The lower value of $r_1$ for trans-compared to cis-\(\beta\)-methylstyrene, indicative of a greater reactivity of the former with the \(p\)-chlorostyrene carbonium ion, can be rationalized on the basis of steric inhibition in the cis isomer towards the achievement of coplanarity for stabilization of the incipient carbonium ion in the transition state of the addition reaction. A closely analogous effect, but considerably enhanced, is observed in free-radical copolymerization and explained on this basis in Section 12.2.3.

Absolute propagation rate constants for both self-addition and cross-addition in copolymerization reactions involving several different monomers, each initiated with iodine, have been determined, and the rate constants are listed in Table 14-11.\(^{123}\) Rate constants for self-addition are listed in the diagonal row extending from the top left-hand column to the bottom right-hand column, while all other values in the table are for cross-addition. Within the series of styrene derivatives, the relative reactivity order is identical for both the monomers and the carbonium ions as follows: \(\text{p-OCH}_3 > \text{p-CH}_3 > \text{p-H} > \text{p-Cl}\). The same type of behavior has been observed in the copolymerization of styrene and \(p\)-chlorostyrene in the same solvent initiated by perchloric acid.\(^{195}\) In contrast, for the two alkyl vinyl ethers in Table 14-11, the reactivity orders are opposite for the monomers (isobutyl > 2-chloroethyl) compared to the propagating carbonium ion species (2-chloroethyl > isobutyl). As mentioned in Section 14.A.2.2, the identity in monomer and endgroup-ion reactivity orders for the styrene derivatives is in sharp contrast to the normal observation in free-radical polymerization that, because of resonance stabilization, the more reactive the monomer, the less reactive the radical and vice versa. One rationalization was mentioned in Section 14.A.2.2, and another which has been offered is that the rate controlling step in copolymerization reactions of styrene monomers is not covalent bond formation, but is formation of a complex between the incoming monomer and the endgroup ion pair.\(^{123}\)

### 14.A.5. Stereoregular Polymerization

One of the first stereoregular polymerization reactions, if not the first which was recognized as such, was accomplished by the cationic polymerization of isobutyl vinyl ether initiated with boron trifluoride etherate in liquid propane.\(^{196}\) Schildknecht reported in 1948 that the poly(vinyl isobutyl ether) formed by carrying out this reaction at temperatures of \(-80\) to \(-60^\circ\text{C}\) was crystalline, and the crystallinity was correctly attributed to an ordered arrangement of the alkoxy pendant groups along the polymer chain backbone. It was proposed at the time that the regular arrangement of alkoxy groups consisted of blocks of repeating units of
alternating configurations, now termed a syndiotactic structure, but X-ray
diffraction studies carried out in 1956 indicated that an isotactic structure
was more likely.197

Since 1948, crystalline polymers of many other vinyl ether monomers
have been prepared with the same and other catalysts in both homogeneous
and heterogeneous systems.198,199 In 1949, a cationic polymerization
reaction, also initiated with boron trifluoride etherate, was reported to
yield crystalline polymers of \( \alpha,\rho \)-dimethylstyrne,200 and these results have
since been verified and extended to \( \alpha \)-methylstyrne.201–203 Stannic
chloride initiation was also found to yield crystalline polymers of \( \alpha,\rho \)
dimethylstyrne, but not of \( \alpha \)-methylstyrne. In the \( \text{SnCl}_4 \)-initiated poly-
merization reaction variations in temperature and solvent had little effect
on crystallinity.201

14.4.5.1. Stereoregular Polymerization of Vinyl Ethers

The preparation of crystalline or crystallizable polymers of vinyl ether
monomers by homogeneous cationic polymerization reactions initiated
with \( \text{BF}_3 \cdot 
(\text{C}_2 \text{H}_5)_{n} \) and related catalysts has been extended to the
\( \text{methyl} \),204 isopropyl,205 \( n \)-butyl,205 \( t \)-butyl,206,207 benzyl,208 and tri-
methylsilyl209 vinyl ethers. Both isotactic and syndiotactic polymers can be
prepared from \( t \)-butyl vinyl ether by changing the polarity of the solvent,
indicating that the degree of dissociation of the endgroup ion pair has an
important influence on the stereochemistry of the propagation reaction.210
Nonpolar solvents, which favor both the formation of intimate ion pairs
and monomer–counterion association, are required for isotactic polymer
formation.211 In most cases, the polymerization reaction is carried out at
low temperatures in a nonpolar solvent, although with \( \text{methyl} \) vinyl ether a
crystalline polymer is obtained only in the presence of chloroform.204
Homogeneous stereoregular polymerization of \( n \)-butyl vinyl ether has also
been accomplished at low temperatures with soluble alkyl aluminum
halides such as \( \text{Al} \left( \text{C}_2 \text{H}_5 \right)_{3} \text{Cl} \), \( \text{Al} \left( \text{C}_2 \text{H}_5 \right)_{3} \text{Cl} \), \( \text{Al} \left( \text{C}_2 \text{H}_5 \right) \text{F} \), \( \text{Al} \left( \text{C}_2 \text{H}_5 \right)_{3} \text{Br} \), and
\( \text{Al} \left( \text{OC}_2 \text{H}_5 \right) \text{Cl} \).212–214

Several stereochemical mechanisms have been suggested to account for
the formation of stereoregular vinyl ether polymers. In one, the carboxonium
ion is considered to be in an \( sp^3 \) configuration (14-78) because of coordina-
tion with the counterion, and the monomer molecule enters the reaction
zone along a plane directly above the backbone carbon–carbon bond of the
last repeating unit in the active polymer chain, Reaction (14-78).215,216 To
minimize steric hindrance, the monomer molecule enters from this direc-
tion with an orientation in space such that the alkoxy group on the mon-
mer and the alkoxy group on the active polymer chain endgroup are furthest
away from each other (14-78). Insertion of the monomer between the car-
bonium ion and the counterion in this manner (14-79) results in the forma-
tion of an isotactic placement.

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_2=\text{CH} & \rightarrow \\
\text{CH}_2\text{CH} \text{CH}_3 & \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\end{align*}
\]

(14-78)

(14-79)

Two alternative mechanisms have been proposed in which the carboxonium
ion endgroups on active chains form six-membered ring structures by
coordination of the carboxonium ion with the alkoxy group on the third
repeating unit back along the chain, Reaction (14-80). In one proposed me-

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \text{CH}_2\text{CH}_2 & \rightarrow \\
\text{CH}_2\text{CH} \text{CH}_3 & \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\end{align*}
\]

(14-80)

anism, steric control results from a preferred equatorial configuration of the
alkoxy group of the terminal unit, Reaction (14-80).217 An isotactic place-
ment is formed because the monomer must approach the coordinated
carbonium ion from the rear, which is the axial direction (14-81). In the

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \text{CH}_2\text{CH}_2 & \rightarrow \\
\text{CH}_2\text{CH} \text{CH}_3 & \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\end{align*}
\]

(14-81)

other mechanism involving this type of cyclic intermediate, steric control
is determined by interaction of the counterion with both existing and
newly forming carbonium ions in the transition state, Reaction (14-82).\textsuperscript{198}

The orientation of the monomer and the coordination of the counterion

\[
\text{HCH}_2\text{CH} = \text{CH} + \text{CH}_2\text{=CH} \rightarrow \text{HCH}_2\text{CH} = \text{CH} \quad \text{(14-82)}
\]

with the incipient carbonium ion are believed to lock the existing carbonium ion into a configuration which ultimately results in the formation of an isotactic sequence.

\textbf{14.A.5.2. Optically Active Polymers}

Asymmetric induction has been used to stereoregulate the cationic polymerization of olefin monomers in order to prepare optically active polymers. In these reactions, \textit{asymmetry is induced} in the substituent groups surrounding the backbone carbon atoms by use of \textit{optically active Lewis base cocatalysts} in the formation of the initiator.\textsuperscript{218} Cocatalysts used successfully for this purpose are listed in Table 14-12, but other attempts

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Asymmetric cocatalyst & Polymerization temp., °C & [\eta] \textsuperscript{b} & [\alpha] \textsuperscript{c} \textsuperscript{,} \textdegree \textsuperscript{c} \\
\hline
(-)\beta-Phenylalanine & -75 & 0.6 & -33.1 \\
(-)\beta-Phenylalanine & -75 & 0.75 & -24.1 \\
(+\beta-Phenylalanine & -75 & 0.7 & +13.1 \\
(+10-Camphorsulphonic acid & -75 & 1.4 & -3.8 \\
(+1Tetramethylammonium & -75 & 0.5 & -2.4 \\
10-camphorsulphonate & -100 & 0.2 & +2.8 \\
\hline
\end{tabular}
\caption{Asymmetric Polymerization of Benzo furan\textsuperscript{a}}
\end{table}

\textsuperscript{a} With aluminum monooethyl dichloride.\textsuperscript{218}
\textsuperscript{b} Determined in toluene at 30°C.
\textsuperscript{c} In benzene.

at preparing optically active polymers by this technique using (-)\alpha-methylbenzyl alcohol, tosyl L-valine, and camphor have failed.\textsuperscript{218}

Optically active polymers have been prepared by the cationic polymerization (14-83) of benzo furan because the repeating units in the polymer obtained from this monomer have no plane of symmetry.\textsuperscript{220,221} The effectiveness of an asymmetric counterion in inducing an asymmetric polymerization reaction and in creating active centers in the polymer backbone is shown by the optical rotation data in Table 14-12.\textsuperscript{218} The most effective cocatalyst according to this data is (-)\beta-phenylalanine. The polymers obtained in these reactions are not crystalline, most probably because of the difficulty involved in reorienting the bulky repeating units in the melt or in solution to form a chain conformation capable of crystallizing.

\textbf{PART B: CARBONYL MONOMERS}

Aliphatic aldehydes, acetone, and substituted ketenes can be polymerized by Lewis acids and protionic acids through the carbonyl double bond to form (14-84) high molecular weight polyacetals and polyketals. Much less

\[
\text{nR_1R_2C=O} \rightarrow \text{[C-O-]}_n \quad \text{(14-84)}
\]

is known about the mechanism of these polymerization reactions than for the cationic polymerization of olefin monomers. The first systematic studies in this field were those conducted by Staudinger on formaldehyde in the late 1920's.\textsuperscript{222} These studies were followed most notably by investigations of the apparent solid-state polymerization of crystalline acetaldehyde in 1936.\textsuperscript{223,224} and by studies on the use of high pressure techniques for the polymerization of long chain aliphatic aldehydes in 1930.\textsuperscript{225} Only very recently have procedures been reported for the carbonyl polymerization of acetone\textsuperscript{226} and dimethylketene,\textsuperscript{227} although unsubstantiated reports for both can be found in the literature of many years back.\textsuperscript{228}

\textbf{14.B.1. ALDEHYDES}

\textbf{14.B.1.1. Formaldehyde}

Formaldehyde can be polymerized to high molecular weight polyoxy-methylene at low temperatures in pure liquid form or in solution in inert solvents such as hydrocarbons, ether, or methylene chloride. Protonic