Table 14-10

Steric Effects in Copolymerization of Alkyl Styrene Monomers (M_2) with *p*-Chlorostyrene (M_1)[a]

Substituent in styrene monomer (M_2)	r_1	r_2
α-CH_3	0.35	15
p-CH_3	0.22	4.5
p-C_2H_5	0.29	4.1
Styrene[b]	0.34	2.0
trans-β-CH_3	0.74	0.32
cis-β-CH_3	1.0	0.32
β-C_2H_5	0.88	0

[a] Initiated with $SnCl_4$ in $C_6H_5NO_2$–CCl_4(1:1) solvent mixture at 0°C.[188]

[b] Initiated with $AlBr_3$.

Table 14-11

Absolute Rate Constants in Cationic Copolymerization Reactions[a]

Carbonium ion	Rate constants, liters mole^{-1} min^{-1} for several monomers: *p*-Chlorostyrene	Styrene	*p*-Methylstyrene	*p*-Methoxystyrene	2-Chloroethyl vinyl ether	Isobutyl vinyl ether
p-Chlorostyrene[b]	0.071	0.16	0.37	—	—	—
Styrene[b]	0.088	0.22	1.1	—	0.073	—
p-Methylstyrene[c]	0.88	1.4	5.7	19	1.1	—
p-Methoxystyrene[c]	—	—	82	350	32	—
2-Chloroethyl vinyl ether	—	8.1	6.4	145	290	580
Isobutyl vinyl ether	—	—	—	—	195	390

[a] Initiated with I_2 in 1,2-dichloroethane at 30°C.[123]

[b] For the copolymerization of styrene (M_1) and *p*-chlorostyrene (M_2) in the same solvent at 25°C: $k_{11} = 1050$, $k_{12} = 525$, $k_{22} = 290$, and $k_{21} = 670$ liters mole^{-1} min^{-1}; initiated with $HClO_4$.[195]

[c] For the copolymerization of *p*-methylstyrene (M_1) and *p*-methoxystyrene (M_2) with the same initiator in carbon tetrachloride at 30°C: $k_{11} = 0.031$, $k_{12} = 0.31$, $k_{22} = 7.4$, $k_{21} = 0.74$ liters mole^{-1} min^{-1}.[186]

The lower value of r_1 for *trans*- compared to *cis*-β-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: *p*-OCH_3 > *p*-CH_3 > *p*-H > *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

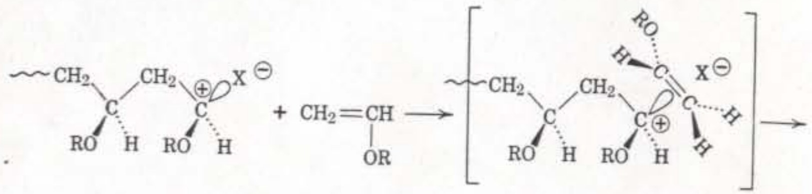
One of the first stereoregular polymerization reactions, if not the first which was recognized as such, was accomplished by the cationic polymerization of isobutyl vinyl ether initiated with boron trifluoride etherate in liquid propane.[196] Schildknecht reported in 1948 that the poly(vinyl isobutyl ether) formed by carrying out this reaction at temperatures of −80 to −60°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 α,p-dimethylstyrene,[200] and these results have since been verified and extended to α-methylstyrene.[201–203] Stannic chloride initiation was also found to yield crystalline polymers of α,p-dimethylstyrene, but not of α-methylstyrene. In the $SnCl_4$-initiated polymerization reaction variations in temperature and solvent had little effect on crystallinity.[201]

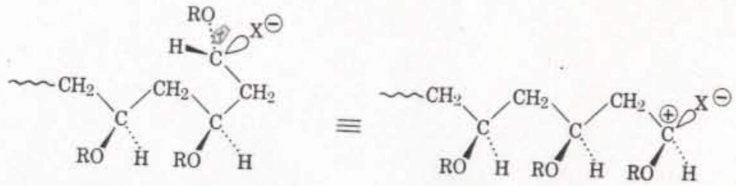
14.A.5.1. Stereoregular Polymerization of Vinyl Ethers

The preparation of crystalline or crystallizable polymers of vinyl ether monomers by homogeneous cationic polymerization reactions initiated with $BF_3 \cdot O(C_2H_5)_2$ and related catalysts has been extended to the methyl,[204] isopropyl,[205] n-butyl,[205] t-butyl,[206, 207] benzyl,[208] and trimethylsilyl[209] 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 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 $Al(C_2H_5)Cl_2$, $Al(C_2H_5)_2Cl$, $Al(C_2H_5)F_2$, $Al(C_2H_5)Br_2$, and $Al(OC_2H_5)Cl_2$.[212–214]

Several stereochemical mechanisms have been suggested to account for the formation of stereoregular vinyl ether polymers. In one, the carbonium ion is considered to be in an sp^3 configuration (14-78) because of coordination 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 direction with an orientation in space such that the alkoxy group on the monomer and the alkoxy group on the active polymer chain endgroup are furthest away from each other (14-78). Insertion of the monomer between the carbonium ion and the counterion in this manner (14-79) results in the formation of an isotactic placement.

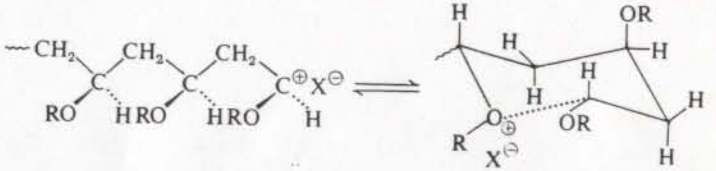


(14-78)

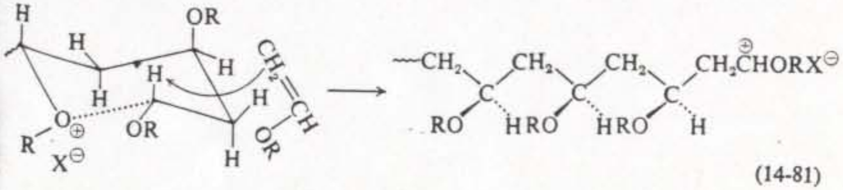


(14-79)

Two alternative mechanisms have been proposed in which the carbonium ion endgroups on active chains form six-membered ring structures by coordination of the carbonium ion with the alkoxy group on the third repeating unit back along the chain, Reaction (14-80). In one proposed mechanism, steric control results from a preferred equatorial configuration of the alkoxy group of the terminal unit, Reaction (14-80).[217] An isotactic placement is formed because the monomer must approach the coordinated carbonium ion from the rear, which is the axial direction (14-81). In the other mechanism involving this type of cyclic intermediate, steric control is determined by interaction of the counterion with both existing and

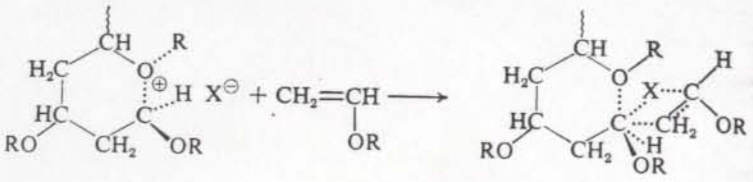


(14-80)



(14-81)

newly forming carbonium ions in the transition state, Reaction (14-82).[198] The orientation of the monomer and the coordination of the counterion



(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.

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, asymmetry is induced in the substituent groups surrounding the backbone carbon atoms by use of optically active Lewis base cocatalysts in the formation of the initiator.[218] Cocatalysts used successfully for this purpose are listed in Table 14-12, but other attempts at preparing optically active polymers by this technique using (−)α-methylbenzyl alcohol, tosyl L-valine, and camphor have failed.[219]

Table 14-12

Asymmetric Polymerization of Benzofuran[a]

Asymmetric cocatalyst	Polymerization temp., °C	$[\eta]$[b]	$[\alpha]_p$[c]
(−)β-Phenylalanine	−75	0.6	−33.1
(−)β-Phenylalanine	−75	0.75	−24.1
(+)β-Phenylalanine	−75	0.7	+13.1
(+)10-Camphorsulphonic acid	−75	1.4	−3.8
(+)Tetramethylammonium 10-camphorsulphonate	−75	0.5	−2.4
(−)Brucine	−100	0.2	+2.8

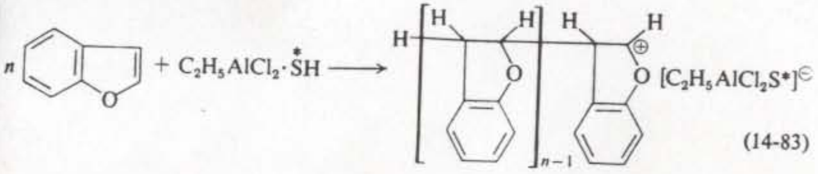
[a] With aluminum monoethyl dichloride.[218]

[b] Determined in toluene at 30°C.

[c] In benzene.

benzofuran

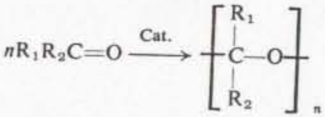
Optically active polymers have been prepared by the cationic polymerization (14-83) of benzofuran because the repeating units in the polymer obtained from this monomer have no plane of symmetry.[220, 221] The effectiveness of an asymmetric counterion in inducing an asymmetric polymerization reaction and in creating active centers in the polymer backbone is shown by the optical rotation data in Table 14-12.[218] The most effective cocatalyst according to this data is (−)β-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.



(14-83)

PART B: CARBONYL MONOMERS

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



$$nR_1R_2C{=}O \xrightarrow{\text{Cat.}} \left[\begin{array}{c} R_1 \\ | \\ -C-O- \\ | \\ R_2 \end{array} \right]_n \qquad (14\text{-}84)$$

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.[222] These studies were followed most notably by investigations of the apparent solid-state polymerization of crystalline acetaldehyde in 1936[223, 224] and by studies on the use of high pressure techniques for the polymerization of long chain aliphatic aldehydes in 1930.[225] Only very recently have procedures been reported for the carbonyl polymerization of acetone[226] and dimethylketene,[227] although unsubstantiated reports for both can be found in the literature of many years back.[228]

14.B.1. ALDEHYDES

14.B.1.1. Formaldehyde

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