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Polymerization of Vinyl Derivatives of the Main Group Elements

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ABSTRACT

A survey of selected novel hybrid organic-inorganic polymers obtained by polymerization and copolymerization of main group compounds containing vinyl groups is presented. Examples from groups 13 through 16 are discussed with an emphasis on synthesis and quantitative reactivity studies.

This is a review of main group inorganic vinyl monomers that polymerize via the vinyl group. Selected examples of monomers, where the main group entity is separated from the vinyl function by other groups, will also be presented. These polymers will have a carbon chain backbone with pendant inorganic groups. The first section involves group 13, specifically the vinylborazines and vinylcarboranes. The second section covers group 14 (Si, Ge, Sn, and Pb). The third section covers group 15, focusing on phosphazenes, phosphonic acid esters, and phosphonic oxides. The last section will cover the vinylsulfoxides. The purpose of this review is to draw together much of the significant work done in this area, focusing on homopolymerization, copolymerizations, mechanisms, and reactivity in a widespread but not comprehensive manner. Relative monomer reactivity in copolymerization is commonly discussed in terms of reactivity ratios. These quantities may be defined as the ratio of the homo- to crosspropagation rate constants; thus, for monomer 1, $r_1 = k_{11}/k_{12}$. Since copolymer composition is kinetically controlled, a combination of $r_1 > 1$ and r_2 (k_{22}/k_{21}) < 1 will yield a copolymer rich in monomer 1. If, on the other hand, both r values equal 1, then a random copolymer results. In the rare case where both r values are significantly greater than 1, the copolymer will have a block-like structure. Reactivity ratios may be converted to the qualitative but useful set of quantities, the Alfrey-Price parameters, Q and e. The Q value is a measure of resonance stabilization, and the e value is a measure of polarity. These are relative values, using styrene ($Q = 1.00$; $e = -0.80$) as the reference standard. The Alfrey-Price parameters are used to analyze electronic effects in olefins and to predict r values for new copolymerization reactions. If an e value is more positive than styrene, then the substituent is more electron withdrawing than styrene. If the e value is more negative than styrene, then the substituent is a stronger electron donor. If a Q value is greater than that for styrene, then there is more conjugation than with styrene; if it is less than that for styrene, then there is less conjugation than with styrene. The one cautionary note that should be added is that reactivity ratio data have not been critically evaluated. It is now well-known that reactivity ratios determined by linearization methods may be in error, so older work, in particular, may not be up to contemporary standards. Transition metal vinyl polymers have been reviewed extensively and will not be covered here [1–4].

GROUP 13. VINYLBORANE AND CARBORANE POLYMERS

O-Carborane and several of its C-alkyl derivatives do not polymerize in the solid state or in benzene

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Dedicated to Prof. James Cullen Martin on the occasion of his sixty-fifth birthday.

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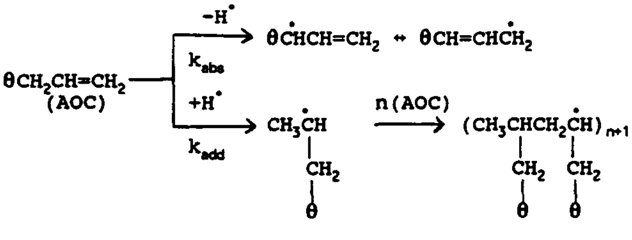
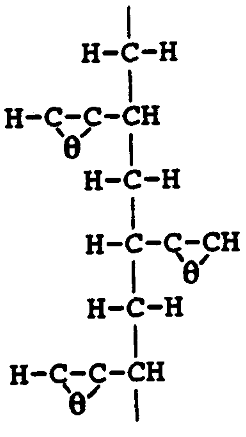
solution [5]. However, alkenyl-substituted carboranes do have the ability to undergo polymerization when subjected to gamma radiation. In the gamma ray irradiation of C-substituted alkenyl derivatives of 1,2-diacarba-closo-dodecaborane, the main products are oligomers, with the degree of polymerization varying between 5 and 10 depending on the temperature [6]. When 1-alkenyl-o-carborane is irradiated with gamma rays, low molecular weight polymers are produced [7].

1-Vinyl-1,2-dicarba-closo-dodecaborane-11 (1-vinyl-o-carborane) is polymerized in 51% yield in a head-to-tail fashion at 31°C with no detectable side products when subjected to gamma ray irradiation [5,8–10]. This polymerization is a bulk reaction governed by a free radical mechanism, and so the degree of polymerization is limited by chain transfer [11].

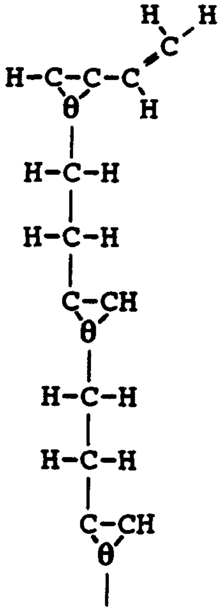
In the study of the mechanism of the polymerization of 1-allyl-o-carborane, the expected hydrogen atom abstraction from the alkenyl group to form an allylic-type radical was found; this was followed by hydrogen atom addition to the allene to form a propyl-type radical [6]. With the propyl radical as the propagating species, a saturated oligomer is formed in a free radical chain process which is characterized by chain transfer [6]. From electron spin resonance studies, it is known that organic unsaturated compounds subjected to ionizing radiation give radicals formed from the addition of hydrogen atoms to the unsaturated bond. In the case of vinyl monomers, the radicals resulting from addition have been considered to initiate radiation-induced polymerization [12]. The termination of growing vinyl carborane polymers is by a bimolecular chain transfer process [6].



θ = polyhedral cage

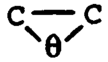


Type 1



Type 2

The polyhedral cage structure is represented here by:



The free radical mechanism when applicable to 1-vinyl-o-carboranes produces two types of polymers. The first (type 1) is a styrene type of polymer with pendant o-carborane side groups on a polyethylene backbone [11,13]. Hydrogen atom addition, as described below, probably initiates the formation of this first polymer [14]. The second (type 2) of polymer has an incorporation of the o-carborane cage in the backbone via linkage of a cage boron and an aliphatic carbon. The initiation and propagation steps for the formation of this second polymer are unknown. There must be a radical centered on the boron cage formed in the process in order to obtain this product [13]. An increase in electron density in the cage from the substituent would stabilize a cage centered radical and favor formation of the type 2 polymer. Semiempirical molecular orbital (INDO) calculations of the dipole moments indicate that the substituents do transfer electron density into the cage [13]. Zhigack and Chikishev have obtained a 71% yield of the first type of polymer by irradiation. They obtained a molecular weight between 5000–6000 [15].

A 1:3 solution of 1-vinyl-o-carborane and styrene using styrene as the solvent produces a copolymer that is 2:9 carborane to styrene when exposed to gamma radiation. This copolymerization is 1.4 times faster than the styrene homopolymerization under the same conditions [7]. The product is the type 1 polymer discussed earlier; the type 2 polymer is not observed.

The thermal degradation of poly(vinylpentaborane), which is obtained from $C_2H_3B_5H_8$, is the first step in a new route to boron carbide [16–18].

$$5BN + 2CH_4 + 9H_2$$
$$NH_3 \uparrow 1000°$$
$$[CH(B_5H_8)CH_2]n$$
$$\text{Ar 8 hrs} \downarrow 1000°$$
$$5/4\ B_4C + 3/4\ CH_4 + 3H_2$$

These studies indicate that vinylpentaborane polymers can be prepared in high yield in either soluble or cross-linked form and are excellent polymeric precursors to B_4C and other boron-based ceramic materials. Pyrolysis of poly(vinylpentaborane) in an ammonia atmosphere leads to a high ceramic yield of boron nitride. This appears to be a two-step process with poly(vinylborazanaphthalene), $[CH(B_5N_5H_7)CH_2]_2$, as an intermediate [17,18]. The formation of boron nitride and boron carbide is an example of a case where preparation from a polymer precursor may be more advantageous than traditional ceramic processes. Traditional methods are limited and thus there has been increasing interest in developing polymer pyrolyses as routes to ceramic materials [19].

Vinylborazine Polymers

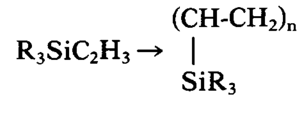
The other important set of vinyl monomers in group 13 is the vinylborazines. Early studies have shown that trivinylborazines are easily polymerized, but the products were not examined in detail [20]. N-Phenyl-B-vinylborazine does not homopolymerize due to steric crowding by the phenyl groups, but it will undergo copolymerization with styrene. Crude reactivity ratio determinations suggest that the reactivity of N-phenyl-B-vinylborazine is similar to that of styrene [21].

A number of B-trivinyl-N-triorganoborazine copolymers with methyl methacrylate, styrene, vinyl acetate, diallyl phthalate, ethyl acrylate, acrylonitrile, and many others have been prepared using radical initiators [22]. More recently, Jackson and Allen studied the polymerization of vinylorganoborazines. They have prepared a series of B-vinyl, allyl, and *p*-vinylphenyl borazines [23], and attempts have been made to carry out radical polymerization of these monomers. Only the *p*-vinylphenyl derivatives undergo homopolymerization and copolymerization with styrene [24]. A further structure-reactivity correlation is that cross-linked materials were observed for the N-methyl borazines and soluble polymers for the N-phenyl borazines. This observation suggests chain transfer at the N-methyl sites. The inability of the vinylborazine to undergo polymerization may be explained by steric crowding at the vinyl group by groups on the adjacent nitrogen (and hence low ceiling temperature) or the absence of significant π-electron delocalization from the olefin by the borazine ring. In the latter case, the vinyl group could not stabilize a radical and therefore the monomer would be difficult to polymerize. The vinylborazine, $N_3B_3Me_5CH{=}CH_2$, does undergo a slow thermal vinyl polymerization at elevated temperatures [25]. Sneddon has recently reported the preparation of alkenylborazines, $(R(H)C{=}CH_2)\text{-}B_3N_3H_5$, which were used to prepare polymeric and ceramic materials [18,26]. A thermal polymerization of vinylborazine, $N_3B_3H_5CH{=}CH_2$, leads to the formation of an insoluble polymer. Soluble, low molecular weight (~900) oligomers can be obtained if the polymerization is conducted in the presence of $B_3N_3H_6$. Free radical initiated (AIBN) polymerization of $N_3B_3H_5CH{=}CH_2$ leads to soluble poly(B-vinylborazine), with M_w ranging from 5000 to 23,000. Some branching may occur [26]. Spectroscopic evidence shows that polymerization occurs through the olefinic center. Similar polymers were prepared from β-alkenylborazines. Pyrolysis of these materials leads to a high ceramic yield of boron nitride [18,26]. The reactivity studies for the styrene copolymerization give values of r_1 (styrene) $= 4.02$ and r_2 (vinylborazine) $= 0.078$. The large disparity in reactivity of these isoelectronic species strongly suggests a low degree of mesomeric interaction between the vinyl group and the borazine ring.

GROUP 14. VINYLSILANE POLYMERS

Vinylsilanes were polymerized as early as 1953 when Wagner and Bailey oligomerized trichlorovinylsilane to tetramers. The cationic catalysts used were $AlCl_3$, $FeCl_3$, $ZnCl_2$, and BCl_3. Without catalysts, 90% conversion at 290°C was realized [27]. Since then, there have been extensive studies on these polymers. This section will cover homopolymers, copolymers, provide a discussion of branching and the related mechanism, and give a table of some reactivity data.

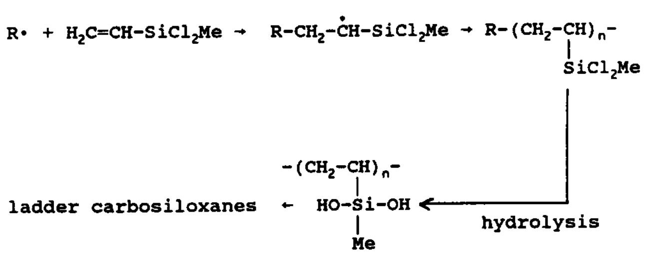
Trichlorovinylsilane will homopolymerize by the methods previously mentioned and by hydrolytic polycondensation [28,29]. The polymerization of $C_2H_3SiCl_3$ with t-BuLi leads to complex products that have been analyzed by GC/MS and GC/IR spectroscopy. The reaction pathway to these products has also been studied [30]. Triethoxyvinylsilane undergoes homopolymeration with di-tert-butylperoxide at 130°C with 100% conversion to form a viscous liquid polymer, which is soluble in most organic solvents and has a molecular weight range 5000–8000 [27]. Ethyl(vinyl)silane polymerizes with a $VCl_4/Al(Et)$ catalyst [31]. Vinylsilanes have also been known to homopolymerize when subjected to gamma irradiation [31,32].



$$R_3SiC_2H_3 \rightarrow \underset{\displaystyle SiR_3}{\overset{\displaystyle (CH\text{-}CH_2)_n}{|}}$$

The ionic polymerization of trimethylvinylsilane and other triorganovinylsilanes with organolithium catalysts produces high molecular weight polymers [33–39]. The polymerization proceeds rapidly, and the molecular weight depends on the ratio of monomer concentration to initiator concentration. The presence of lithium butoxides has a marked effect on the anionic polymerization of trimethylvinylsilane. As the amount of lithium butoxide increases, the amount of polymer decreases [40,41]. The degree of polymerization in the butyllithium catalyzed system varies from 3 to 30 [42]. Khodzhevano and Semenov report the formation of poly(vinyltrimethylsilane) by use of EtLi with $M_w = 5.6 \times 10^5$ and $M_n = 2.9 \times 10^5$ [42,43]. Another account reports that the anionic polymerization of trimethylvinylsilane produces low molecular weight polymers at temperature less than 100°C due to chain transfer to monomer [44]. The reaction of trimethylvinylsilane and metallic lithium in a hydrocarbon solvent for 20 hours gave only 30% conversion. The initial radical anion couples to form a dianion which is the propagating species [45]. The deviations of these systems from classical living polymerization behavior are believed to be due to chain transfer to momer and polymer, leading to double bonds and branching in the chain [35]. Poly(vinyltrimethylsilane), prepared by a variety of methods, is soluble in cyclohexane, toluene, diethyl ether, THF, chloroform, and methylene chloride [46].

Radical initiation of the polymerization of vinyl(methyl)dichlorosilane leads to an intermediate polymer which undergoes hydrolysis to produce materials believed to be (on the basis of IR spectroscopy) ladder carbosiloxanes [47].



While not strictly main group vinyl derivatives, silylstyrene derivatives have also attracted attention; therefore, selected recent work in this area will be mentioned. The radical polymerization of a wide range of *para*-substituted styrenes, $CH_2{=}CH_2C_6H_4$-*p*-R (R=Si_2Me_5 [48,49], Si_3Me_7 [49], Si_4Me_9 [49], $CH_2Si_2Me_5$ [49]), has been reported. Anionic initiation has been used for $CH_2{=}C(Me)C_6H_4$-*p*-R (R=$Si_2Me_4CH_2CH{=}CH_2$, $SiMe_2(CH_2)_nSi(CH_2CH{=}CH_2)Me_2$ (n=1,2)) [50]. The anionic homopolymerization of $CH_2{=}CHC_6H_4$-*p*-$Si(OR)Me_2$(R=Me, *i*Pr) gives polymers with a polydispersity of approximately 1.1 [51]. A living polymer with a polydispersity of 1.08–1.19 is obtained when $CH_2{=}CHC_6H_4$-*p*-$SiMe_2H$ is polymerized under anionic conditions with oligo (α-methylstyryl) dilithium (or disodium, dipotassium) [52].

Not all vinylsilanes will homopolymerize. There have been unsuccessful attempts to homopolymerize dimethylvinylsilane and divinylmethylsilane [53]. The monomers $CH_2{=}CX\text{-}SiMe_3$ (X=Ph, Cl, COOH) do not undergo homopolymerization by traditional radical, cationic, or anionic techniques [54]. These monomers are expected to be similar in reactivity to styrene, vinyl chloride, vinyl bromide, and acrylic acid. It has been proposed that the lack of polymer formation is the result of steric crowding [54]. Vinyltriethoxysilane and vinyltris(methoxy ethoxy)silane do not undergo homopolymerization when initiated by benzoyl peroxide [55]. This may be due to the aforementioned steric contribution or the electronic isolation of the vinyl group (and hence lack of stable radical formation) by the nonconjugating silicon center.

The anionic polymerization of α-(trimethoxylsilyl)-1,3-butadiene gives a polymer which does not undergo chain transfer or termination, thus producing stable living polymers at −78°C. This allowed for the preparation of well-defined polymers with controlled molecular weight and narrow molecular weight distribution [59]. The polymer microstructure was determined by comparing the ^{1}H NMR and ^{13}C NMR spectra of the polymer to those of model compounds [59]. In contrast to the behavior of butadiene and isoprene, the reaction exhibits 1,4 regiospecificity with the stereoisomer distribution shown below:

E form 70%

Z form 30%

The microstructure is of interest, because the physical properties of the polydienes depend on the structure of the repeating units.

Organometallic ($SnCl_4$/$EtAlCl_2$) catalyzed polymerization of vinylsilyl ethers with bulky substituents leads to polymers having 66% heterotactic triads [66]. A study of the oligomerization of vinylsilanes with various acceptor substituents on silicon by use of Zeigler-Natta types of catalysts indicates that the substituents do not have a significant effect on the structure of the products [67]. The silanes studied were trimethoxyvinylsilane, methyldimethoxyvinylsilane, and trichlorovinylsilane.

The Zeigler-Natta and anionic polymerizations of triorganovinylsilanes by organolithium reagents in bulk or organic solvents give secondary reactions that lead to branched polymers. The degree of branching increases with time and temperature and limits chain growth [33,35,68–71].

There are several accounts that discuss the mechanism of the anionic polymerization of vinylsilanes [34,37,38,73]. Trimethylvinylsilane undergoes anionic polymerization in cyclohexane in a manner similar to that of styrene or dienes except for the occurrence of a termination step (which will be discussed at the end of this section) [74]. The silicon center stabilizes alpha carbanions due to lone pair/σ hyperconjugation, making silicon substituted olefins good candidates for anionic polymerization.

The thermodynamics of the polymerization of organosilanes have been studied. The ΔH, ΔS, ΔG, heat capacity, stabilization energies, and phase transitions have been determined for the homopolymerization of $Me_3SiCH{=}CH_2$, $Me_2(Ph)SiCH{=}CH_2$, and $Me_2(PhCH_2)SiCH{=}CH_2$ [38]. The kinetics of organovinylsilane polymerization have also been studied [45].

There are much more extensive accounts of vinylsilane copolymerization. Trichlorovinylsilane copolymerizes with propylene, isobutylene, and styrene with use of a BF_3 catalyst. It also copolymerizes with vinyl acetate, methyl methacrylate, and acrylonitrile with a peroxide catalyst [27]. The above reactions result in polymers with only a small incorporation of silicon. Diacetoxymethylvinylsilane and diethoxymethylvinylsilane copolymerize with styrene, with AIBN as an initiator, to give high conversion in bulk and in toluene [56]. The diethoxy monomer has a higher reactivity ratio than the diacetoxy species, indicating that it is the more reactive of the two silyl monomers toward styrene [56]. Trimethyl and trimethoxyvinylsilane will cooligomerize with ethylene, propylene, and butadiene with use of a metal catalyst [57,58].

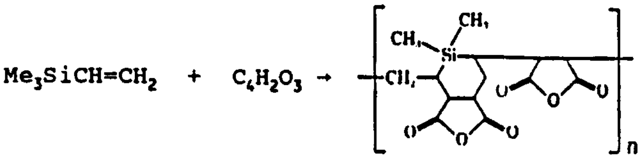
The copolymerization of vinyl(methyl)-dimethylaminosilanes with styrene, α-methylstyrene, and isoprene occurs by an anionic mechanism with n-BuLi as the catalyst. The amino groups are inert to the catalyst, and, after the polymerization, remain very reactive toward electrophilic reagents [60].

Trimethylvinylsilane and dimethylphenylvinylsilane copolymerize with butadiene in the presence of a lithium catalyst. The methyl and phenyl substituents display significantly different effects on the rate of copolymerization and on the relative concentration of silane in the copolymer [61].

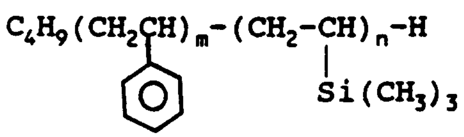
Trimethylvinylsilane, dimethylphenylvinylsilane [62], and vinyl(methyl)diacetoxysilane [64] will undergo radical addition copolymerization with styrene. In the anionic copolymerization of dimethylphenylsilane with styrene [63], it has been proposed that the phenyl group increases the reactivity of the silane by increasing the polarizability of the multiple bond. This could lead to greater reactivity in anionic copolymerization [63]. In radical copolymerization, the phenyl group increases the reactivity twofold [62]. Aromatic substituents have an inductive effect which can also facilitate the ethyllithium catalyzed anionic polymerization of vinylsilanes. This effect is seen in the increasing reactivity in this series: trimethylvinylsilane, benzyldimethylvinylsilane, dimethylphenylvinylsilane, and finally, most reactive, triphenylvinylsilane [37]. Hyperconjucative interactions of silicon–carbon bonds with the vinyl group can also lead to stabilization of anionic intermediates.

In the radical copolymerization of trimethylvinylsilane and dimethylphenylvinylsilane with styrene and methyl methacrylate, as the concentration of silane increases, the yield and molecular weight decrease [62]. This may indicate significant chain transfer involving the silane monomer or polymer.

Trimethylvinylsilane and dimethyldivinylsilane will copolymerize with maleic anhydride to produce an alternating copolymer [53]. Anionic copolymerization of trimethylvinylsilane



and styrene allows for formation of the diblock copolymers shown below. The copolymers, which have been characterized by GPC and



$$C_4H_9(CH_2\underset{C_6H_5}{CH})_m\text{-}(CH_2\text{-}\underset{Si(CH_3)_3}{CH})_n\text{-}H$$

^1H NMR spectroscopy, contain about 0.1 mole fraction of the vinylsilane [65].

The substituents on the olefinic carbon of the vinylsilane have a significant effect on copolymerization. The monomers $H_2C{=}C(X)SiMe_3$ (X=Ph, Br, Cl, COOH) copolymerize slowly with styrene, acrylonitrile, and methyl methacrylate due to steric limitations [54].

An account of the rates, cross linking, properties, and thermal stability of the ethylene/$H_2C{=}CSiR_3$ system (R=$OSiMe_3$, OEt, OBu, OC_9H_{19}, Et, Ph, OC_2H_4OEt, OPhMe) has been reported [72].

The reactivity ratios for many vinylsilanes and their comonomers are listed in Table 1. Copolymerization of trimethylvinylsilane and dimethylphenylvinylsilane with styrene and methyl methacrylate gives r values indicating that styrene and methyl methacrylate homopolymerize until al-

TABLE 1 Reactivity Data for Vinylsilane VS_1R_3[a]

Monomer 1	r_1	*Monomer 2*	r_2	*Conditions*[b]	*Reference(s)*
VMe_3Si	0	styrene	26	AIBN	75
VMe_3Si	0.01 ± 0.01	styrene	24 ± 4	benzoyl peroxide	62
VMe_3Si	0.02	butadiene	23	n-BuLi[c]	177, 179, 180
VMe_3Si	0.02 ± 0.01	methyl methacrylate	34 ± 4	benzoyl peroxide	62
VMe_3Si ether	0.21 ± 0.004	t-butyl vinyl ether	1.6 ± 0.04	toluene[d]	176
VMe_3Si ether	0.24 ± 0.06	t-butyl vinyl ether	1.45 ± 0.009	nitroethane[d]	176
VMe_3Si ether	1.37 ± 0.06	i-butyl vinyl ether	0.34 ± 0.03	toluene[d]	176
VMe_3Si ether	1.08 ± 0.05	i-butyl vinyl ether	0.35 ± 0.03	nitroethane[d]	176
VMe_3Si ether	1.40 ± 0.10	n-butyl vinyl ether	0.18 ± 0.03	toluene[d]	176
VMe_3Si ether	1.04 ± 0.09	n-butyl vinyl ether	0.32 ± 0.09	nitroethane[d]	176
$VPhMe_2Si$	1.07	butadiene	0.62	n-BuLi[c]	179
$VPhMe_2Si$	0.04 ± 0.01	methyl methacrylate	30.5 ± 5	benzoyl peroxide	62
$VPhMe_2Si$	0.03 ± 0.01	styrene	30.6 ± 6	benzoyl peroxide	62
$VPhMe_2Si$	0.06	styrene	5.7	n-BuLi[c]	62
$VPhMe_2Si$	1.3	styrene	0.54	n-BuLi[c]	62
VPhSiH	0	styrene	5.7	AIBN	75
$AllylMeSiH_2$	0	styrene	36	AIBN	75
$AllylPhSiH_2$	0	styrene	29	AIBN	75
p-$VPhMe_2SiH_2$	0	styrene	0.91	AIBN	75
p-$VPhMe_2Si$	1.00	styrene	0.56	AIBN	76
p-$VPhSi_2Me_5$	1.13	styrene	0.71	benzoyl peroxide	48
$V(MeO)_3Si$	0	vinyl chloride	0.8	benzoyl peroxide	175
$V(MeO)_3Si$	0	acrylonitrile	6.0	benzoyl peroxide	175
$V(EtO)_3Si$	0	acrylonitrile	4.72	benzoyl peroxide	55
$V(EtO)_3Si$	0	acrylonitrile	4.75	benzoyl peroxide	175
$V(EtO)_3Si$	0	vinyl chloride	0.9	benzoyl peroxide	175
$V(EtO)_3Si$	0	styrene	13 ± 1	benzoyl peroxide	174
$V(EtO)_3Si$	0	styrene	22 ± 5	AIBN	75
$V(isopropyl)_3Si$	0	vinyl chloride	0.8	benzoyl peroxide	175
$V(isopropyl)_3Si$	0	acrylonitrile	6.5	benzoyl peroxide	175
$V(aceto)_3Si$	0	styrene	3.55 ± 0.2	benzoyl peroxide	174
V(tris-MeO)-(EtO)Si	0	acrylonitrile	2.45	benzoyl peroxide/bulk	55
$VMe(EtO)_2Si$	0	styrene	11.7 ± 0.1	bulk	56
$VMe(EtO)_2Si$	0.13 ± 0.06	styrene	5.7 ± 0.2	toluene	56
$VMe(EtO)_2Si$	0	vinyl chloride	1.2	benzoyl peroxide	174
$VMe(EtO)_2Si$	0	acrylonitrile	6.0	benzoyl peroxide	175
$Vet(EtO)_2Si$	0	vinyl chloride	1.0	benzoyl peroxide	175
$Vet(EtO)_2Si$	0	acrylonitrile	0.9	benzoyl peroxide	175
$VPh(EtO)_2Si$	0	vinyl chloride	0.7	benzoyl peroxide	175
$VPh(EtO)_2Si$	0	acrylonitrile	8.3	benzoyl peroxide	175
$VMe(aceto)_2Si$	0	styrene	10.4 ± 0.03	bulk	56
$VMe(aceto)_2Si$	0	styrene	4.01 ± 0.03	toluene	56
$VMe(aceto)_2Si$	0	acrylonitrile	2.26 ± 0.25	bulk	56
$(Me_3SiO)_3SiV$	0.1	styrene	60.0	benzoyl peroxide	177
$(Me_3SiO)_2SiVMe$	0.1	styrene	60.0	benzoyl peroxide	177
$(Me_3SiO)SiVMe_2$	0.1	styrene	60.0	benzoyl peroxide	177
$(Me_3SiO)_3SiV$	0.1	acrylonitrile	8.0	benzoyl peroxide	177
$(Me_3SiO)_2SiVMe$	0.1	acrylonitrile	8.0	benzoyl peroxide	177
$(Me_3SiO)SiVMe_2$	0.1	acrylonitrile	8.0	benzoyl peroxide	177
$(Me_3SiO)_3SiV$	0.01	vinyl acetate	0.99	benzoyl peroxide	177
$(Me_3SiO)_2SiVMe$	0.01	vinyl acetate	0.99	benzoyl peroxide	177
$(Me_3SiO)SiVMe_2$	0.01	vinyl acetate	0.99	benzoyl peroxide	177
$(Me_3SiO)_3SiV$	0.1	N-vinyl pyrrolidone	4.0	benzoyl peroxide	177
$(Me_3SiO)_3SiV$	0.50	vinyl chloride	0.9	benzoyl peroxide	177
$(Me_3SiO)_2SiVMe$	0.50	vinyl chloride	0.9	benzoyl peroxide	177
$(Me_3SiO)_3SiV$	0.20	perfluorovinyl chloride	0.05	benzoyl peroxide	177
$(Me_3SiO)_2SiVMe$	0.20	perfluorovinyl chloride	0.05	benzoyl peroxide	177

[a] V = vinyl.

[b] *Radical initiation unless otherwise noted.*

[c] *Anionic initiation.*

[d] *Cationic initiation.*

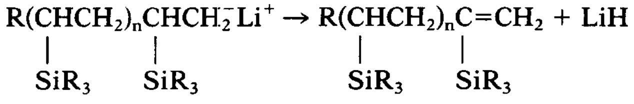
TABLE 2 Alfrey-Price Parameters for Vinylsilanes

System (Silane/Comonomer)[a]	*Q (Silane)*	*e (Silane)*	*Reference*
p-VPhMeSiH$_2$/styrene	1.1	−0.8	75
p-VPhMe$_2$Si/styrene	0.97	−0.04	76
p-VPhSi$_2$Me$_5$/styrene	0.96	−.33	47
Me$_3$SiVEt$_2$O/*i*-Bu-VEt$_2$O	0.18	−2.39	77
V(EtO)$_3$Si/styrene	0.03	+0.1	77
VMe$_3$Si/styrene	0.03	−0.1	77

[a] V = vinyl.

most all the organic monomers are used up, and then the silane addition occurs [62]. Table 2 lists some reported Alfrey-Price parameters, *Q* and *e*, which show that, in the radical copolymerization of triethoxyvinylsilane and trimethylvinylsilane with styrene, the silicon centers display an essential absence of conjugation ($Q = 0.03$), thus confirming previous proposals concerning lack of stabilization of a radical vinylsilane. The $CH_2{=}CHC_6H_4$-*p*-Si(Me)H$_2$ styrene copolymer has Alfrey-Price parameters very similar to those of styrene ($Q = 1.1$; $e = -0.8$) [75]. When the silane is $CH_2{=}CHC_6H_4$-*p*-Si(H)Me$_2$, the *Q* value (0.97) representing the degree of conjugation is very similar to that of styrene but the *e* value, −0.04, indicates that the −Si(H)Me$_2$ substituted phenyl group is more electron withdrawing than styrene. The pentamethyldisilyl, Si$_2$Me$_5$, function also shows a significant polar effect ($e = -.33$) but no resonance effect ($Q = 0.96$) as a substituent on styrene [48]. Triethoxyvinylsilane and trimethylvinylsilane have similar *Q* values (0.03), indicating they are very similar and exhibit little conjugative interactions. Triethoxyvinylsilane has an *e* value of +0.1, indicating that the substituent is more electron withdrawing than styrene, while trimethylvinylsilane ($e = -0.1$) is a weaker electron donor than styrene [77].

Vinylsilanes undergo anionic polymerization in a manner similar to styrene; thus, the presence of an electron withdrawing group, such as a phenyl substituent, increases the reactivity. The phenyl group increases the polarizability of the silicon center leading to greater reactivity in anionic processes [63]. As previously noted, silicon has the ability to stabilize α-carbanions. One difference between the polymerization of styrene and the polymerization of vinylsilanes is the presence of a termination step as shown below [34,74].



$$R(\underset{SiR_3}{CH}CH_2)_n\underset{SiR_3}{CH}CH_2^-Li^+ \rightarrow R(\underset{SiR_3}{CH}CH_2)_n\underset{SiR_3}{C}{=}CH_2 + LiH$$

While vinylsilanes have the ability to homopolymerize and copolymerize by both radical and anionic methods, the lack of radical stabilization and the effective stabilization of α-carbanions by silicon make anionic initiation the method of choice. The broad range of reactivity and *Q*/*e* values (Tables 1 and 2) indicates that the substituents on the silane, together with the extensive hyperconjugative interactions, make silanes candidates for a wide range of polymerization reactions. Numerous studies of vinylsiloxanes and siloxystyrenes and their role as cross-linking sites in poly(siloxane) chemistry have appeared in the literature but are beyond the scope of this review. Two recent systems which have been reported are of interest. An oligomeric copolymer has been prepared by the reaction of styrene and the vinylcyclosiloxane, $CH_2{=}CHSi(Me)OSiPh_2OSiPh_2O$. Polymers with longer siloxane chains are available from the reaction of these oligomers with (Me$_2$SiO)$_4$/KOH [78]. Poly(*p*-siloxystyrenes) have also been prepared [49].

Vinylgermanium Polymers

Although not as extensively studied as silicon polymers, there are vinyl polymers prepared from the heavier elements of group 14. There are several reports of the Zeigler-Natta polymerization of vinylgermanium compounds [79–81], but, overall, the work is scarce. Methylacrylyltriethylgermanium has been polymerized using AIBN or benzoyl peroxide as an initiator [82]. There are other reviews of the polymerization of organogermanium compounds [83,84]. The scarcity of work done in this area may be due to the difficulty and expense in preparing trimethylvinylgermanium [85], but some germanium polymers have been reported. $Me_3GeCH_2CH{=}CH_2$ polymerizes at 120°C and 6000 atm with use of a (Me$_3$CO)$_2$ catalyst to yield 34% of a liquid oligomer with a molecular weight of 560 [86]. $Et_3GeCH_2CH{=}CH_2$ polymerizes under the same conditions to yield 64% of an oily material with MW 780 [86]. $Me_3GeCH_2C(Me){=}CH_2$ does not polymerize under the same conditions. Germanyl substituted styrenes, $CH{=}CHC_6H_4$-*p*-R (R=GeMe$_3$, Ge$_2$Me$_5$, CH$_2$GeMe$_3$, CH$_2$Ge$_2$Me$_5$, SiMe$_2$OGeMe$_3$) have been polymerized using radical initiation [49].

Vinyltin Polymers

Organotin polymers and copolymers have received significantly more attention due to their use as long-lived, film-forming resinous antifouling coatings which exhibit steady leaching of the organotin compounds [87]. Polymers and copolymers of trialkyltin acrylate and methacrylate have wide-spread use as antibacterial, antifungal, and antifouling coatings [88,89]. Recent environmental concerns about the role of organotin compounds in natural waters will probably result in a decreased emphasis on the use of these materials in the future. There are several reviews on the Zeigler-Natta polymerization of vinyltin compounds [79–81,90].

The radical copolymerization [91–94] of $CH_2{=}C(Me)C(O)O\text{-}SnBu_3$ with $H_2C{=}C(Me)C(O)OR$ (R = Me, Pr, Bu) gives reactivity ratios of (0.79, 0.58), (0.58, 0.9), and (0.65, 0.68), respectively [88] (also see Table 3). These *r* values, being less than 1, indicate that monomers prefer to add to each other rather than to themselves, producing a significant incorporation of both monomers in the polymer. A reasonable set of reactivity ratios for tributyltin acrylate with methyl methacrylate is (0.40, 2.2), with propyl acrylate (0.32, 1.71), with butyl acrylate (0.20, 1.65), and with acrylonitrile (0.24, 1.01) [89,93]. The *r* values for methyl methacrylate and butyl acrylate are greater than 1, indicating that they exhibit preferential homopropagation rather than cross-propagation with tributyltin acrylate. The reactivity ratios (Table 3) for the radical copolymerization of tributyltin acrylate or methyl methacrylate with styrene, allyl methacrylate, butyl methacrylate, acrylonitrile, N-

TABLE 3 Reactivity Ratios for Vinyltin Copolymers

Monomer 1	r_1	*Monomer 2*	r_2	*Conditions*[a]	*Reference*
Tributyltin methacrylate	1.747	methyl acrylate	0.664	AIBN	91
Tributyltin methacrylate	1.259	ethyl acrylate	0.606	AIBN	91
Tributyltin methacrylate	0.846	butyl acrylate	0.572	AIBN	91
Tributyltin methacrylate	0.79	methyl methacrylate	0.58	AIBN	88
Tributyltin methacrylate	0.58	propyl methacrylate	0.9	AIBN	88
Tributyltin methacrylate	0.65	butyl methacrylate	0.08	AIBN	88
Tributyltin methacrylate	0.49	styrene	0.51	AIBN	88
Tributyltin methacrylate	4.408	vinyl acetate	0.017	AIBN	95
Tributyltin methacrylate	3.100	N-vinyl pyrrolidone	0.438	AIBN	95
Tributyltin methacrylate	0.465	acrylonitrile	0.467	AIBN	91
Triphenyltin methacrylate	0.69	acrylonitrile	0.16	AIBN	87
Triphenyltin methacrylate	0.76	styrene	0.47	AIBN	87
Triphenyltin methacrylate	1.22	N-vinyl pyrrolidone	0.36	AIBN	87
Triphenyltin methacrylate	2.58	methyl acrylate	0.66	AIBN	98
Triphenyltin methacrylate	2.37	ethyl acrylate	0.43	AIBN	98
Triphenyltin methacrylate	1.27	butyl acrylate	0.39	AIBN	98
Triphenyltin methacrylate	0.68	butyl methacrylate	0.83	AIBN	98
Triphenyltin methacrylate	0.94	methyl methacrylate	0.79	AIBN	98
Tributyltin maleate	0.05	styrene	15.4	AIBN	97
Tributyltin maleate	0.01	methyl methacrylate	6.7	AIBN	97
Tributyltin maleate	0.11	butyl acrylate	9.39	AIBN	97
Tributyltin maleate	0.06	acrylamide	122.4	AIBN	97
Tributyltin acrylate	0.401	methyl methacrylate	2.197	AIBN	89
Tributyltin acrylate	0.82	methyl acrylate	1.46	AIBN	97
Tributyltin acrylate	0.03 ± 0.06	methyl acrylate	0.82 ± 0.07	AIBN	92
Tributyltin acrylate	0.51 ± 0.09	methyl acrylate	1.97 ± 0.15	emulsion	101
Tributyltin acrylate	0.41 ± 0.07	ethyl acrylate	0.89 ± 0.15	emulsion	101
Tributyltin acrylate	0.08	ethyl acrylate	0.75 ± 0.04	AIBN	92
Tributyltin acrylate	0.323	propyl acrylate	1.73	AIBN	89
Tributyltin acrylate	0.196	butyl acrylate	1.65	AIBN	89
Tributyltin acrylate	0.15 ± 0.08	butyl acrylate	0.70 ± 0.01	AIBN	92
Tributyltin acrylate	0.15 ± 0.08	butyl acrylate	0.70 ± 0.01	AIBN	93
Tributyltin acrylate	0.42 ± 0.11	butyl acrylate	0.18 ± 0.39	emulsion	101
Tributyltin acrylate	0.49 ± 0.05	octyl acrylate	0.67 ± 0.09	emulsion	101
Tributyltin acrylate	0.22 ± 0.11	octyl acrylate	0.60 ± 0.03	AIBN	92
Tributyltin acrylate	0.234	acrylonitrile	1.008	AIBN	89
Tributyltin acrylate	0.10 ± 0.05	acrylonitrile	0.99 ± 0.18	AIBN	93
Tributyltin acrylate	2.567	vinyl acetate	0.006	AIBN	95
Tributyltin acrylate	0.513	N-vinyl pyrrolidone	0.01	AIBN	95
Tributyltin acrylate	0.82	acrylamide	0.11	AIBN	97
m-(Tributyltin)styrene	.03	styrene	18.5	AIBN	104
m-(Tributyltin)styrene	.01	ethyl acrylate	10.4	AIBN	104
m-(Tributyltin)styrene	.03	methyl methacrylate	0.69	AIBN	104
m-(Tributyltin)styrene	.38	vinyl acetate	5.33	AIBN	104
m-(Tributyltin)styrene	4×10^{-5}	acrylonitrile	4.88	AIBN	104

[a] Radical initiation.

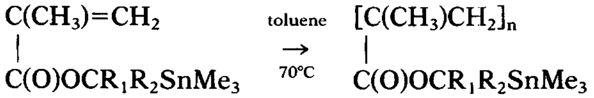
vinylpyrrolidone, and vinyl acetate have been reported [87,95,96]. The reactivity ratios and the *Q* and *e* values for the radical copolymerization of tri-n-butyltin maleate/acrylate/methacrylate with methyl methacrylate, styrene, butyl acrylate, acrylamide, and methyl acrylate have also been reported [97]. The reactivity ratios for the radical copolymerization of triphenyltin methacrylate with acrylonitrile, styrene, N-vinylpyrrolidone, n-butyl methylacrylate, and acrylic and methacrylic acid esters have also been reported (see Table 3) [87,98,99].

As can be seen in Table 3, tributyltin methacrylate [91] and triphenyltin methacrylate [98] have *r* values greater than 1 when they undergo copolymerization with methyl acrylate and ethyl acrylate. Similarly, tributyltin methacrylate with vinyl acetate, N-vinylpyrrolidone, and acrylonitrile has *r* values greater than 1. These *r* values indicate that the tin monomers prefer to homopropagate rather than crosspropagate in these reactions; thus, the polymer will have a higher concentration of the tin monomer. Styrene, methyl methacrylate, butyl acrylate, and acrylamide have very large *r* values in the copolymerization with tributyltin maleate, indicating that the copolymer formed will contain more of the organic monomer than tin. The reactivity ratios for tributyltin acrylate with alkyl methylacrylate, alkyl acrylates, acrylonitrile, and styrene indicate that the copolymers will have a random distribution of monomer with a tendency toward alternation as the ester alkyl chain length increases [96]. Since many of these radical copolymerization reactions have low values for r_1 and r_2, a tendency toward alternating behavior might be expected.

The copolymerizations of $R_3SnOC(O)C(Me)=CH_2$ and $R_2Sn[OC(O)C(Me)=CH_2]_2$, where R = Me, to C_8H_{17} and phenyl have been reported [100]. Tributyltin acrylate and methyl, ethyl, butyl, and octyl acrylate have been copolymerized by emulsion copolymerization using 1% ammonium sulfate and 8% emulsifier at 72°C [101].

The homopolymerization of tributyltin methacrylate using radical initiators gives an atactic polymer. Poly(tributyltinmethacrylate-co-styrene) was prepared by free radical copolymerization and the reactivity ratios determined as follows: r_1 (M_1, styrene) = 0.51; r_2 (tin) = 0.49. The *Q* and *e* values for the tin compound were found to be 0.78 and 0.38 [102]. Isotactic and enriched syndiotactic homopolymers can be prepared from the reactions of poly(methacrylic acids) with tributyltin oxide [10].

Another class of tin polymers has been reported. The monomer, 1-(Me_3Sn)alkyl methacrylate, has the tin atom bound to C-1 on the ester not on the oxygen as in other tin compounds. This monomer will undergo radical catalyzed homopolymeration and copolymeration with methyl methacrylate to form a random copolymer [103].



$$\begin{array}{c} C(CH_3)=CH_2 \\ | \\ C(O)OCR_1R_2SnMe_3 \end{array} \xrightarrow[70^\circ C]{\text{toluene}} \begin{array}{c} [C(CH_3)CH_2]_n \\ | \\ C(O)OCR_1R_2SnMe_3 \end{array}$$

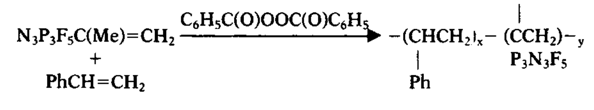
Stannylstyrenes have also recently attracted attention. Radical homopolymerization of $CH_2=CHC_6H_4$-*p*-CH_2SnMe_3 has been reported [49] as has the copolymerization of $CH_2=CHC_6H_4$-*m*-$SnBu_3$ with styrene, ethyl acrylate, methyl methacrylate, vinyl acetate, and acrylonitrile [104]. Reactivity studies in the latter system suggest the importance of steric and polar contributions of the tri-n-butyltin fragment to the propagation behavior of the olefin [104]. Vinyltin compounds have also been polymerized using alkyllithium catalysts [104].

Vinyllead Polymers

There are several older reviews covering vinyllead polymers [66,80,81]. The radical polymerization of $Ph_2Pb(methacrylate)_2$ was initiated with AIBN or a peroxide [105]. One of the uses for lead-containing olefin polymers is to produce radiation shields [106,107]. Lead polyester and lead acrylate polymers are also used as an impregnating agent for treating the imperfections of cast and sintered metal parts to be used in nuclear devices [108]. Future developments in this area will depend on the balance of useful applications vs. environmental concerns relative to lead toxicity.

GROUP 15. VINYLPHOSPHAZENE POLYMERS

Work in the area of the polymerization of vinylphosphazenes is relatively recent, with one of the important aspects of these polymers being their flame retardant nature [109,110]. The monomer $P_3N_3F_5C(Me)=CH_2$ does not homopolymerize under radical, anionic, or cationic initiation but does undergo radical copolymerization with styrene [111]. The *Q* and *e* values for the propenyl phosphazene are 0.21



$$\begin{array}{c} N_3P_3F_5C(Me)=CH_2 \\ + \\ PhCH=CH_2 \end{array} \xrightarrow{C_6H_5C(O)OOC(O)C_6H_5} -\begin{array}{c} (CHCH_2)_x \\ | \\ Ph \end{array} - \begin{array}{c} CH_3 \\ | \\ (CCH_2) \\ P_3N_3F_5 \end{array}-_y$$

and 0.18, respectively, and the reactivity ratios are available (see Tables 4 and 6). The copolymers from 2-(2-propenyl)-pentafluorocyclotriphosphazene and vinylbenzyl chloride or styrene have been prepared with a phosphazene content between 6% and 40% [111,112]. The difficulty in polymerizing vinyl-phosphazenes has been attributed, in part, to the high polarity of the olefin. Thus, work has been directed toward decreasing the polarity of the ole-

TABLE 4 Reactivity Data for Vinylphosphazene Copolymers

Monomer 1	*r_1*	*Monomer 2*	*r_2*	*Conditions*	*Reference*
$N_3P_3F_5C(CH_3)=CH_2$	1.35	styrene	2.20	AIBN	111
$N_3P_3F_5C(OC_2H_5)=CH_2$	0.19	styrene	3.04	AIBN	126
para-$N_3P_3F_5C_6H_4C(CH_3)=CH_2$	0.28	styrene	0.41	AIBN	117
meta-$N_3P_3F_5C_6H_4C(CH_3)=CH_2$	0.28	styrene	0.58	AIBN	117
$N_3P_3Cl_5OC_6H_4C_6H_4CH=CH_2$	2.4	styrene	0.36	AIBN	124
$N_3P_3Cl_5OC_6H_4C_6H_4CH=CH_2$	2.1	MMA	0.23	AIBN	124
$N_3P_3Cl_5O(CH_2)_2OC(O)C(CH_3)=CH_2$	1.08	MMA	0.46	AIBN	121

TABLE 5 Penultimate Reactivity Data for (α-Methylethenylphenyl)pentafluroocyclotriphosphazenes

Comonomers	*r_1*	*r_1'*	*r_2*	*r_2'*	*Reference*
MMA-I	0.70	0.23	0.38	2.80	117
MMA-II	1.23	0.32	0.0	39.50	117
STY-I	0.63	0.18	0.63	0.095	117
STY-II	0.58	0.87	0.15	0.88	117

MMA = methyl methacrylate; STY = styrene; I = *para*-$N_3P_3F_5C_6H_4C(CH_3)=CH_2$; and II = *meta*-$N_3P_3F_5C_6H_4C(CH_3)=CH_2$.

fin. This can be done in two ways. The strong electron withdrawing effect of the phosphazene [113–115] can be counterbalanced by placement of an electron donating group on the olefin. Another method is to place an insulating group between the olefin and the phosphazene ring, as in the case of phosphazene derivatives of α-methylstyrene [115,116]. The radical copolymerization of an example of these types of monomers, 3- and 4-(α-methylethenylphenyl) pentafluorocyclotriphosphazene, ($N_3P_3F_5C_6H_4C(CH_3)=CH_2$), for example, with styrene and methyl methacrylate leads to flame retardant copolymers with up to 66% and 44% phosphazene content, respectively [117]. The amount of phosphazene monomer incorporated into a copolymer is the same for the *meta* or *para* derivatives of the monomers. The methyl methacrylate copolymerization does not fit a terminal model, and reactivity studies indicate that penultimate behavior, i.e., the effect of the next to last monomer unit on reactivity, is observed [117]. The reactivity ratios for the monomers have been computed using programs [118] for both terminal and penultimate models. The penultimate parameters are listed in Table 5. Recent studies have employed oxygen atoms to separate the organofunctional unit from the phosphazene. The radical polymerization of vinyloxy- [119,120] and methacryloyl ethenedioxy pentachlorocyclotriphosphazenes [120], $N_3P_3Cl_5OR$ ($R=CH=CH_2,(CH_2)_2OC(O)C(CH_3)=CH_2$), leads to high and moderate molecular weight polymers, respectively. The methacryloyl ethenedioxy derivative undergoes copolymerization with methyl methacrylate. The reactivity parameters (r_1, r_2; Q, e) show significant polarity effects of the phosphazene on the olefin in spite of being separated by several atoms [121]. Inoue and co-workers have explored the homo- and copolymerization of 4′-vinyl-4-biphenylyloxy phosphazenes, $N_3P_3X_5OC_6H_4C_6H_4CH=CH_2$ (X=F, Cl) [122–124]. The homopolymerization rates are identical for the chloro and fluoro derivatives, indicating the absence of significant electronic perturbation of the vinyl group by the phosphazene [123]. Copolymerization of the chloro derivatives with styrene and methyl methacrylate occurs readily. The reactivity parameters (Tables 4 and 6) suggest a polar but not mesomeric effect of the phosphazene [124]. Preliminary data on the homo- and copolymerization of $2,2^1$-$N_3P_3Cl_4$(*i*-C_3H_7)R ($R=CH(OH)C_6H_4CH=CH_2$, $CH(OC(O)C(CH_3)=CH_2CH_3)$) have been presented [125]. Mediation of the electron withdrawing effect of the phosphazene by modification of the olefin has been

TABLE 6 Alfrey-Price Parameters for Vinylphosphazenes

System (Phosphazene/Comonomer)	*Q (Phosphazene)*	*e (Phosphazene)*	*Reference*
$N_3P_3F_5C(CH_3)=CH_2$/styrene	0.21	0.18	111
$N_3P_3F_5C(OC_2H_5)=CH_2$/styrene	0.18	−0.06	126
para-$N_3P_3F_5C_6H_4C(CH_3)=CH_2$/styrene	0.72	0.72	117
meta-$N_3P_3F_5C_6H_4C(CH_3)=CH_2$/styrene	0.63	0.58	117
$N_3P_3Cl_5OC_6H_4C_6H_4CH=CH_2$/styrene	2.0	−0.39	124
$N_3P_3Cl_5O(CH_2)_2OC(O)C(CH_3)=CH_2$/MMA	0.96	1.24	121

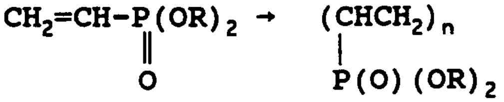
studied using 2-(α-ethoxyvinyl)pentafluorocyclotriphosphazene. The reactivity ratios and the Q and e values (Tables 4 and 6) obtained in the styrene and methyl methacrylate copolymerization of the ethoxyvinylphosphazene show that the electronic behavior of the olefin is closer to that of vinyl acetate than to that of a vinyl ether [126].

Vinylphosphine Oxides

The polymers and copolymers of vinylphosphine oxides, $RR'(C_2H_3)P{=}O$, have been used to produce flame retardant materials. Although most of the work has been done on copolymers, a homopolymer with R= R'= Ph has been reported [127]. Diphenylvinylphosphine oxide has been polymerized by a free radical process in solution and in bulk to give low molecular weight products [128–130]. Even with anionic polymerization of this monomer with organometallic catalysts, polymers with molecular weights only up to 10,000 are obtained [131]. The highest molecular weights, up to 30,000, were observed when the polymerization was induced by X-rays [132,133]. The reactivity ratios for the free radical copolymerization of diphenylvinylphosphine oxide (M_2) with acrylonitrile (M_1) have been found to be r_1 = 3.8 and r_2 = 0.16 (see Table 7). With vinyl acetate (M_1), the ratios are r_1 = 0.38 and r_2 = 1.7 [135]. For the diphenylvinylphosphine oxide-acrylonitrile and diphenylvinylphosphine oxide-vinyl acetate systems, the Q and e values were found to be (0.068, 0.49) and (0.059, 0.44), respectively [135]. A copolymerization of diphenylvinylphosphine oxide and methyl methacrylate using benzoyl peroxide as the radical initiator produced an oligomer with a molecular weight of 5400. A characteristic shared by these copolymers is that, as the amount of vinylphosphine oxide in the copolymer increases, the intrinsic viscosity and hence molecular weight of the copolymer decreases [135].

Vinylphosphonic Acid Esters

Polymers and copolymers of vinylphosphonic acid esters, $C_2H_3P(O)(OR)_2$, are used to produce fire resistant cotton, nylon, cellulose acetate-Vinylon, and acrylic textiles [136–140]. Some physical properties of these compounds have been reported [141]. Homopolymerization can be carried out using various initiation methods.



$$\mathrm{CH_2{=}CH{-}\underset{\underset{O}{\|}}{P}(OR)_2 \rightarrow \underset{\underset{P(O)\,(OR)_2}{|}}{(CHCH_2)_n}}$$

The light initiated polymerization of dimethyl, diisobutyl, and diethylvinylphosphonic acid esters using di-tert-butylperoxide as the initiator has been reported [147]. Reactivity ratios and activation energies are also given [163]. In another account, bis(2-chloroethyl) vinylphosphonic acid ester was polymerized in a Zeigler-Natta process [142–144]. The kinetics were measured, and interactions between the vinylphosphonic acid ester and the aluminum compounds are proposed [145]. The highest yield of polymer is obtained when the phosphonic acid ester to aluminum ratio is 10:1. The rate increases as the size of the alkyl group increases.

Bis(2-chloroethyl) vinylphosphonic acid ester can also be polymerized using gamma rays which induce a free radical reaction [146]. Diethyl and dimethyl vinylphosphonic acid esters have undergone radical initiated homopolymerization using AIBN as the initiator [147]. Moldable polymers with high heat stability are produced when $H_2C{=}CR{-}P(O)R'_2$ (R=H, Me; R_2=OEt, OPh, SEt, NMe_2) poly-

TABLE 7 Reactivity Data for Vinylphosphine Oxide and Vinylphosphonic Acid Ester Copolymerization with Organic Monomers

Monomer 1[a]	r_1	*Monomer 2*	r_2	*Conditions*	*Reference*
$Ph_2VP(O)$	0.16	acrylonitrile	3.8	benzoyl peroxide	135
$Ph_2VP(O)$	1.7	vinyl acetate	0.38	benzoyl peroxide	135
$VP(O)(OPh)_2$	0.2	methyl acrylate	3.1	radical	153
$VP(O)(OPh\text{-}o\text{-}NO_2)_2$	0.13	methyl acrylate	3.5	radical	153
$VP(O)(OCH_2CH_2Cl)_2$	0.13	acrylonitrile	7.3	radical	155
$VP(O)(OCH_2CH_2Cl)_2$	0.37 ± 0.1	vinyl chloride	0.26 ± .5	radical	156
$VP(O)(OCH_2CH_2Cl)_2$	0.47	vinyl acetate	0.33	bulk, radical	167
$VP(O)(OCH_2CH_2Cl)_2$	2.7	styrene	2.04	radical	160
$VP(O)(OBu)_2$	0	styrene	1.7	radical	160
$VP(O)(OEt)_2$	0.88 ± .02	acrylic acid	3.7 ± 0.2	bulk, UV	163
$VP(O)(OBu)_2$	0.87 ± 0.16	acrylic acid	3.99 ± 0.34	bulk, UV	163
$VP(O)(O\text{-}iBu)_2$	0.47 ± 0.08	acrylic acid	2.91 ± 0.3	bulk, UV	163
$VP(O)(O\text{-}iBu)_2$	0	styrene	2.5	radical	160

[a] V = vinyl.

TABLE 8 Alfrey-Price Parameters for Vinylphosphine Oxide and Vinylphosphonic Acid Esters

System (Phosphorus/Comonomer)[a]	*Q (P)*	*e (P)*	*Reference*
$\mathrm{Ph_2VP(O)}$/acrylonitrile	0.068	0.49	135
$\mathrm{Ph_2VP(O)}$/vinyl acetate	0.059	0.44	135
$\mathrm{VP(O)(OPh)_2}$/methyl acrylate	0.16	−0.71	153
$\mathrm{VP(O)(OPh\text{-}O\text{-}NO_2)_2}$/methyl acrylate	0.16	−0.54	153
$\mathrm{VP(O)(OCH_2CH_2Cl)_2}$/acrylonitrile	0.06	+0.98	155
$\mathrm{VP(O)(OCH_2CH_2Cl)_2}$/vinyl acetate	0.06	+1.1	167
$\mathrm{VP(O)(OCH_2CH_2Cl)_2}$/vinyl chloride	0.23	−1.73	156

[a] V = vinyl.

merization is initiated using Grignard reagents [148]. The in situ catalyzed thermal polymerization of bis(2-chloroethyl) vinylphosphonic acid ester with lauroyl peroxide can be used to produce materials with high flame resistance [149].

There have been a number of studies of the copolymerization of vinylphosphonic acid esters with various organic comonomers. The copolymerization of bis(2-chloroethyl) vinylphosphonic acid ester with ethylene can be effected in both solution and bulk [150]. The homopolymerization of diphenyl and bis(2-chloroethyl) vinylphosphonic acid esters proceeds at a high reaction rate. Copolymerizations of these two monomers with ethylene is slower than the homopolymerization but faster than that of ethylene copolymerized with dibutyl and diisobutyl vinylphosphonic acid ester. This difference in reactivity is related to differences in polarity. Copolymerization reactions proceed at an overall slower rate than the homopolymerizations due to two competing chain transfer reactions. At low concentrations, the predominant reaction is the intramolecular cyclization leading to the formation of stable phosphorus radicals. At high concentrations, the intramolecular abstraction of hydrogen predominates [151].

In the copolymerization of diphenyl and bis(2-chloroethyl) vinylphosphonic acid esters with methyl acrylate, the polarity of the substituents has an effect on the reaction rate and viscosity [152]. Bis(2-chloroethyl) vinylphosphonic acid ester copolymerizes faster than diphenyl vinylphosphonic acid ester with methyl acrylate. The copolymerization of vinyl acetate and diethyl vinylphosphonic acid ester using radical initiation has been reported to have the reactivity parameters [134]. For the copolymerization of diphenyl vinylphosphonic acid ester with methyl acrylate, the reactivity ratios are 0.20 and 3.1, respectively (Table 7). The Q and e values of the phosphonic acid ester (Table 8) are 0.16 and −0.71 [153]. The copolymerization of bis-(o-nitrophenyl) vinylphosphonic acid ester with methyl acrylate yields reactivity ratios of 0.13 and 3.5, respectively. The Q and e values are 0.15 and −0.54, respectively [153,154]. In the free radical copolymerization of bis(2-chloroethyl) vinylphosphonic acid ester with acrylonitrile, the reactivity ratios were found to be 0.13 and 7.3, respectively. The Q and e values were 0.06 and 0.98 [155]. Block copolymers derived from methyl, ethyl, propyl and allyl vinylphosphonates, and acrylonitrile all have self-extinguishing properties when subjected to flames [156].

The copolymerization of bis(2-chloroethyl) vinylphosphonate (monomer 1) and vinyl chloride gives r_1 (0.37 ± 0.1) and r_2 (0.26 ± 0.5), respectively [157]. Di(β-chloroethyl) vinylphosphonic acid ester can also be copolymerized in bulk using AIBN as the initiator [158]. The copolymerization of styrene (monomer 1) with dimethyl, diethyl, and bis(β-chloroethyl) vinylphosphonic acid esters gives r_1 values in the range of 2.45–6.32 and r_2 values in the range of 0.015–0.183 [159]. The reactivity ratios for styrene and di(β-chloroethyl) vinylphosphonic acid ester are 2.04 and 2.7 [160]. For styrene and dibutyl vinylphosphonic acid ester, the r values are 1.7 and 0 [160]. For styrene and di(isobutyl) vinylphosphonic acid ester, the r values are 2.5 and 0 [160]. Clearly, significant electronic perturbations of the olefin result from changes in alkyl group electronegativity.

For the copolymerization of styrene and $\mathrm{H_2C{=}CHZP(O)(OR)_2}$, where Z = p-$\mathrm{C_6H_4}$, p-$\mathrm{C_6H_4CH_2}$-, p-$\mathrm{C_6H_4CH_2CH_2}$- and R = $\mathrm{Me_3Si}$, Et, the reactivity ratio data for both anionic and radical initiations are given [161]. For Z = Me, Br, OAc, $\mathrm{CO_2Et}$ and R = Me, Et, r values and Q/e parameters are reported [162]. For the copolymerization of methyl methacrylate with $\mathrm{H_2C{=}CR\text{-}P(O)(OR')_2}$ (R = Me, Br, $\mathrm{CO_2Et}$ and R′ = Me, Et), r, Q, and e values have been reported [162]. Block copolymers from methyl, ethyl, propyl, and allyl vinylphosphonates all have self-extinguishing properties when subjected to flames [156].

The copolymerization of acrylic acid with diethyl vinylphosphonic acid ester gives r values of (3.7 ± 0.2) and (0.88 ± 0.02). For acrylic acid with dibutyl and di(isobutyl) vinylphosphonic acid ester, r values are (3.99 ± 0.34), (0.87 ± 0.16), (2.91 ± 0.3), and (0.47 ± 0.08) [163]. The preceding data were obtained under bulk conditions using UV radiation. Acrylic acid with diethyl vinylphosphonic acid ester in benzene, dioxane, or $\mathrm{MeCO_2Et\text{-}H_2O}$ gives r values in the range of 1.30–3.80 for acrylic acid and 0.21–0.48 for the vinylphosphonic acid ester [164–166]. The reactivity ratios for the copolymerization of vinyl acetate and bis(2-chloroethyl) vinylphosphonic acid ester under free radical, bulk conditions are 0.47 and 0.33, respectively. Again, the electronic effect of the chloroalkyl group is noted. The Q and e values were determined to be 0.06 and 1.1 [167]. For dimethyl and diethyl vinylphosphonic acid ester with vinyl acetate, the r values are in the range of 0.74–0.85 and 0.04–0.09, respectively [159].

There are a number of other unusual co-oligomers and copolymers which can be found in the literature, such as vinyl chloride-bis(2-chloroethyl) vinylphosphonic acid ester-ethyl acrylate copolymer [168], allylphosphonic acid and diethylene glycol copolymers [169], phenyl allylphosphonic acid ester with poly(ethylene fumarate maleate) [151], plus many others [170,171].

On inspection of the comonomers that react with the vinylphosphonic acid esters (Table 7), the larger *r* values for the comonomers indicate that the comonomer will prefer to add to itself rather than to the vinylphosphonic acid ester. Thus, the copolymers formed will have a larger incorporation of the comonomer than the vinylphosphonic acid ester. The reduced homopolymerization reactivity and the preferential reactivity of organic comonomers in radical copolymerization suggest significant parallels to the vinylsilanes, and, consequently, similar electronic constraints may be operative. The low *Q* values indicate minimal mesomeric interactions of the vinyl group with the phosphorus center, and the wide range of *e* values indicates the ease of perturbation of vinyl polarity by changes in other substituents on the phosphorus center.

GROUP 16

At this point, the distinction between inorganic and organic substituents becomes unclear, so we will only briefly consider one class of recently explored systems which have a Group 16 substituent.

Vinylsulfoxides

Alkylation and other electrophilic reactions of lithio-β-sulfinyl carbanions are generally stereoselective. The anionic polymerization of vinylsulfoxides is interesting, because stereoregularity of the polymer is expected for several reasons. First, the S–O bond is highly polar and coordinates strongly with metal counterions. Thus, the polymerization can be compared to the polymerization of polar molecules, such as methacrylates and 2-vinylpyridines, where such coordination has been shown to strongly affect the stereochemistry. Also, the sulfinyl group is chiral, and reactions of lithio-β-sulfinyl carbanions with electrophiles tend to be stereoselective [172]. Using 1-lithio-1-(phenylsulfinyl)-ethane as the initiator, vinylphenylsulfoxide was completely converted to polymer. Polymerization of racemic vinylphenylsulfoxide forms an atactic polymer, while the polymerization of optically enriched vinylphenylsulfoxide forms a highly stereoregular, optically active polymer. The monomer is configurationally stable under the polymerization conditions, and stereoselective polymerization is possible [173].

It is clear from the material presented in this review that polymerization, or copolymerization, of vinyl (and *p*-vinylphenyl) main group derivatives represents an effective methodology for the synthesis of hybrid organic-inorganic polymers. These novel materials often exhibit some of the characteristics of the inorganic entity, which results in useful modifications of a traditional organic polymer. Studies of the reactivity patterns of the main group monomers allow for some insight into the electronic perturbations of the olefin by the inorganic entity.

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