6) must be used as initiators (*20*). Tertiary amines, quarternary ammonium salts, and even quarternary ammonium alkoxides, do not initiate higher aldehyde polymerizations (*20*). It has not yet been established that the polymerization does not occur because these initiators do not initiate or because propagation cannot proceed with quarternary gegenions.

Anionic aldehyde polymerization is different from cationic polymerization, in that the cyclic trimer is not formed under these conditions. In fact, no side reaction occurs under the polymerization conditions in hydrocarbon solvents, even at room temperature. At higher temperatures (boiling xylene), the Tishchenko reaction, a hydride transfer reaction of the aldehyde dimer to form the ester, is the predominant reaction with aluminum alkyls and

TABLE 6

Polymerization of Aldehydes to Crystalline Isotactic Polymers[a] (*20*)

Aldehyde	Yield[b]
Acetaldehyde	++
Propionaldehyde	+++
n-Butyraldehyde	+++
Isobutyraldehyde	+++
n-Valeraldehyde	+++
n-Heptaldehyde	+++
n-Octaldehyde	++
Chloral	+++
3-H-Perfluoro-propionaldehyde	+++
Phenylacetaldehyde	+++
3-Methoxy-propionaldehyde	+++
Cyclohexaldehyde	++

[a] Initial reaction temperature, −75°; initiator, potassium triphenylmethoxide; solvent, propylene; solvent monomer ratio, 4:1.

[b] +++ = good yield; ++ = ≈ 50% yield.

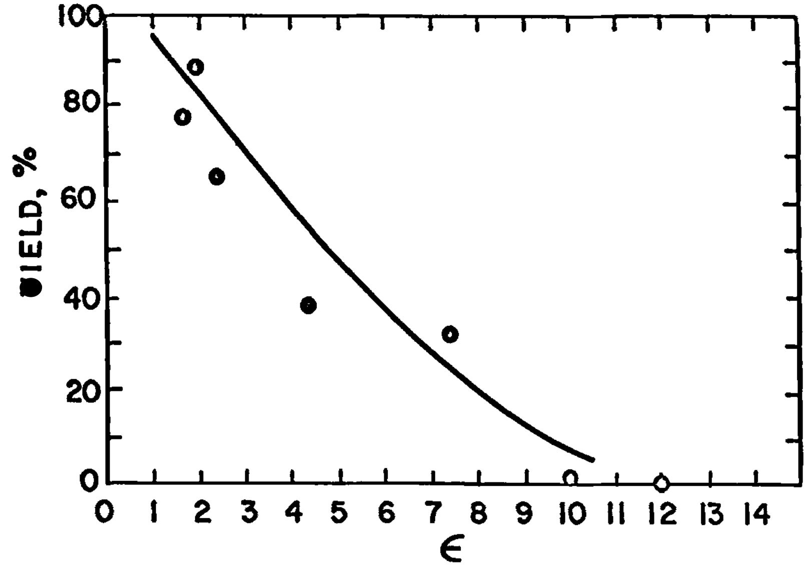


FIG. 3. Influence of the dielectric constant ε of various solvents upon the polymerization of *n*-butyraldehyde. Initial reaction temperature, −75°; time, 1/2 hr; initiator, potassium triphenylmethoxide, 0.14 mole-%; solvent, *n*-butyraldehyde, ratio 4:1.

butyllithium. In the case of acetaldehyde ethyl acetate is the major reaction product.

Solvents also affect the anionic aldehyde polymerization, because they change the position of the monomer/polymer equilibrium. Figure 3 shows the influence of some solvents on the anionic higher-aldehyde polymerization. It can be seen that solvents of low dielectric constant gave the highest yield of aldehyde polymer. Solvents of higher dielectric constants, particularly solvents of higher complexing power, such as ether, are rather poor solvents for the aldehyde polymerization. Solvents of even higher dielectric constant and protic solvents prevent aldehyde polymerization.

At the proper temperature, the polymerization of aldehydes (for example, *n*-butyraldehyde) is fast; it is essentially complete in 5 min. Only a small amount of diffusion-controlled polymerization occurs after 10 min, and for practical purposes the equilibrium is reached. When polymerizations are carried out at various temperatures, it can be shown that no polymer is obtained above −18°C (Fig. 4). This temperature agrees well with the ceiling temperature, which was estimated for the polymerization of higher aliphatic aldehydes.

Higher aldehydes, when polymerized with anionic initiators, give a crystalline, insoluble polymer, in contrast to the polymers obtained by cationic polymers, which are amorphous, elastomeric, and soluble. This statement should be qualified, however, because the size and bulkiness of the aldehyde side chain determines the portion of the polymer which consists of the crystalline, insoluble fraction. For example, when acetaldehyde is polymerized with potassium triphenyl methoxide under standard conditions, the acetaldehyde polymer is opaque, somewhat sticky, and tacky. It can be extracted with acetone, leaving 45% of crystalline polymer. The soluble portion, again, can be fractionated into fractions of higher and lower crystallinity. The most soluble, amorphous fraction is sticky and of relatively low molecular weight (4×10^4).[*] By contrast, polymerizations with cationic initiators give soluble

---

[*] It is interesting to note that polymerization of acetaldehyde under the same conditions with more active initiators, such as butyllithium, actually gave a polyacetaldehyde that is almost completely soluble and of low molecular weight. The reason for this decrease in stereoregularity is not known, but it is probably due to a local temperature increase.

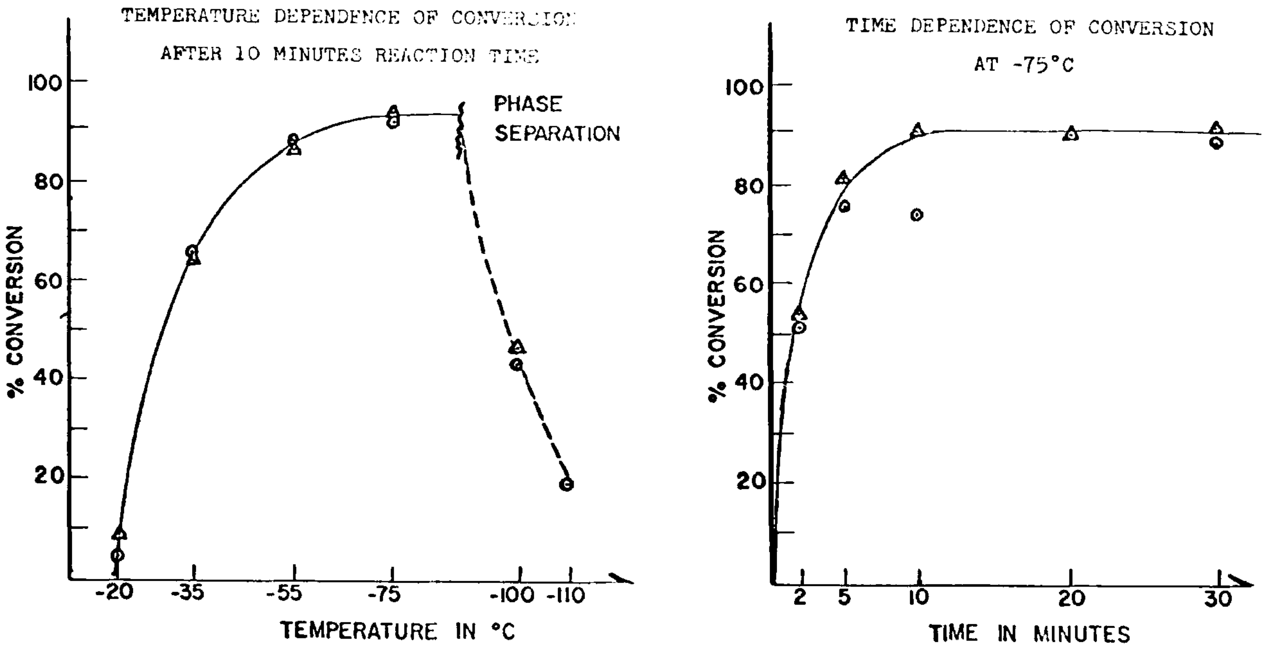


FIG. 4. Conversion in *n*-butyraldehyde polymerization, potassium triphenylmethoxide (0.2 mole-%) as initiator in 25% pentane solutions. △, by gas chromatography; ○, isolated and weighed (*20*).

and usually very high-molecular-weight polyacetaldehyde. A trace of crystalline, insoluble polymer was obtained on rare occasions.

Polymers of aliphatic aldehydes with a longer side chain, such as *n*-butyraldehyde, isobutyraldehyde, and *n*-heptaldehyde, gave polymers that had no soluble fraction when potassium triphenyl methoxide was used as initiator. Cationic polymerization gave in many cases polymers whose insoluble fraction was 10 to 20% (*n*-butyraldehyde with $SnBr_4$ as initiator), but in some cases no insoluble fraction was obtained.

The nature of the alkali metal gegenion plays an important role in the stereoregularity of the polymerization of some olefins, such as styrene and butadiene (*45*). It was therefore interesting to see how different cations influence the stereoregularity of the higher-aldehyde polymerization (Table 7). This case was studied with *n*-butyraldehyde as the monomer. Triphenyl methoxides were prepared from the lithium, sodium, potassium, and cesium metals (*20*). Although the lithium and cesium compounds were not very soluble in toluene, their activity as initiators was

TABLE 7
Alkali-Metal Initiators for Aldehyde Polymerization[a]

Anion	Lithium	Sodium	Potassium	Cesium
Methoxide	x(O)	x(O)	—	—
Ethoxide	x	—	—	—
Isopropoxide	x	x	—	—
n-Butoxide	x	—	—	—
sec-Butoxide	x	x	x	—
tert-Butoxide	x	x	x	—
Cyclohexoxide	—	x	x	—
Benzoxide	—	x	x	—
Diphenyl methoxide	—	x	x	—
Triphenyl methoxide	x	x	x	x
Phenoxide	—	x(O)	—	—
Benzophenone ketyl	—	x	x	—
Dimethyl formamide	—	x	x	—
Acetylacetonate	—	—	x	—
Butyl	x	—	—	—
Alkali metal	x	x	x	—

[a] Key: x, used as initiator, polymerization occurred; x(O), used as initiator, no polymerization; —, was not prepared (*20*).

qualitatively the same as the soluble sodium and potassium salts. With all four initiators the poly-*n*-butyraldehydes obtained had the same high crystallinity, and all four polybutyraldehyde samples did not have a soluble fraction.

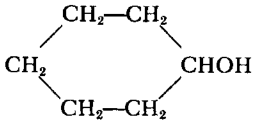
As discussed in the case of cationic polymerization, the polymerization of higher aldehydes give crystalline polymers with organoaluminum compounds under conditions that seem to favor anionic polymerization. Furukawa and his school (*41,42*) have greatly contributed to the understanding of the polymerization of acetaldehyde with organoaluminum compounds.

It should be pointed out that the polymerization of aldehydes with organoaluminum compounds (*43*) proceeds in hours, rather than in minutes as in the case of alkali metal alkoxides (*44*).

It has been found that organoaluminum compounds with one small alkoxy group, such as —OCH_3, in Et_2AlOMe produce a

TABLE 8

Polymerization of Acetaldehyde by Triethylaluminum–Alcohol Systems[a] (*46*)

	Polymer	
Alcohol	Yield, %	Insoluble fraction, %[b]
None[c]	39	15
CH_3CH_2OH	36	14
$CH_3(CH_2)_2OH$	59	22
$CH_3(CH_2)_3OH$	45	22
$CH_3(CH_2)_7OH$	44	34
$(CH_3)_2CHCH_2OH$	35	29
$(CH_3)_2CHOH$	75	78
$CH_3CH_2CH(CH_3)OH$	62	79
	29	45
$(CH_3)_3COH$	14	86

[a] Reaction conditions: CH_3CHO, 0.25 mole; $Al(C_2H_5)_3$ and alcohol, each 0.0025 mole; *n*-hexane, 20 ml; polymerization at −78°C for 44 hr.

[b] Percentage of the methanol-insoluble fraction based on the total polymer.

[c] Polymerization by $Al(C_2H_5)_3$ alone.

small amount of crystalline polyacetaldehyde. As the size and the bulkiness and the number of the alkoxy groups increases, the stereoregularity of the resulting polyacetaldehyde made with these initiators increases (*46*) (Table 8).

Similar results were also obtained by Tani et al. (*47–49*), who reacted triethylaluminum with aromatic amines, amides, and ketones. Polyacetaldehyde with high stereoregularity was obtained with 1:2 reaction products of Et_3Al with these compounds.

It has also been found that RAlOR′Cl (*50*) and Ziegler-type initiators from Et_3Al and $TiCl_4$ (*26*) gave almost completely crystalline polyaldehydes.

It should be pointed out, however, that great care must be taken in working with polymers made with organoaluminum compounds. Aluminum compounds are retained obstinately by

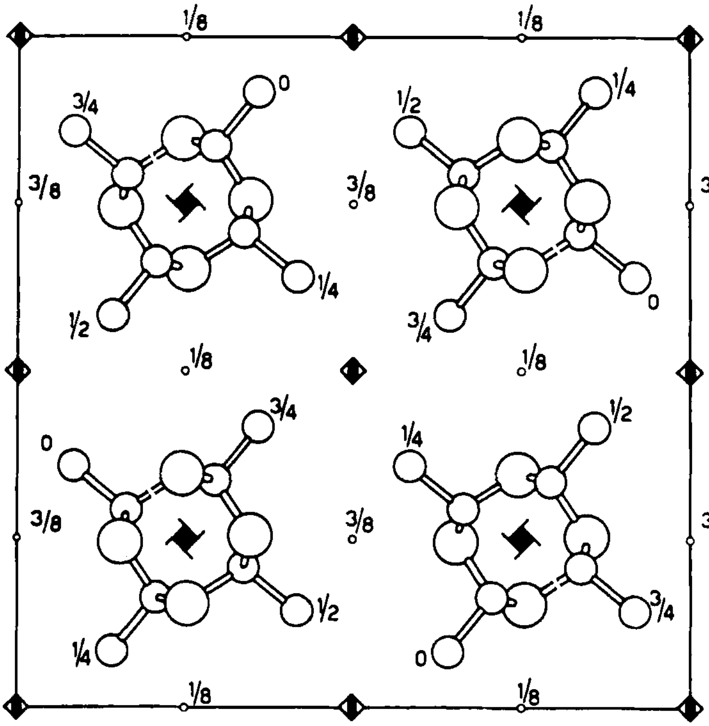


FIG. 5. Model of isotactic polyacetaldehyde. Projection on (001). [From J. Furukawa and T. Saegusa, *Polymerization of Aldehydes and Oxides*, Wiley (Interscience), New York, 1963.]

aldehyde polymers and must be removed; otherwise, it is not proper to call these polymers true aldehyde polymers. High melting point with decomposition and insolubility of the polymers, especially in the case of a low-yield polymerization, should be taken with great caution.

It was early recognized that in the polymerization of higher aldehydes a new asymmetric center was formed at the addition of each new monomer unit. Polyacetals should, therefore, be capable of existing in stereoregular forms similar to the stereoregularity in polyolefins. It appeared probable that the crystalline polyaldehydes were the stereoregular form of the higher polyaldehydes (*21*).

Natta and his school (*51*,*52*) have shown that this is the case. They have shown by elegant x-ray studies that crystalline polyaldehydes are the isotactic polymers of higher aldehydes (Fig. 5).

No syndiotactic polyaldehyde has yet been prepared or isolated. When polymerizations were carried out under conditions that would favor the formation of syndiotactic polymer, namely in solvents of higher dissociating power for the growing ion pairs on the chain end, no polymer was obtained with anionic initiators. Only trimers were obtained with cationic initiators. Low-temperature free-radical polymerization, another technique for the preparation of syndiotactic vinyl polymers, is ineffective in aldehyde poly-

TABLE 9

Melting Points and Crystal Structure of Crystalline Isotactic Polyaldehydes

Monomer	Polyaldehyde m.p., °C.	Monomer units per repeat unit	Identity period, A
CH_3CHO	165[a] (decomp.), 180[b] (decomp.)	4_1	4.8[d]
$CH_3(CH_2)_2CHO$	225[a] (decomp.)	4_1	4.8[d]
$CH_3(CH_2)_3CHO$	155 (85)[a]	—	—
$CH_3(CH_2)_5CHO$	150 (75)[a]	—	—
$CH_3(CH_2)_6CHO$	35[a]	—	—
$(CH_3)_2CH{\cdot}CHO$	> 260 (decomp.)[a]	4_1	5.2[d]
CH_2O[c]	178	9_5	16.2

[a] (*20*).

[b] M. Letort, private communication (1961).

[c] Added for comparison.

[d] (*52*).

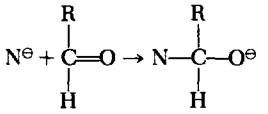
merization, because aldehydes, as far as is known, do not undergo free-radical polymerization.

Isotactic polyacetaldehydes crystallize in a fourfold helix with a repeat distance of 4.8 A. The more bulky polyisobutyraldehyde has a repeat distance of 5.2 A (Table 9). The unit cell contains four monomer chains.

Soluble "atactic" polyacetaldehyde has been studied by high-resolution NMR techniques and was found to be mainly heterotactic but to have excess isotactic linkages. The details of this work will be discussed in another paper.

MECHANISM OF ANIONIC ALDEHYDE POLYMERIZATION

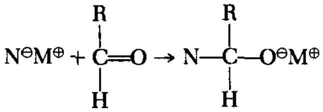
Anionic aldehyde polymerization is initiated by the attack of the nucleophilic initiator on the carbonyl carbon of the aldehyde, forming an alkoxide [Eq. (3)]:



$$N^{\ominus} + \overset{\displaystyle R}{\underset{\displaystyle H}{C}}{=}O \rightarrow N{-}\overset{\displaystyle R}{\underset{\displaystyle H}{C}}{-}O^{\ominus} \qquad (3)$$

where R is an alkyl and N is a nucleophile. Propagation proceeds by the subsequent nucleophilic attack of the alkoxide on a new monomer molecule, forming a new alkoxide. It is, therefore, not necessary to use initiators with a nucleophilicity much higher than that of alkoxides for the initiation of aldehyde polymerization. The actual initiator of anionic aldehyde polymerization is an alkoxide, regardless of the apparent initiator used, and the propagation proceeds via polymeric alkoxides.

All anionic polymerizations of aliphatic aldehydes seem to proceed by an ion-pair mechanism and to have a definite gegenion:



$$N^{\ominus}M^{\oplus} + \overset{\displaystyle R}{\underset{\displaystyle H}{C}}{=}O \rightarrow N{-}\overset{\displaystyle R}{\underset{\displaystyle H}{C}}{-}O^{\ominus}M^{\oplus}$$

where R is an alkyl, N is a nucleophile, and M is a metal. Several detailed mechanisms have been proposed in the last few years.

They should be mentioned here without being discussed in detail. One mechanism (*3,4*) takes into account the fact that polymers precipitate from the solution and that alkali metal cations are the counterions. It suggests that the stereoregular polymerization of the aldehyde forms the isotactic helix directly. Monomer is coordinated by the gegenion, and more than one monomer (probably two) are involved in the transition state. This mechanism does not account for the possible association of the alkali cation with other initiator molecules, forming such ionic associates as are known for lithium *tert*-butyl and lithium *tert*-butoxide (*17*) in solution $[Li^+(Li_3R_4)^-]$.

Another mechanism (*42*), specifically for organoaluminum initiation of aldehyde polymerization, claims a Meerwein complex as the transition state of polymerization. This mechanism is similar to the mechanism which was proposed for the Meerwein-Ponndorff reduction and Oppenauer oxidation and is a coordination-type insertion mechanism.

A variation of this mechanism (*40*) tries to explain the stereoregularity of the aldehyde polymerization by suggesting that a multicenter metal cation is involved in bringing about the proper stereoregular placement of the monomer. This mechanism is particularly favored for aluminum and zinc organic compounds as initiators. It does not take into account the stereochemistry of the already formed polymer chain and the structure of the monomer solution around the growing chain.

It is very important that the structure of the solution in close proximity to the growing ends and the solvation of the transition state of polymerization receive adequate attention in discussions of stereoselective polymerization mechanisms.

STABILITY OF HIGHER-ALDEHYDE POLYMERS

Compared to hydrocarbon polymers, polyaldehydes are very unstable and revert to monomer rather easily (*53–55*). This is caused by the low ceiling temperature of polymerization.

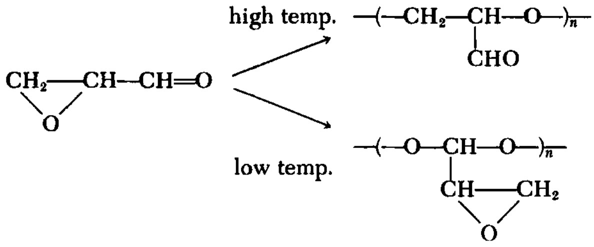
The stability of higher-aldehyde polymers can be substantially increased by end-capping the polymers. This can be done by converting the unstable hydroxyl and alkoxide ends into stable ether and ester ends. It is not always enough to end-cap the chain ends, because polyaldehydes are very susceptible both to random chain cleavage by acidolysis and to autooxidation. Consequently, antioxidants and thermal stabilizers must also be added for the proper stabilization of polyaldehydes. Capped and stabilized, crystalline polyaldehyde can be brought into solution and the solution properties determined. Solution viscosities have been determined in tetrahydronaphthalene at elevated temperatures, and inherent viscosities of up to 0.85 have been reported for poly-*n*-butyraldehyde (56).

Isotactic polyaldehydes melt with decomposition. The higher members of the polyaldehyde series can be melted without decomposition (Table 9). The lower and branched isotactic polyaldehydes are high-melting, even more high-melting than the corresponding isotactic polyolefins, and sometimes decompose before melting can be observed. A relatively high loading of thermal stabilizer is needed in studies of these polyaldehydes at higher temperatures.

POLYMERS OF FUNCTIONALLY SUBSTITUTED ALDEHYDES

Polymers of higher aldehydes having a hydrocarbon side chain have received the chief attention of most investigators. Certain aldehydes with some functionality in the side chain have also been investigated. Prominent among these investigations is the work of Goodman (57) on optically active aldehyde polymers derived from citronellal. He showed that the optical activity of the monomer is greatly enhanced when it is made into a polymer, and he also showed that this polymer could be depolymerized to the monomer without any loss of optical activity of the monomer.

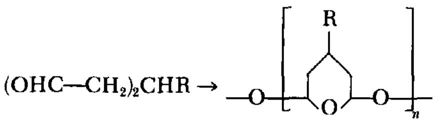
Glycidaldehyde (58) was polymerized to two types of polymer, the polyacetal at low temperature and the polyether at high temperature:



Recently β-cyanopropioaldehyde was successfully polymerized (59). Polyoxymethylenes with a carbon-carbon double bond in the side chain have been prepared. Suberaldehyde has been polymerized (*60*). Poly(vinyl)oxymethylene was obtained (*61*) by treating acrolein with cyanide ion at low temperature. This polymer is a polyacetal, is unstable to acid, and undergoes random cleavage, but, curiously, does not seem to degrade by unzipping of the chain.

DIALDEHYDE POLYMERS

Dialdehydes, particularly glyoxal (*62*), have been known for a long time to give polymers of ill-defined structure. More interesting polymers were obtained from glutaraldehyde (*63,64*) and 3-phenyl (*65*) and 3-methyl-substituted (*66,67*) glutaraldehydes and succinaldehyde (*64*). With both acids and bases these dialdehydes cyclopolymerize to polyacetals containing mainly pyrane or tetrahydrofuran rings:



Normal aldehyde polymerization, which leaves pendent aldehyde groups, occurs besides cyclopolymerization. The amount of free aldehyde groups depends upon the reaction conditions and the initiators used.

COPOLYMERIZATION

Higher aldehydes undergo copolymerization with formaldehyde and with each other. The copolymers with each other may be rubbery or crystalline, depending upon the initiator and the amount of comonomer used. Most of these copolymers are not very well defined. Copolymer compositions usually have been based on chemical analyses and on some spectral evidence obtained from unfractionated products. Therefore, there is no guarantee of homogeneity of the copolymers or even of actual copolymerization.

Formaldehyde–acetaldehyde copolymers (*68,69*) become more rubbery with increasing acetaldehyde content and also show a decrease in thermal stability. Acetaldehyde can be copolymerized by BF_3 initiation with a number of aldehydes to give a modified, elastomeric polyacetaldehyde (*70*).

Attempts have been made to obtain isotactic copolymers. *n*-Butyraldehyde and isobutyraldehyde were copolymerized and gave a crystalline polymer in high yield (3). It is presumably an isotactic copolymer.

Stabilization has been achieved in formaldehyde copolymers by introducing a zipper jammer randomly along the polymer chain. Epoxides and cyclic formals are the favored comonomers.

The successful copolymerization of these comonomers with higher aldehydes has not yet been reported. A recent report indicates, however, that acetaldehyde and other higher aldehydes have been copolymerized with isocyanates (*71*). The incorporation of these urethane linkages is said to have given improvements in thermal stability.

Acknowledgment

I am indebted to Dr. H. C. Miller for many stimulating discussions.

REFERENCES

1. O. Vogl, *Polymer Preprints*, **7**(**1**), 217 (1966).
2. O. Vogl and W. M. D. Bryant, *J. Polymer Sci.*, **A2**, 4633 (1964).
3. O. Vogl and W. M. D. Bryant, *Plastiques*, **2**(3), 224 (1965).
4. F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 331 (1950).
5. O. Vogl, *J. Polymer Sci.*, **46**, 241 (1960).
6. P. W. Bridgeman and J. B. Conant, *Proc. Natl. Acad. Sci. U.S.*, **15**, 680 (1929).
7. J. B. Conant and C. O. Tongberg, *J. Am. Chem. Soc.*, **52**, 1659 (1930).
8. J. B. Conant and W. R. Peterson, *J. Am. Chem. Soc.*, **54**, 628 (1932).
9. A. Novak and E. Whalley, *Can. J. Chem.*, **37**, 1710, 1718 (1959).
10. M. Letort, *Compt. Rend.*, **202**, 767 (1936).
11. M. W. Travers, *Trans. Faraday Soc.*, **32**, 246 (1936).
12. O. Vogl, *Advan. Chem. Ser.*: **52**, 67 (1966).
13. H. Staudinger, *Trans. Faraday Soc.*, **32**, 249 (1936).
14. G. B. B. M. Sutherland, A. R. Philpotts, and G. H. Twigg, *Nature*, **157**, 257 (1946).
15. H. A. Rigby, C. J. Danby, and C. N. Hinshelwood, *J. Chem. Soc.*, **1948**, 234.
16. M. Letort and J. Petry, *J. Chim. Phys.*, **48**, 594 (1951).
17. A. J. Richard, thesis, Nancy, France, 1955.
18. O. Vogl, *J. Polymer Sci.*, **A2**, 4591 (1964).
19. G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, and G. Moraglio, *J. Am. Chem. Soc.*, **77**, 1708 (1955).
20. O. Vogl, *J. Polymer Sci.*, **A2**, 4607 (1964).
21. O. Vogl, Belg. Pat. 580,553 (1959); priority USA, 8/18/58.
22. J. Furukawa, T. Saegusa, T. Tsuruta, and H. Fujii, Fr. Pat. 1,268,322 (1961); priority Japan, 11/6/59.
23. G. Natta, P. Chini, G. Mazzanti, and A. Brizi, Belg. Pat. 597,373 (1961); priority Italy, 11/24/59.

24. E. G. Brame, R. S. Sudol, and O. Vogl, *J. Polymer Sci.*, **A2,** 5337 (1964).
25. J. Brandrup and M. Goodman, *J. Polymer Sci.*, **B2,** 123 (1964).
26. J. Furukawa and T. Saegusa, *Polymerization of Aldehydes and Oxides*, Wiley (Interscience), New York, 1963.
27. O. Vogl in *The Polymer Chemistry of Synthetic Elastomers*, J. Kennedy and E. Tornqvist, eds. in press.
28. R. Hallmann, *Z. Physik. Chem. (Leipzig)*, **43,** 130 (1903).
29. J. Furukawa, T. Saegusa, T. Tsuruta, H. Fujii, and T. Tatano, *J. Polymer Sci.*, **36,** 546 (1959).
30. J. Furukawa, T. Saegusa, T. Tsuruta, H. Fujii, A. Kawasaki, and T. Tatano, *Makromol. Chem.*, **33,** 32 (1960).
31. J. Furukawa, T. Saegusa, T. Tsuruta, H. Fujii, A. Kawasaki, and T. Tatano, *J. Chem. Soc. Japan Ind. Chem. Sect.*, **62,** 1925 (1959).
32. K. Weissermel and W. Schmieder, *Makromol. Chem.*, **51,** 39 (1962).
33. H. Takida and K. Noro, *Chem. High Polymers (Japan)*, **21,** 23, 109 (1964).
34. H. Takida and K. Noro, *Chem. High Polymers (Japan)*, **20,** 705, 712 (1963).
35. T. Miyakawa and N. Yamamoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **65,** 390 (1962).
36. J. N. Koral and B. W. Song, *J. Polymer Sci.*, **54,** S34 (1961).
37. S. Ishida, *J. Polymer Sci.*, **62,** 1 (1962).
38. S. Ohta, T. Saegusa, and J. Furukawa, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **67,** 608 (1964).
39. J. Furukawa, T. Saegusa, and H. Fujii, *Makromol. Chem.*, **44/46,** 398 (1961).
40. J. Furukawa, paper presented at the Gordon Conference on Polymers, New London, N.H., July 1962, and at the meeting on Mechanism of Stereospecificity, Moretonhampstead, Devon, England, May 1962.
41. H. Fujii, I. Tsukuma, T. Saegusa, and J. Furukawa, *Makromol. Chem.*, **82,** 32 (1965).
42. H. Fujii, T. Saegusa, and J. Furukawa, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **65,** 695 (1962).
43. E. J. Vandenberg, U.S. Pat. 3,208,975 (1965).
44. O. Vogl, unpublished results.
45. J. E. Mulvaney, C. G. Overberger, and A. M. Schiller, *Advan. Polymer Sci.*, **3,** 106 (1961).
46. J. Furukawa, T. Saegusa, and H. Fujii, Abstract 94, IUPAC Symposium on Macromolecular Chemistry, Paris 1963.
47. H. Tani and N. Oguni, *J. Polymer Sci.*, **B2,** 123 (1964).
48. H. Tani, T. Aoyagi, and T. Araki, *J. Polymer Sci.*, **B2,** 921 (1964).
49. H. Tani, H. Yasuda, and T. Araki, *J. Polymer Sci.*, **B2,** 933 (1964).
50. G. Mazzanti, private communication, 1962.
51. G. Natta, G. Mazzanti, P. Corradini, P. Chini, and I. W. Bassi, *Atti Accad. Nazl. Lincei Rend. Classe Sci. Fis. Mat. Nat.*, **28,** 8, 18, 284 (1960).
52. G. Natta, P. Corradini, and I. W. Bassi, *J. Polymer Sci.*, **51,** 505 (1960).
53. O. Vogl, *Chem. Ind. (London)*, **1961,** 748.
54. D. L. Funck and O. Vogl, U.S. Pat. 3,001,966 (1961).
55. O. Vogl, Brit. Pat. 894,399 (1962).
56. O. Vogl, *J. Polymer Sci.*, **A2,** 4623 (1964).
57. M. Goodman and A. Abe, *J. Polymer Sci.*, **59,** S 37 (1962).

58. W. J. Sullivan, U.S. Pat. 3,067,174 (1962).
59. H. Sumimoto and K. Kobayashi, *J. Polymer Sci.*, **A1**, *Polymer Chem.*, **4**, 907 (1966).
60. J. N. Koral and E. M. Smolin, *J. Polymer Sci.*, **Al**, 2831 (1963).
61. R. C. Schulz, G. Wegner, and W. Kern, *Angew. Chem.*, **78**, 613 (1966).
62. W. T. Brady and H. R. O'Neal, *J. Polymer Sci.*, **B2**, 649 (1964).
63. C. G. Overberger, S. Ishida, and H. Ringsdorf, *J. Polymer Sci.*, **62**, S1 (1962).
64. W. W. Moyer, Jr., and D. A. Grev, *J. Polymer Sci.*, **B1**, 29 (1963).
65. K. Meyersen, R. C. Schulz, and W. Kern, *Makromol. Chem.*, **58**, 204 (1962).
66. C. Aso and Y. Aito, *Bull. Chem. Soc. Japan*, **35**, 1426 (1962).
67. C. Aso, A. Furuta, and Y. Aito, *Makromol. Chem.*, **84**, 126 (1965).
68. H. F. Mark and N. Ogata, *J. Polymer Sci.*, **A1**, 3439 (1963).
69. M. Letort, *Chim. Ind. (Paris)*, **89**, 155 (1963).
70. Consortium für Electrochemie, Brit. Pat. 876,956 (1961); German Appl. 6/30/59; Fr. Pat. 1,262,179 (1961); Belg. Pat. 592,462 (1960).
71. H. Takida and K. Noro, *Chem. High Polymers (Japan)*, **22**, 463 (1965).

Received by editor September 9, 1966
Submitted for publication September 9, 1966