Kirk-Othmer Encyclopedia of Chemical Technology.

VINYL ETHER MONOMERS AND POLYMERS

Because of the strong electron-donating oxygen, the polymerization of vinyl ethers (VE) can be readily accomplished using cationic initiators, resulting in polymers and copolymers that have the potential for significant variety. However, only poly(methyl vinyl ether) (PMVE)) achieved commercial success among the homopolymers, and its commercial importance has faded (1). Divinyl ethers are emerging as important ingredients in radiation-cured coatings (2), whereas copolymers of methyl vinyl ether (MVE) and maleic anhydride, easily prepared by free-radical initiation, continue to be valued as ingredients in personal care and pharmaceutical products (3).

The observation in 1949 (4) that isobutyl vinyl ether (IBVE) can be polymerized with stereoregularity ushered in the stereochemical study of polymers, eventually leading to the development of stereoregular polypropylene. In fact, vinyl ethers were key monomers in the early polymer literature. For example, ethyl vinyl ether (EVE) was first polymerized in the presence of iodine in 1878 and the overall polymerization was systematically studied during the 1920s (5). There has been much academic interest in living cationic polymerization of vinyl ethers and in the unusual compatibility of poly(MVE) with polystyrene.

1. Monomers

The most general commercial process for the manufacture of mono- and divinyl ethers, developed by Reppe in the 1930s at BASF, is by treating alcohols with acetylene under pressure of ≥ 6.8 atm (100 psi) at temperatures of 120–180°C in the presence of catalytic amounts of the corresponding metal alcoholate. Although this is a simple reaction to visualize, the danger of handling acetylene under pressure in concentrated form requires sophisticated equipment and should only be attempted experimentally in an appropriately barricaded high pressure autoclave (6).

$$\mathrm{HC{\equiv}CH} \overset{\mathrm{ROM}}{\rightarrow} (\mathrm{ROCH=CHM}) \overset{\mathrm{ROM}}{\rightarrow} \mathrm{ROCH=CH_2 + ROM}$$

Alternatively, thermal cracking of acetals or metal-catalyzed transvinylation can be employed. Vinyl acetate or MVE can be employed for transvinylation and several references illustrate the preparation especially of higher vinyl ethers by such laboratory techniques. Special catalysts and conditions are required for the synthesis of the phenol vinyl ethers to avoid resinous condensation products (6, 7). Direct reaction of ethylene with alcohols has also been investigated (8).

1.1. Monomer Properties

Some physical properties of the lower homologues of vinyl ether are presented in Table 1.

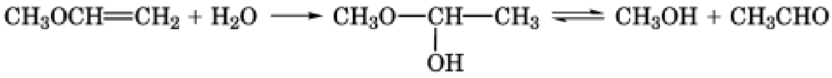
Table 1. Physical Properties of the Lower Vinyl Ethers[a]

	Methyl vinyl ether	Ethyl vinyl ether	Isopropyl vinyl ether	*n*-Butyl vinyl ether	Isobutyl vinyl ether
CAS Registry Number	[107-25-5]	[109-92-2]	[926-65-8]	[111-34-2]	
odor	sweet, pleasant	pleasant	pleasant	pleasant	pleasant
boiling point, °C	5.5	35.6	55–56	94.3	83
freezing point, °C	−122	−115.3	−140	−112.7	−132.3
specific gravity at 20/4°C	0.7511	0.753	0.753	0.778	0.767
refractive index, n_D^{25}	1.3947	1.3734	1.3829	1.3997	1.3946
solubility in water at 20°C, wt %	0.97	0.039	0.6	0.1	0.1
flash point, °C	−56[b]	−18[c]		0.55	−9.4
heat of vaporization at 101.3 kPa		367		316	323

[a] Ref. 6.
[b] Cleveland open cup.
[c] Tag open cup (ASTM D1310).

1.2. Reactions of Vinyl Ethers

Vinyl ethers undergo the typical reactions of activated carbon–carbon double bonds. A key reaction of VEs is acid-catalyzed hydrolysis to the corresponding alcohol and acetaldehyde, ie, addition of water followed by decomposition of the hemiacetal. For example, for MVE, the reaction is



$$CH_3OCH{=}CH_2 + H_2O \longrightarrow CH_3O{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}CH_3 \rightleftharpoons CH_3OH + CH_3CHO$$

To avoid this reaction during storage, VEs are often stabilized using small amounts of bases such as triethanol amine.

MVE is a reactive flammable gas and must be handled safely. A detailed review of VE handling issues is available (6).

The principal reaction of vinyl ethers to be considered in this article is cationic polymerization.

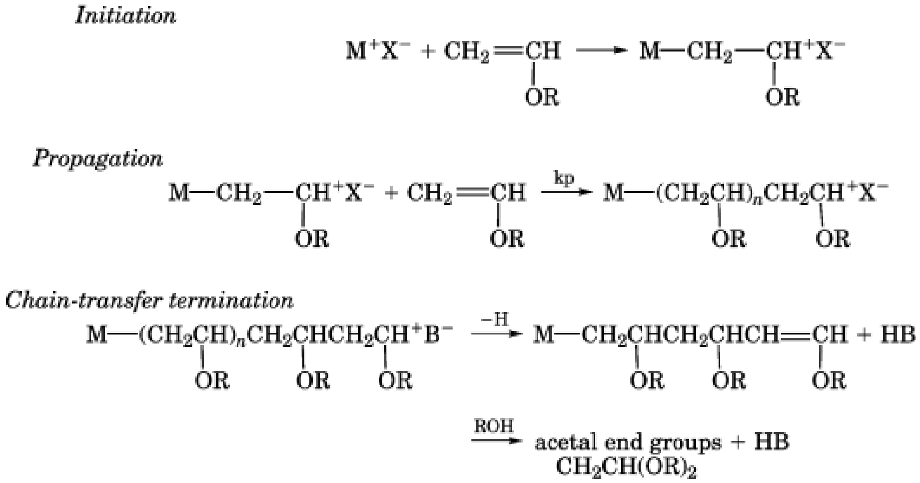
2. Homopolymerization

VEs such as MVE polymerize slowly in the presence of free-radical initiators to form low mol wt products of no commercial importance (9). Examples of anionic polymerization are unknown, whereas cationic initiation promotes rapid polymerization to high mol wt polymers in excellent yield and has been extensively studied (10).

A typical cationic polymerization is conducted with highly purified monomer free of moisture and residual alcohol, both of which act as inhibitors, in a suitably dry unreactive solvent such as toluene with a Friedel-Crafts catalyst, eg, boron trifluoride, aluminum trichloride, and stannic chloride. Usually low temperatures (-40 to -70°C) are favored in order to prevent chain-transfer or sidereactions.

Complexation of the initiator and/or modification with cocatalysts or activators affords greater polymerization activity (11). Many of the patented processes for commercially available polymers such as poly(MVE) employ BF_3 etherate (12), although vinyl ethers can be polymerized with a variety of acidic compounds, even those unable to initiate other cationic polymerizations of less reactive monomers such as isobutene. Examples are protonic acids (13), Ziegler-Natta catalysts (14), and actinic radiation (15, 16).

Initiation is an electrophilic addition of a cation across the double bond, but because of the poor nucleophilicity of the initiator's counterion, propagation is favored over termination. Chain transfer to more nucleophilic species such as fortuitous moisture or impurities such as alcohols either limits propagation or, if such impurities are present in sufficient quantities, totally inhibits polymerization. As the temperature of a particular polymerization is increased, molecular weight drops off quickly because the propagating carbocation can transfer its β-proton to the counterion or to fresh monomer. This results in terminal unsaturation or acetal end groups. The mechanism can be illustrated as follows:



Initiation

$$\mathrm{M^+X^- + CH_2{=}\underset{OR}{CH} \longrightarrow M{-}CH_2{-}\underset{OR}{CH}{}^+X^-}$$

Propagation

$$\mathrm{M{-}CH_2{-}\underset{OR}{CH}{}^+X^- + CH_2{=}\underset{OR}{CH} \xrightarrow{kp} M{-}(CH_2\underset{OR}{CH})_nCH_2\underset{OR}{CH}{}^+X^-}$$

Chain-transfer termination

$$\mathrm{M{-}(CH_2\underset{OR}{CH})_nCH_2\underset{OR}{CH}CH_2\underset{OR}{CH}{}^+B^- \xrightarrow{-H} M{-}CH_2\underset{OR}{CH}CH_2\underset{OR}{CH}CH{=}\underset{OR}{CH} + HB}$$

$$\xrightarrow{\mathrm{ROH}} \text{acetal end groups} + \mathrm{HB} \quad \mathrm{CH_2CH(OR)_2}$$

In the presence of cationic initiators, the possibility for loss of pendant ether groups to form free alcohol is another side reaction that usually results in color formation because of the highly conjugated products formed.

$$\text{poly(vinyl ether)} \xrightarrow{\text{several steps-HOR}} \mathrm{{-}(CH{=}CH)_n{-}CH{=}\underset{OR}{CH}}$$

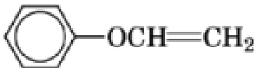
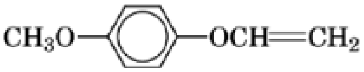
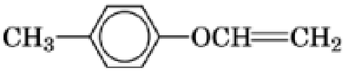
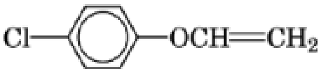
This reaction is favored by higher reaction temperatures and polar solvents. Another degradation reaction common to ethers is oxidation, especially when the α-carbon is branched (17). Polymeric ethers of all types must not be exposed to oxygen, especially in the presence of transition metals because formation of peroxides can become significant.

2.1. Monomer Reactivity

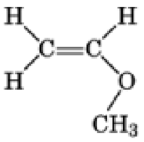
The nature of the side chain R group exerts considerable influence on the reactivity of vinyl ethers toward cationic polymerization. The rate is fastest when the alkyl substituent is branched and electron-donating. Aromatic vinyl ethers are inherently less reactive and susceptible to side reactions. These observations are shown in Table 2.

The same order of reactivity is also found for reactions such as acid-catalyzed hydrolysis; a closer look at the structure of these vinyl ether homologues suggests the reason.

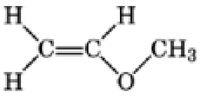
Table 2. VE Monomer Reactivity

Monomer	CAS Registry Number	Relative reactivity	Formula
	Alkyl vinyl ethers[a]		
ethyl vinyl ether	[109-92-2]	1.00	$CH_3CH_2OCH{=}CH_2$
t-butyl vinyl ether	[926-02-3]	12.5	$(CH_3)_3COCH{=}CH_2$
isopropyl vinyl ether	[926-65-8]	5.4	$(CH_3)_2CHOCH{=}CH_2$
2-chloroethyl vinyl ether	[110-75-8]	0.44	$ClCH_2CH_2OCH{=}CH_2$
	Aryl vinyl ethers[b]		
phenyl vinyl ether	[766-94-9]	1.00	
p-methoxyphenyl vinyl ether	[4024-19-5]	2.38	
p-methylphenyl vinyl ether	[1005-62-5]	1.82	
p-chlorophenyl vinyl ether	[1074-56-2]	0.278	

[a] Ref. 18.
[b] Ref. 19.



syn



anti

Syn- and anti-orientations are possible and there is evidence that the anti-orientation does not favor orbital overlap; such an orientation is favored with larger branched-chain substituents. A ^{13}C-nmr study found that the π-electron density on the vinyl β-carbon is lower as the reactivity of the monomer increases (20). Methyl vinyl ether exists almost entirely in the syn-structure, a favorable orbital overlap situation, and MVE for this reason is less reactive to both polymerization and hydrolysis (21).

This is a puzzling situation because it is expected that a higher electron density on the β-carbon would lead to greater reactivity toward an approaching carbocation. Obviously the reactivity of the carbocation terminus toward an approaching vinyl ether monomer is another factor in determining the reactivity of a particular vinyl ether during cationic polymerization. Most models designed to explain why low electron density on the β-vinyl

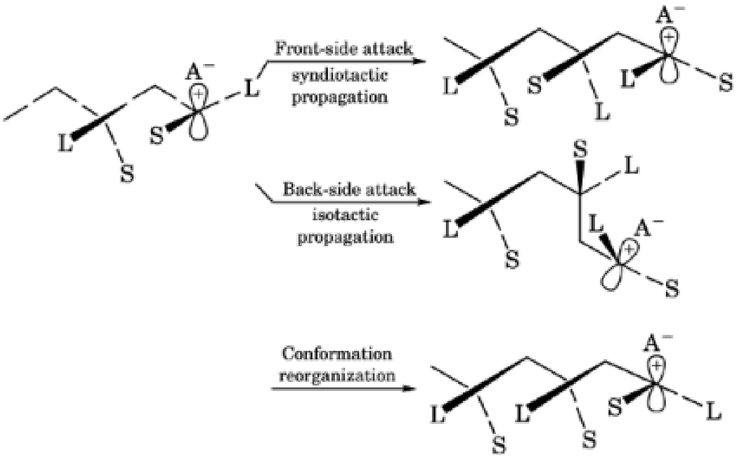


Fig. 1. Effect of ion pairing on stereochemistry of propagation for alkyl vinyl ethers, where L is large substituent; S, small substituent.

carbon produces a more reactive vinyl ether suggest that a cyclic π-complex transition state is involved. Such an intermediate allows the α-carbon to benefit from the higher level of electron density as the new carbocation terminus forms (10).

2.2. Stereoregular Polymerization

Chemists at GAF Corporation were first to suggest that stereoregularity or the lack thereof is responsible for both nontacky and crystalline or tacky and amorphous polymers generated from IBVE with $BF_3{:}O(C_2H_5)_2$, depending on the reaction conditions (22, 23). In addition, it was shown that the crystalline polymer is actually isotactic (24). Subsequently, the reaction conditions necessary to form such polymers have not only been demonstrated, but the stereoregular polymerization has been extended to other monomers, such as methyl vinyl ether (25, 26).

In order to generate stereoregular (usually isotactic) polymers, the polymerization is conducted at low temperatures in nonpolar solvents. A variety of soluble initiators can produce isotactic polymers, but there are some initiators, eg, $SnCl_4$, that produce atactic polymers under isotactic conditions (26). The nature of the pendant group can influence tacticity; for example, large, bulky groups are somewhat sensitive to solvent polarity and can promote more crystallinity (14, 27).

The low temperature limitation of homogeneous catalysis has been overcome with heterogeneous catalysts such as modified Ziegler-Natta (28) solid-supported protonic acids (29, 30) and metal oxides (31). Temperatures as high as 80°C in toluene can be employed to yield, for example, crystalline poly(IBVE) with Cr_2O_3 (31).

It has been suggested that the mechanism of stereoregular vinyl ether polymerization heavily depends on the degree of association of the counterion with the growing terminal carbocation (32, 33). Figure 1 illustrates the predicted most-stable configuration of the ultimate and penultimate units of a growing chain. It indicates how an incoming monomer can approach the carbocation terminus from either the front- or back-side attack, which attack is prevalent depends on the tightness of the growing ion pair and the steric requirements of the particular vinyl ether monomer. Front-side attack is favored by a loose ion pair associated with polar solvents, whereas a back-side attack is favored by nonpolar solvents where a tight ion pair prevails.

3. Living Polymerization

Ever since the demonstration that the initiation system of hydrogen iodide and molecular iodine (HI/I_2) induces living polymerization of VE monomers (34), numerous studies have been performed to extend the scope of this type of VE polymerization. Living polymerization is characterized by an increasing number-average molecular weight as the monomer is consumed. The rate of M_n increase is inversely proportional to the initial concentration of hydrogen iodide, not iodine, and the molecular weight distribution (MWD) of the polymer is very narrow throughout the course of the polymerization ($M_w/M_n < 1.1$). Thus, this type of polymerization can be stopped and started by consumption or addition of fresh monomer. It is similar to ethylene oxide/propylene oxide (EO/PO) anionic polymerization in this regard, but the initiation system is longer lived (see Polyethers).

The mechanism proposed (35) consists of the reaction of HI across the double bond, followed by activation with molecular iodine. This weakens the C–I bond, making the α-carbon cationic enough to insert monomer and propagate polymerization. However, without fresh monomer, the polymerization stops, but without termination. The stability of the terminus of the polymer suppresses side reactions such as chain transfer and termination. The iodine is a weak Lewis acid, but because of the nucleophilicity of the iodide, the carbon–iodide bond remains intact. Other weak Lewis acids can perform the same function; for example, the HI/Zn_2I_2 system (36) and the $C_2H_5AlCl_2$/ester and ether systems (37–39) afford living polymerization at higher temperatures and rates. An overview of the design of initiating systems has been published (40).

Living VE polymerization is usually terminated by addition of alcohols, phenols, amines, etc, that can replace iodide. Without some base present to neutralize generated HI, an aldehyde end group forms if moisture is present because of acid-catalyzed hydrolysis (41).

Details of the mechanism of living polymerization have been refined continually (42), and a dormant species has been shown to be crucial for such polymerization. The dormant species is in equilibrium with the active species and the ratio can determine MWD and hence the quality of the living process (43).

The living polymerization process offers enormous flexibility in the design of polymers (40). It is possible to control terminal functional groups, pendant groups, monomer sequencing along the main chain (including the order of addition and blockiness), steric structure, and spatial shape.

More recent examples include end-functionalized multiarmed poly(vinyl ether) (44), MVE/styrene block copolymers (45), and star-shaped polymers (46–48). With this remarkable control over polymer architecture, the growth of future commercial applications seems entirely likely.

4. Homopolymer Properties

Physical properties, which depend on molecular weight, the nature of the alkyl group, the nature of the initiator, stereospecificity, and crystallinity, range from viscous liquids, through sticky liquids and rubbery solids, to brittle solids. Polyethers with long alkyl side chains are waxy, however, as the alkyl group in such cases dominates physical properties.

As shown in Table 3, the glass-transition temperatures of the amorphous straight-chain alkyl vinyl ether homopolymers decrease with increasing length of the side chain. Also, the melting points of the semicrystalline poly(alkyl vinyl ether)s increase with increasing side-chain branching.

Poly(methyl vinyl ether) [34465-52-6], because of its water solubility, continues to generate commercial interest. It is soluble in all proportions and exhibits a well-defined cloud point of 33°C. Like other polybases, ie, polymers capable of accepting acidic protons, such as poly(ethylene oxide) and poly(vinyl pyrrolidone), each monomer unit can accept a proton in the presence of large anions, such as anionic surfactants, HI_3, or polyacids, to form a wide variety of complexes.

Table 3. Glass-Transition Temperature of Amorphous Poly(Vinyl Ether)s and Melting Points of Crystalline Poly(Vinyl Ether)s[a]

Poly(alkyl vinyl ether)	CAS Registry Number	T_g, °C	Mp, °C
poly(methyl vinyl ether)	[34465-52-6]	−34	144
poly(ethyl vinyl ether)	[25104-37-4]	−42	
poly(isopropyl vinyl ether)	[25585-49-3]	−3	191
poly(*n*-butyl vinyl ether)	[25232-87-5]	−55	
poly(isobutyl vinyl ether)	[9003-44-5]	−19	170
poly(2-ethylhexyl vinyl ether)	[29160-05-2]	−66	
poly(*n*-pentyl vinyl ether)		−66	
poly(*n*-hexyl vinyl ether)	[25232-88-6]	−77	
poly(*n*-octyl vinyl ether)	[25232-89-7]	−80	
poly(*t*-butyl vinyl ether)	[25655-00-9]		238

[a] Ref. 6.

Table 4. Commercial Vinyl Ether Homopolymers[a, b]

Vinyl ether	Physical form	Specific viscosity, η_{sp}	Trademark	Manufacturer	Uses
methyl	viscous liquid, balsam-like	0.68	Lutonal M	BASF	plasticizer for coatings; aqueous tackifier
	viscous liquid, balsam-like	0.3–0.5	Gantrez M	ISP	plasticizer for coatings; aqueous tackifier
ethyl	viscous liquid	1.0	Lutonal A	BASF	plasticizer for cellulose nitrate and natural-resin lacquers
	elastomeric solid		PVEE[c]	Union Carbide	pressure-sensitive adhesive base
isobutyl	high polymer viscous liquid	1.0	Lutanol I	BASF	tackifier for adhesives
	viscous liquid	0.1–0.5	Gantrez B	ISP	tackifier for adhesives
	elastomeric solid	2–6	Oppanol C	BASF	pressure-sensitive adhesive base
octadecyl	waxy solid[d]		V-Wax	BASF	polishes and waxes

[a] Refs. 12 and 49.
[b] Some viscous–liquid polymers are also supplied as high solids solutions, eg, 70% in toluene.
[c] Solid and solutions supplied.
[d] Low degree of polymerization, mp 50°C.

5. Commercial Aspects

Although no longer of significant commercial interest, the characteristics of some of the amorphous homopolymers commercially available at one time or another are illustrated in Table 4. No crystalline polymers are known to have been commercialized. This lack of commercial success results from the economically competitive situation concerning vinyl ether polymers versus other, more readily available polymers such as those based on acrylic and vinyl ester monomers.

The commercial situation in the late-1990s is surprising, considering the inherently inexpensive cost of the monomer raw materials, the apparent simplicity of manufacture, and the wide variety of vinyl ether monomers possible from the vast assortment of commercially available alcohols. Several bright spots in this technology have emerged, however; the field of radiation-curable coating formulations based on vinyl ether monomers is being actively pursued, and living cationic polymerization and polymer–polymer compatibility, especially of PMVE and polystyrene, are intensively studied.

Table 5. Reactivity Ratios in the Copolymerization of *n*-Butyl Vinyl Ether (M_1) with Another Vinyl Ether (M_2)[a, b]

M_2 $CH_2{=}CH{-}OR$	r_1	r_2	$1/r_1$	log $1/r_1$
CH_3	5.67 ± 0.02	0.47 ± 0.02	0.18	−0.745
C_4H_6	2.17 ± 0.15	0.24 ± 0.17	0.46	−0.337
C_2H_6	2.05 ± 0.05	0.75 ± 0.02	0.49	−0.310
n-C_3H_7	1.35 ± 0.15	0.99 ± 0.10	0.74	−0.131
n-C_4H_9	1.00	1.00	1.00	0.00
n-C_6H_{13}	0.95 ± 0.02	1.38 ± 0.03	1.05	0.021
i-C_4H_9	0.73 ± 0.15	1.48 ± 0.10	1.37	0.137
$C_6H_5CH_2$	0.72 ± 0.05	1.61 ± 0.08	1.40	0.146
i-C_3H_7	0.38 ± 0.07	2.77 ± 0.10	2.63	0.420
C_6H_{11}	0.29 ± 0.02	3.80 ± 0.02	3.44	0.537
$C_6H_5CHCH_3$	0.38 ± 0.10	1.40 ± 0.10	2.63	0.420
t-C_4H_9	0.19 ± 0.02	9.67 ± 0.05	5.26	0.721

[a] Ref. 51.

[b] Total monomer, 20 mmol; $C_2H_5AlCl_2$, 0.05 mmol; total volume of the reaction mixture, 23 mL in toluene at −78°C

6. Copolymerization

VEs do not readily enter into copolymerization by simple cationic polymerization techniques; instead, they can be mixed randomly or in blocks with the aid of living polymerization methods. This is on account of the differences in reactivity, resulting in significant rate differentials. Consequently, reactivity ratios must be taken into account if random copolymers, instead of mixtures of homopolymers, are to be obtained by standard cationic polymerization (50, 51). Table 5 illustrates this situation for butyl vinyl ether (BVE) copolymerized with other VEs. The rate constants of polymerization (kp) can differ by one or two orders of magnitude, resulting in homopolymerization of each monomer or incorporation of the faster monomer, followed by the slower (assuming no chain transfer).

VEs can also copolymerize by free-radical initiation with a variety of comonomers. According to the Q and e values of 0.023 and -1.77 (isobutyl vinyl ether), VEs are expected to form ideal copolymers with monomers of similar Q and e values or alternating copolymers with monomers such as maleic anhydride (MAN) that have high values of opposite sign ($Q = 0.23$; $e = +2.25$).

For bulk copolymerization of methyl, octyl, dodecyl, and octadecyl vinyl ethers using benzoyl peroxide as initiators at 40–100°C with the following comonomers (M_1), where r_2 is 0 in all cases (6), the values of r_1 are

M_1	r_1
acrylonitrile	0.8–1
butyl maleate	0–0.1
maleic anhydride	0.0
methyl acrylate	2.7–3
methyl methacrylate	10
styrene	>50
vinyl acetate	3.4–3.7
vinyl chloride	1.7–2.2
vinyldene chloride	1.3–1.5

Both MAN and VE do not readily homopolymerize by themselves by a free-radical mechanism. If each by itself is initiated with significant quantities of initiator at high temperature and with neat monomer, high yields of oligomer or low mol wt polymer is possible under these extreme conditions. However, when mixed together, the mixture can polymerize explosively even without initiation to high mol wt polymers (52). Early on, workers interested in this alternating polymerization recognized that the resulting polymer, even with varying ratios of monomer, remained 1:1 in monomer ratio, and that the rate of polymerization was at maximum when the monomers were polymerized at a 1:1 mole ratio. In fact, MAN and VE formed a charge-transfer complex (CTC) whose concentration could be measured in the uv. This species is found to be at a maximum when the monomers are at a 1:1 ratio. Hence the idea is that the CTC of MAN + VE is the active *in situ* monomer and this accounts for the complete alternating tendency found in the polymer regardless of monomer feed composition.

Evidence against this idea has fueled a long-enduring controversy. Several detailed review articles have appeared concerning this subject (53–55). However, in trapping experiments in the presence of donor and acceptor monomers that are known to form CTC, no evidence can be found for the concerted addition of the CTC (56, 57). This suggests that the mechanism for alternation results from the interaction of an electron-acceptor terminal radical and an electron-donor monomer or the reverse, an electron-donor terminal radical and an electron-acceptor monomer, because of a decrease in the activation energy of cross-propagation (58). Alternatively, a convincing argument has been presented for the formation of diradicals or zwitterionic C_4 intermediates depending on substituents and conditions instead of a CTC (59). The current evidence supports a definite intermediate such as the CTC or C_4 diradical (60). Furthermore, the reality is that such alternating polymerizations can be reliably carried out with monomers such as vinyl ethers and electron-withdrawing monomers such as maleic anhydride, regardless of the actual mechanism. The alternating copolymers of MVE and MAN have achieved commercial success.

6.1. MVE/MAN Copolymers

Various mol wt grades of poly(methyl vinyl ether-*co*-maleic anhydride) (PMVEMA) are available from International Specialty Products, Inc. (formerly GAF Corp.), under the trade name of Gantrez. Table 6 illustrates the M_w and MWD found for commercially available polymers. As can be seen, high molecular weights are readily achieved.

Table 6. Absolute Molecular Weights and Molecular Weight Distributions of Gantrez AN (PMVEMA)[a, b]

Gantrez sample	M_w	M_n	M_w/M_n
AN-119	2.16×10^5	7.98×10^4	2.71
AN-139	1.08×10^6	3.11×10^5	3.47
AN-149	1.25×10^6	4.85×10^5	2.58
AN-169	1.98×10^6	9.60×10^5	2.06
AN-179	2.40×10^6	1.13×10^6	2.12

[a] Refs. 61 and 62.

[b] Samples from size-exclusion chromatography/low angle laser light scattering (sec/lalls).

PMVEMA, supplied as a white, fluffy powder, is soluble in ketones, esters, pyridine, lactams, and aldehydes, and insoluble in aliphatic, aromatic, or halogenated hydrocarbons, as well as in ethyl ether and nitroparaffins. When the copolymer dissolves in water or alcohols, the anhydride group is cleaved, forming the polymers in free acid form or the half-esters of the corresponding alcohol, respectively. Table 7 illustrates the commercially available alternating copolymers and derivatives.

When hydrolyzed in water, the resulting diacid exhibits two pK_as ($\sim$3 and 8); the half ester as expected has one pK_a typical of polycarboxylic acids. A cross-linked version of this polymer, referred to as Stabileze, thickens a variety of formulations by expanding its hydrodynamic volume when neutralized. Because of the low pK_a of the vicinal diacids, Stabileze acquires a negative charge at lower pH than competitive cross-linked polyacrylic acids (carbomers). This allows for efficient thickening at lower pHs similar to that found on moist

Table 7. Commercially Available Alternating Copolymers

Polymer	CAS Registry Number	Trade name	Supplier	Application
poly(methyl vinyl ether-*co*-maleic anhydride-*co*-decadiene)		Stabileze	ISP	cosmetic/pharmaceutical thickener
poly(methyl vinyl ether-*co*-maleic anhydride (PMVEMA)	[9011-16-9]	Gantrez AN	ISP	adhesives, coatings, pharmaceutical tablet binder
butyl half-ester	[54578-91-5]	Gantrez ES-425	ISP	hairspray fixatives
ethyl half-ester	[50953-57-4]	Gantrez ES-225	ISP	hairspray fixatives
isopropyl half-ester	[31307-95-6]	Gantrez ES-335	ISP	hairspray fixatives
hydrolyzed (free acid)	[25153-40-6]	Gantrez S-95, S-97	ISP	thickener, protective colloid, dispersant
disodium salt	[9019-25-4]	Gantrez DS-1935; Sokalan CP-2	ISP; BASF	phosphate replacement in detergents (sequestrant)
mixed Ca and Na salts		MS-955	ISP	denture adhesive
poly(isobutyl vinyl ether-*co*-vinyl chloride)	[25154-85-2]	Caroflex MP-45	BASF	marine paints (film former)
poly(isobutyl vinyl ether-*co*-methyl acrylate-*co*-acrylonitrile)		Acronal 430D	BASF	polymer additive
poly(octadecyl vinyl ether-*co*-maleic anhydride	[28214-64-4]	Gantrez AN-8194	ISP	release coatings

skin, which in turn allows products to perform at optimum pH as desired by skin-care product formulators (63).

The effect of varying the degree of polymer neutralization on the conformations assumed by the poly(alkyl vinyl ether-*co*-maleic acid)s has been studied (64–66). The polyacids of this family with methoxy or ethoxy groups are random coils at all degrees of neutralization. The polyacids with intermediate-size alkoxy, ie, butoxy through octoxy, undergo at a particular degree of neutralization a conformational transition from a compact state, stabilized by hydrophobic forces, to a random coil. With small side groups such as methyl or ethyl, the potential for interaction is minimal. Consequently, as neutralization proceeds even to a small extent, repulsive forces predominate. However, when the pendant groups are hydrophobic, they can interact with each other in the same manner as surfactants, and this energy is sufficient to overcome charge repulsion but only to the point where repulsive forces overcome such hydrophobic interactions. Once this threshold is reached, the polymer uncoils to produce, ultimately, a polyelectrolyte with maximum charge separation.

International Specialty Products (ISP) supplies ethyl, isopropyl, and *n*-butyl half-esters of PMVEMA as 50% solutions in ethanol or 2-propanol. Typical properties are shown in Table 8. These half-esters do not dissolve in water but are soluble in dilute aqueous alkali and in aqueous alcoholic amine solutions. The main application for the half-esters is in hairsprays where they combine excellent hair-holding properties at high humidity without making the hair stiff or harsh. These half-esters are easily removed during shampooing, have a very low order of toxicity, and form tack-free films that exhibit good gloss, luster, and sheen (see Hair preparations).

Table 8. Typical Properties of Alcohol Solutions of the Half-Esters of PMVEMA

Property	Gantrez ES/225; SP/215	Gantrez ES-335-I	Gantrez ES-425 A-425	Gantrez ES-435
alkyl group of monoester	ethyl	isopropyl	butyl	butyl
physical form	clear, viscous liquid	clear, viscous liquid	clear, viscous liquid	clear, viscous liquid
activity, % solids	50 ± 2	50 ± 2	50 ± 2	50 ± 2
solvent	ethanol	2-propanol	ethanol	2-propanol
acid number, 100% solids	275–300	255–285	245–275	245–275
density, g/cm^3	0.983	0.957	0.977	0.962

7. Health and Safety Factors

Poly(methyl vinyl ether-*co*-maleic anhydride) and their monoalkyl ester derivatives have been shown on rabbits to be neither primary irritants nor primary sensitizers to skin and eyes. The acute oral toxicities on white rats of the two copolymers are, respectively, 29 g/kg and 25 g/kg body weight.

8. Applications

8.1. Radiation-Curable Coatings

The discovery and utilization of onium salt photoinitiators made possible the 1990s enthusiastic commercial interest in cationic radiation-curable vinyl ether coatings (49). The advantage over the older acrylic formulations is insensitivity to air (oxygen), fast cure, and excellent adhesion to metal and wood. In addition, the cationic mechanism allows both vinyl ether and epoxy monomers and oligomers to cure together. Although vinyl ethers are faster than epoxies, they accelerate the rate of overall polymerization even though an interpenetrating network of the two polymers is most likely the end result (67).

A wide variety of monovinyl and divinyl ethers are commercially available for this application, which allows the formulator greater latitude. For example, triethylene glycol divinyl ether [76-12-8] (DVE-3) and 1,4-cyclohexanedimethanol divinyl ether [17351-75-6] (CHVE) can be combined as reactive diluents, with each contributing quite different properties to the subsequently cured coating. CHVE offers hard brittle films, whereas DVE-3 produces films that have greater flexibility. DVE-3 is also a good solvent for the photoinitiator. More recently, the propenyl ether of propylene carbonate [130221-78-2] (PEPC) has been commercialized and specifically developed as a solubilizer for such initiators (68). Combinations of both divinyl ethers offer superior coatings that have controllable levels of flexibility, hardness, and solvent resistance (69). Their trade names are Rapi-Cure DVE-3, CHVE, PEPC, etc.

Vinyl ethers can also be formulated with acrylic and unsaturated polyesters containing maleate or fumarate functionality. Because of their ability to form alternating copolymers by a free-radical polymerization mechanism, such formulations can be cured using free-radical photoinitiators. With acrylic monomers and oligomers, a hybrid approach has been taken using both simultaneous cationic and free-radical initiation. A summary of these approaches can be found in Table 9.

International Specialty Products has been especially active in promoting and developing this technology. Success with the development of such coatings requires significant help with formulation details and the reader is referred to the appropriate trade literature for greater detail (70).

Table 9. Properties of Vinyl Ether-Based Formulations for Radiation-Curing Coating[a]

Property	Cationic	Radical	Hybrid
monomer type	vinyl ether	vinyl ether	vinyl ether
oligomer type	epoxy and vinyl ether	maleate	acrylate
cure speed in			
air	fast	slow	fast
N_2	fast	moderate	fast
adhesion to			
metal	excellent	poor	poor
wood	excellent	excellent	excellent
post-cure	slight	none observed	none observed
formulation latitude	moderate	moderate	wide

[a] Ref. 67.

8.2. Polymer–Polymer Compatibility

Frequently when polymers are mixed together they are immiscible because the combinatorial entropy of mixing is too small to overcome the enthalpy changes, which are usually positive. This small entropy of mixing is a result of the high mol wt nature of the component polymers. If the component polymers exhibit a specific interaction such as hydrogen bonding, Van der Waals, or electrostatic, etc, then miscibility can occur (71). In the case of PMVE–polystyrene, the blend presents a lower critical solution temperature (LCST) and the miscibility region depends on the molecular weight of the polymers. The interaction in this case is between the electrons of the ether groups and the aromatic polystyrene ring. In fact, PMVE can function as a diluent for isotactic polystyrene enhancing spherulite formation (72). Depending on the molecular weight and tacticity of the PMVE employed, separated regions of crystallized PMVE can function as reinforcement for polystyrene blends and offer improved plastic properties (73).

Derivatives of styrene such as poly(α-methylstyrene) results in immiscibility with PMVE. Only when hydrogen-bonding sites are incorporated into the poly(α-methylstyrene) can miscibility be re-established (74). Such hydrogen-bonding monomers, eg, vinyl phenol, can be incorporated in a variety of incompatible copolymers, resulting in modified copolymers now miscible with PMVE (75). Small-molecule polymer analogues have been employed with inverse gas chromatography to predict polymer compatibility with PMVE. This predictive technique shows that PMVE is compatible with poly(vinyl propionate) and poly(vinyl butyrate), but not with poly(vinyl acetate) (76). Obviously, small-polymer structural changes can have significant impact on compatibility because small energy differences are involved.

Another mechanism of compatibility is hydrogen bonding. Numerous examples illustrate that homogeneous polymer blends are possible when the polymers can interact by an acid–base mechanism. An interesting example of such interactions can be found in solution. For example, the interaction of strong hydrogen-bonding polymers such as poly(acrylic acid) with polybases such as PMVE or PVP in aqueous solution is strongly influenced by the degree of polyacrylic acid (PAA) neutralization (pH). This is because a certain level of cooperativity is required to form a stable complex. Such complexes can be insoluble in water (and homogeneous upon dry-down) even though each polymer by itself is soluble. When such insoluble complexes are titrated with base, a point is reached where the level of interaction is insufficient to counter electrostatic charge repulsion and the complex dissociates and dissolves. Neutralization therefore disrupts this situation of cooperativity, thus accounting for resolubilization of the precipitated complex. Interestingly, only a few anionic groups are necessary for this effect to take place (77–79).

The strong polybase behavior of PMVE is well documented, and interest in this polymer, especially from academic workers, suggests eventual interest industrially. This feature of PMVE cannot be found in acrylates or other inexpensive polymers but is inherent in PMVE polymers.

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