ALLYL MONOMERS AND POLYMERS

1. Introduction

Allyl compounds comprise a large group of ethylenic compounds having unique reactivities and uses often contrasting with those of typical vinyl-type compounds (styrenes, acrylics, vinyl esters and ethers, and related compounds). In allyl compounds the double bond is not substituted by a strong activating group to promote polymerization but is attached to a carbon which generally bears one or more reactive hydrogen atoms, eg,

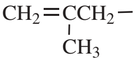
$CH_2{=}CHCH_3$	$CH_2{=}CHCH_2OOCR$	$CH_2{=}CHCHX_2$
propylene	allyl ester	3,3-dihalo-1-propenes

The allylic 1-alkenes, which yield useful polymers by Ziegler-type catalysts, are not discussed here. Unlike monovinyl compounds, monoallyl compounds do not form homopolymers of high molecular weight by free-radical or conventional ionic mechanisms; in general, only viscous liquid homopolymers of limited use have been obtained. This is explained by the low reactivity of the ethylenic double bond together with the high reactivity of hydrogen atoms on the allylic carbon in reducing the molecular weight by degradative chain transfer (1). However, numerous monoallyl compounds, including some that occur in nature, are known outside the polymer field. Examples are allyl sulfur compounds of onions, mustard, and other food flavors; allyl esters used in perfumes; allylic drugs and other compounds of biologic activity; as well as important intermediates for organic syntheses (see ALLYL ALCOHOL AND DERIVATIVES).

In contrast, many allyl compounds containing two or more reactive double bonds yield solid, high molecular weight polymers by initiation with suitable free-radical catalysts. A number of polyfunctional allyl esters have achieved importance in polymerization and copolymerization especially to obtain heat-resistant cast sheets and thermoset moldings. The reactivities of these monomers often permit polymerization in two stages: a solid prepolymer containing reactive double bonds can be molded by heating; then completion of polymerization gives cross-linked articles of superior heat resistance. The most important examples of allyl polymers are the CR-39 or diallyl diglycol carbonate polymers and molding materials based on diallyl phthalates.

Another use is of minor proportions of polyfunctional allyl esters, eg, diallyl maleate, triallyl cyanurate, and triallyl isocyanurate, for cross-linking or curing preformed vinyl-type polymers such as polyethylene and vinyl chloride copolymers. These reactions are examples of graft copolymerization in which specific added peroxides or high energy radiation achieve optimum cross-linking (see COPOLYMERS).

Small proportions of mono- or polyfunctional allylic monomers also may be added as regulators or modifiers of vinyl polymerization for controlling molecular weight and polymer properties. Polyfunctional allylic compounds of high boiling point and compatibility are employed as stabilizers against oxidative degradation and heat discoloration of polymers. Diallyl ammonium salt copolymers are used in water purification and flocculation. Compounds containing one or more methallyl groups

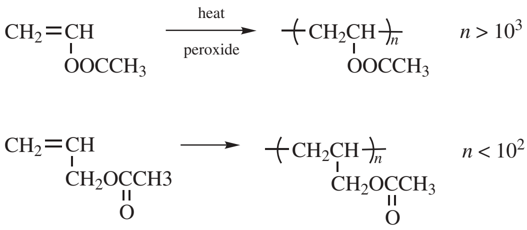


$$CH_2{=}\underset{CH_3}{C}CH_2{-}$$

find relatively little commercial utility.

2. Reactivity of Allyl Compounds

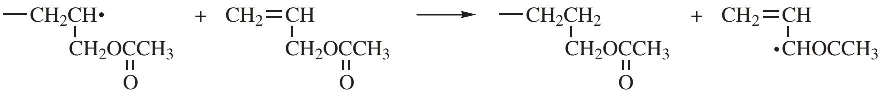
Whereas vinyl acetate [108-05-4] ($C_4H_6O_2$), upon heating with benzoyl peroxide or other free-radical initators, forms solid polymers of high molecular weight, similar treatment of allyl acetate [591-87-7] ($C_5H_8O_2$) gives only viscous liquid polymers.



$$CH_2{=}\underset{OOCCH_3}{CH} \xrightarrow[\text{peroxide}]{\text{heat}} \left(\underset{OOCCH_3}{CH_2CH}\right)_n \qquad n > 10^3$$

$$CH_2{=}\underset{CH_2O\underset{\underset{O}{\|}}{C}CH3}{CH} \longrightarrow \left(\underset{CH_2O\underset{\underset{O}{\|}}{C}CH_3}{CH_2CH}\right)_n \qquad n < 10^2$$

This is explained by the low reactivity of the double bond of the allyl compound together with prevalence of chain termination through reaction of allylic H atoms as shown (2).



$$-\underset{CH_2O\underset{\underset{O}{\|}}{C}CH_3}{CH_2CH\cdot} + CH_2{=}\underset{CH_2O\underset{\underset{O}{\|}}{C}CH_3}{CH} \longrightarrow -\underset{CH_2O\underset{\underset{O}{\|}}{C}CH_3}{CH_2CH_2} + CH_2{=}\underset{\cdot CHOCCH_3}{CH}$$

When vinyl and allyl monomers undergo chain transfer with solvents, so-called telomers may form, generally of rather low molecular weight (1).

Because of the low reactivity and tendency to undergo chain transfer, small additions of most allyl compounds retard polymerization of typical vinyl monomers in free-radical systems (1,3) and may be useful in controlling molecular weight and structure in polymers.

Many polyallyl compounds, upon heating with radical initiators, form solid high polymers in spite of chain transfer and loss of some double bonds by cyclization. With diallyl esters, such as diallyl phthalates, these slower polymerizations can be controlled more readily than in the polymerization of poly-functional vinyl compounds to give soluble prepolymers containing reactive double bonds (1,4). Cyclization in polymerization of diallyl compounds also can occur depending on the reaction conditions (5). In general, more cyclization occurs at lower monomer concentrations in solution and cross-linking is thereby reduced.

Few allyl monomers have been polymerized to useful, well-characterized products of high molecular weight by ionic methods, eg, by Lewis acid or base catalysts. Polymerization of the 1-alkenes by Ziegler catalysts is an exception. However, addition of acidic substances, at room temperature or upon heating, often gives viscous liquid low mol wt polymers, frequently along with by-products of uncertain structure.

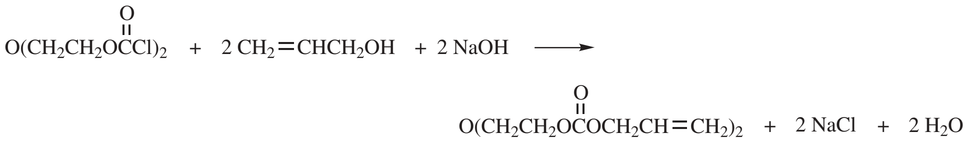
In special cases allyl compounds, such as diallyl [592-42-7], (C_6H_{10}), (1,5-hexadiene) and diallyl ether [557-40-4] ($C_6H_{10}O$), can form high polymers by addition of active hydrogen atoms. The best known case is the polymerization of diallyl with dimercaptans using free-radical initiation (6). These reactions are related to chain transfer and what has been called telocopolymerization (1,7).

Allyl compounds, depending on the structure of substituents, can undergo other reactions such as rearrangements, hydrolysis, and additions. Such reactions that may affect polymerization and have health considerations have been closely studied only with important industrial compounds (1).

3. Diallyl Carbonate Cast Plastics

From a number of diallyl esters investigated, diallyl diglycol carbonate or diethylene glycol bis(allyl carbonate), DADC, was developed to produce by bulk polymerization cast sheets, lenses, and other shapes of outstanding scratch resistance, and optical and mechanical properties. CR-39, a trademark of PPG Industries, is used to describe this material. DADC is the CR-39 monomer [142-22-3] from which CR-39 homopolymer [25656-90-0] $(C_{12}H_{18}O_7)_x$ is made. CR-39 polymers have greater impact resistance and lower density than glass. These polymers are the most important clear, organic optical materials shaped by the casting process and by machining. Many polyfunctional ethylenic monomers have been patented (8,9).

3.1. DADC Monomers. Reaction of allyl alcohol in the presence of alkali with diethylene glycol bis(chloroformate), obtained from the glycol and phosgene, gives the monomer



$$O(CH_2CH_2O\overset{\overset{O}{\|}}{C}Cl)_2 + 2\,CH_2{=}CHCH_2OH + 2\,NaOH \longrightarrow O(CH_2CH_2O\overset{\overset{O}{\|}}{C}OCH_2CH{=}CH_2)_2 + 2\,NaCl + 2\,H_2O$$

In another method, phosgene is gradually passed into 1,2-propylene glycol (9). The chloroformate is washed, dried, and distilled at 266 Pa (2 mm Hg) and added slowly to a mixture of allyl alcohol and pyridine below 15°C. The purified monomer 1,2-propylene glycol bis(allyl carbonate) ($C_{11}H_{16}O_6$) heated with lauroyl peroxide at 70°C gives a hard clear, polymer.

Reaction of allyl chloroformate and diethylene glycol in the presence of alkali with cooling is another method of preparing the diallyl carbonate ester DADC. The properties of diallyl carbonate monomers are given in Table 1.

DADC monomer is a colorless liquid of mild odor and a viscosity of 9 mPa s(=cP) at 25°C. It is low in toxicity, but can produce skin irritation. It is fairly resistant to saponification by dilute alkali. Contact with strong alkali at

Table 1. **Properties of Diallyl Glycol Carbonate Monomers**

Monomer	Molecular formula	CAS Registry Number	Boiling point, °C_{Pa}[a]	n_D^{20}	d_4^{20}
ethylene glycol bis(allyl carbonate)	$C_{10}H_{14}O_6$	[4074-91-3]	122_{133}	1.444	1.114
diethylene glycol bis(allyl carbonate)[b]	$C_{12}H_{18}O_7$	[142-22-3]	160_{266}	1.452	1.143
triethylene glycol bis(allyl carbonate)	$C_{14}H_{22}O_8$		polymerized	1.452	1.135
tetraethylene glycol bis(allyl carbonate)	$C_{16}H_{26}O_9$			1.454	1.133
glycerol tris (allyl carbonate)	$C_{15}H_{20}O_9$			1.456	1.194
ethylene glycol bis(methallyl carbonate)	$C_{12}H_{18}O_6$	[64653-60-7]	142_{266}	1.449	1.110

[a] To convert Pa to mm Hg, multiply by 0.0075.

[b] DADC (CR-39 monomer).

higher temperature produces the more toxic allyl alcohol. Properties are given in Table 2 and the trade literature (10). DADC is soluble in common organic solvents and in methyl methacrylate, styrene, and vinyl acetate. It is partially soluble in amyl alcohol, gasoline, and ligroin. It is insoluble in ethylene glycol, glycerol, and water.

3.2. DADC Homopolymerization. Bulk polymerization of CR-39 monomer gives clear, colorless, abrasion-resistant polymer castings that offer advantages over glass and acrylic plastics in optical applications. Free-radical initiators are required for thermal or photochemical polymerization.

Table 2. **Typical Properties of Commercial DADC Monomer**[a]

Property	Value
appearance	clear, colorless liquid
color, APHA	10
odor	none to slight
specific gravity	$1.15^{20}{}_4$
refractive index, n_D^{20}	1.452
boiling point at 266 Pa[b], °C	166
melting point (supercooled), °C	−4 to 0
viscosity at 25°C, mm^2/s (=cSt)	15
flash point	
Seta closed cup, °C	173
Cleveland open cup, °C	186
water content, slightly hygroscopic, %	0.1

[a] Ref. 10.

[b] To convert Pa to mm Hg, multiply by 0.0075.

Relatively high concentrations of organic peroxide or azo initiators are needed to obtain complete polymerization. After the reaction peak exotherm, polymerization slows down. Initiator concentrations must be high enough to complete conversion. Polymerization is inhibited by oxygen and copper, lead, and sulfur compounds (11).

Bulk polymerization has been studied at relatively low temperatures and in toluene and carbon tetrachloride solutions carried to low conversions (12). The effects of temperature and different organic peroxide initiators have been observed. The molecular weight of soluble polymer after 3% conversion is ca $M_n = 19,000$ and is somewhat dependent on initiator concentration or temperature between 35 and 65°C. With di-2-methylpentanoyl peroxide, polymerization can be carried out at temperatures as low as 13°C. Nuclear magnetic resonance studies of the unsaturated prepolymer show that less than 10% of monomer units undergo cyclopolymerization.

3.3. Casting of DADC. Sheets, rods, and lens preforms are cast from CR-39 or prepolymer syrup by methods similar to those used for methacrylate ester syrups (13). Casting in glass cells with flexible gaskets is described in reference 4. Horizontal cells may be heated at 60–70°C to reach the gel state, and later at 125°C for completing the polymerization of thin sheets. In some cases polymerization of gel shapes can be completed by heating the outside of the mold with additional shaping. Shrinkage between monomer and polymer is about 14%. Under controlled casting conditions, density increases and initiator concentration decreases, as shown in Figure 1.

Many proprietary methods have been developed for casting and shaping DADC, especially for lenses. In one method DADC containing 3.5% diisopropyl percarbonate is prepolymerized by warming to a syrup of viscosity 40–60 mm^2/s

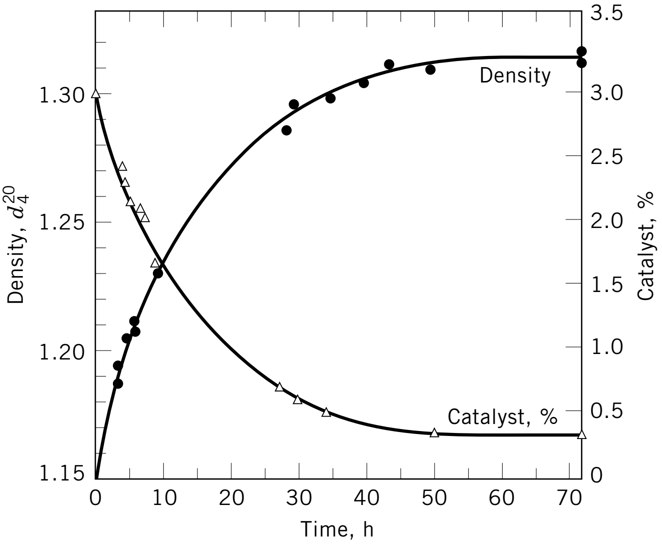


Fig. 1. Bulk polymerization of diethylene glycol bis(allylcarbonate) at 45°C with initial addition of 3.0% diisopropyl percarbonate. Rates of polymerization as measured by density and catalyst consumption decrease with time at a given temperature (14).

(=cSt) (15). Polymerization is continued in a lens for 18 h at 90°C followed by annealing at 120°C.

Scratch resistance of polymer from DADC is improved by novel mixtures of peroxide initiators such as 5% isopropyl percarbonate with 3.5% benzoyl peroxide (16). In order to force completion of polymerization and attain the best scratch resistance in lenses, uv radiation is applied (17). Eyeglass lenses can be made by prepolymerization in molds followed by removal for final thermal cross-linking (18).

Initially, DADC polymers were used in military aircraft for windows of fuel and deicer-fluid gauges and in glass-fiber laminates for wing reinforcements of B-17 bombers. Usage in impact-resistant, lightweight eyewear lenses has grown rapidly and is now the principal application. Other uses include safety shields, filters for photographic and electronic equipment, transparent enclosures, equipment for office, laboratory, and hospital use, and for detection of nuclear radiation.

Many lens casters use the term hard-resin lenses for DADC products. Sheet castings for covers for welding-mask lenses are produced. These covers are resistant to hot metal fragments.

Typical properties of homopolymers from DADC are given in Tables 3 and 4, and in manufacturers' literature (20).

3.4. Coatings. In recent years methods have been developed to improve abrasion resistance of DADC polymer surfaces in optical devices and glazings by means of special coatings. Hard or glasslike coatings may be applied by near-vacuum vapor deposition of quartz (silica) or by hydrolysis of alkoxysilanes. Vapor deposition or sputtering processes of SiO_2 may be facilitated by electron beams or glow discharge. A second class of coatings are elastomeric polymers,

Table 3. **Optical and Electrical Properties of DADC Homopolymer**[a,b]

Property	Value	ASTM method
refractive index at 20°C 589.3 nm, n_D	1.4980	D542
dispersion factor f	0.0084	
Abbe number	59.3	
uv transmission[c], %		
280 nm	6	
300 nm	27	
340 nm	78	
380 nm	88	
visible transmission[c], %		
400–700 nm	89–91	
volume resistivity, $M\Omega$ cm	10.4×10^{14}	D257
dielectric strength, V/μm	13.9	D149
dielectric constant		
10^3 Hz	4.2	D150
10^6 Hz	3.6	D150

[a] Ref. 19.

[b] CAS Registry Number = [25656-90-].

[c] 2.7-mm thickness.

Table 4. **Physical and Mechanical Properties of DADC Homopolymer**[a,b]

Property	Value	ASTM method
density at 20°C, g/cm^3	1.31	D792
tensile strength, MPa[c]	35–41	D638
flexural yield strength, MPa[c]	52–58.6	D790
compressive strength, MPa[c]	155	D695
Izod impact, notched 25°C, J/m[d]	10.7–21.4	D256
hardness		
Barcol, 15 s	25–28	
abrasion		
Taber (X PMMA)[e]	15–20	D1044
thermal conductivity, W/(m · K)	0.21	C177
specific heat, kJ/(kg · K)[f]	2.3	C351
linear coefficient of expansion/°C		
− 40 to 25°C	8.1×10^{-5}	D696
25 to 75°C	11.4×10^{-5}	D696
75 to 125°C	14.3×10^{-5}	D696
heat distortion at 1.8 MPac, °C/10 mL	55–65	D648
glass transition, °C	85	
burn rate, 1.3–2.9-mm thickness, mm/min	0.04	D635

[a] Ref. 19.
[b] CAS Registry Number = [25656-90-0].
[c] To convert MPa to psi, multiply by 145.
[d] To convert J/m to ftlb/in., divide by 53.38.
[e] Reference of poly(methyl methacrylate) = 1.
[f] To convert J to cal, divide by 4.184.

which appear to be scratch-resistant because they heal by slow flow into the scratch depression. According to the Bayer abrader test, some coated DADC lenses are 10 times more resistant than the unmodified homopolymer surfaces. Subcoats and pretreatments of cast polymer surfaces have been patented. Antireflection, antistatic, and antifogging properties may also be improved by such coatings. Photochromic agents and color tints may be incorporated or added in coatings. A photochromic lens called Transitions is are designed to surface and edge in the same manner as lenses made from CR-39 under normal processing procedures (21). Many features such as blue color, uv absorption, and a scratch-resistant coating are inherent in the Transitions (trademark of PPG Industries) lenses (see CHROMOGENIC MATERIALS, PHOTOCHROMIC).

3.5. Modified Polymers and Copolymers. DADC pure monomer and mixtures with small amounts of comonomers or other additions are commercially available for casting. Monomer formulations are available including agents for protecting the eyes against uv light. Another grade is designed to absorb infrared radiation, and several modified monomers give copolymers of increased heat resistance and hardness. Heat-resistant castings have special advantages in high temperature vacuum deposition of scratch-resistant and antireflective coatings and metallization.

DADC may be polymerized industrially with small amounts of other miscible liquid monomers. Some acrylic ester monomers and maleic anhydride may accelerate polymerization. Copolymerization with methacrylates, diallyl phthalates, triallyl isocyanurate, maleates, maleimides, and unsaturated polyesters are among the examples in the early literature. Copolymers of DADC with poly-functional unsaturated esters give castings of high clarity for eyeglass lenses and other optical applications (20).

Various methacrylate esters have been disclosed as modifiers of DADC. Thus methyl methacrylate polymer may be dissolved in DADC and the sheets cast (22). When DADC is copolymerized with methyl methacrylate, a silane derivative may be added to control the release from the mold (23). CR-39 has been copolymerized with benzyl methacrylate and triallyl cyanurate, also with benzyl methacrylate [2495-37-6] and diallyl phthalate (24), and with trifluoroethyl methacrylate by a two-step process (25).

The DADC monomer has been copolymerized with small amounts of polyfunctional methacrylic or acrylic monomers. For example, 3% triethylene glycol dimethacrylate was used as a flexibilizing, cross-linking agent with a percarbonate as initiator (26). CR-39 and diethylene glycol diacrylate containing isopropyl percarbonate were irradiated with a mercury lamp to a 92% conversion and then cured at 150°C (27). By a similar two-step process DADC was copolymerized with methyl methacrylate and tetraethylene glycol dimethacrylate (28).

Light-focusing plastic rods and other optical devices with graduated refractive indexes may use DADC and other monomers (29). Preparation and properties of plastic lenses from CR-39 are reviewed in reference 30.

3.6. Polymeric Nuclear-Track Detectors. DADC polymer is used in solid-state track detectors (SSTD) of nuclear particles, including alpha-particles, fast neutrons, cosmic rays, and ions of elements of atomic number 10 and above. The outstanding sensitivity of the cast polymers in thin sheets and films to diverse types of ionic radiations with a wide range of mass-to-charge ratio has increased applications in nuclear and space sciences, medicine, mining, and ecological research (1). The tracks formed in the polymer are made visible by partial saponification of the polymer with warm aqueous alkali. The resulting surface holes or spots are counted under a light microscope or a scanning device. Polymerization has been optimized to improve sensitivity, resolution, and measurement. Electrons, x rays, and gamma rays are not recorded, but ions of energies above 0.5 MeV are. As little as 1 ppm uranium in river waters can be detected, autoradiographs from alpha particles or other radioactivity in body tissues can be made, and personnel radiation exposures as low as 100 kSv (10 Mrem) can be monitored. SSTD badges of DADC polymer for monitoring exposure to high energy radiations are used in sensitive areas. Commercial SSTD films from CR-39 and modifiers of 5 μm and thicker are available.

Radiation sensitive cast polymers from DADC are also used in resists for microelectronic circuitry. Relief images result from differential rates of solution in alkali induced by exposure to high energy radiations.

4. Other Allyl Carbonate Polymers

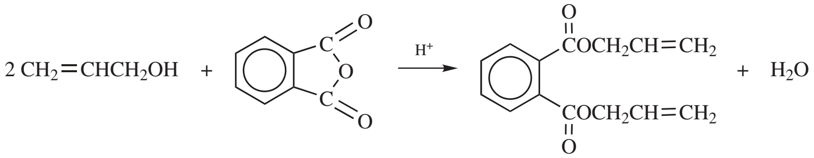
In bulk polymerization triallyl carbonates show less than the 13% shrinkage of CR-39 (31). For example, a trimethylolpropane derivative of average molecular weight 300 was treated with phosgene, and the resulting chloroformate, treated with allyl alcohol, gave a polyfunctional allyl carbonate monomer. The purified monomer was heated with a percarbonate initiator to form a polymer lens.

Similarly, a propoxylated glycerol derivative of molecular weight ca 700 was treated with phosgene and then with allyl alcohol in the presence of a base (32). A polyfunctional allyl carbonate was prepared from Uvithane 893, an oligomer of molecular weight ca 1300 (33). A copolymer of this monomer with CR-39 had better impact strength than that of the homopolymer. Polymers with 1,4-cyclohexane dimethanol bis(allyl carbonate) have been disclosed (34). A lens prepared from equal parts of this monomer and phenyl methacrylate has a refractive index $n_D = 1.565$.

5. Diallyl Phthalates and Their Polymerization

The three isomeric diallyl phthalates are colorless liquids of mild odor, low volatility, and relatively slow polymerization in the early stages. At ca 25% conversion, the viscous liquid undergoes gelation and polymerization accelerates; however, the last monomer disappears at a slow rate.

The monomers are prepared by conventional esterification. Diallyl phthalate (DAP) [131-17-9] is prepared from phthalic anhydride and allyl alcohol:



Properties of two diallyl phthalate monomers, $C_{14}H_{14}O_4$, are given in Table 5. The liquids are soluble in common organic solvents but insoluble in water.

If DAP is partially polymerized by heating with peroxide initiator to give a viscous solution and the polymerization is terminated with methanol and branched soluble prepolymer precipitated (35), the dried prepolymer melts near 90°C and exhibits about one-third of the unsaturation of the monomer. When bulk polymerization is allowed to continue, gelation occurs at about 25%

Table 5. **Properties of Commercial Diallyl Esters**[a]

Property	DAP[b]	DAIP[c]
CAS Registry Number	[131-17-9]	[1087-21-4]
boiling point, °C at 0.53 kPa[d]	161	181
density, g/mL	1.117^{25}	1.124^{20}
refractive index, n_D^{25}	1.518	1.5212
surface tension at 20°C, Pa[e]	3.9	3.54
viscosity at 20°C, mPa s(=cP)	12	17
freezing point, °C	below −70	−3
flash point, °C		171
solubility in gasoline at 25°C, %	24	miscible

[a] Sources: Osaka Soda Company, Hardwick Chemical Company, and FMC Corporation.

[b] Diallyl phthalate.

[c] Diallyl isophthalate.

[d] To convert kPa to mm Hg, multiply by 7.5.

[e] To convert Pa to dyn/cm^2, multiply by 10.

conversion with very rapid polymerization which, however, stops at 65–93% conversion, depending on the initial benzoyl peroxide concentrations. At higher temperatures cross-linking is less complete. Adding diallyl maleate to DAP delays gelation and gives copolymers.

For all three diallyl phthalate isomers, gelation occurs at nearly the same conversion; DAP prepolymer contains fewer reactive allyl groups than the other isomeric prepolymers (36). More double bonds are lost by cyclization in DAP polymerization, but this does not affect gelation. The heat-distortion temperature of cross-linked DAP polymer is influenced by the initiator chosen and its concentration (37). Heat resistance is increased by electron beam irradiation.

Films from prepolymer solutions can be cured by heating at 150°C. Heating the prepolymer in molds gives clear, insoluble moldings (38). The bulk polymerization of DAP at 80°C has been studied (35). In conversions to ca 25% soluble prepolymer, rates were nearly linear with time and concentrations of benzoyl peroxide. A higher initiator concentration is required than in typical vinyl-type polymerizations.

The bulk polymerization of DAP has been studied at 60°C with azobisisobutyronitrile as initiator (39). Branching of the polymer chains is confirmed by enhanced broadening of the molecular weight distribution until gelation occurred at about 25% conversion. In copolymerizations with styrene at 80°C with benzoyl peroxide as initiator the gel time increases with fraction comonomer in the feed. Both the yield of gel and the styrene units in the gel increase with copolymerization time. Heating DAP prepolymer with styrene in benzene solution at 60–100°C with the initiators gives no gelation, but slow formation of polystyrene and copolymer.

Theoretical calculations to predict the conversions at which gelation of polyfunctional monomers occur are reviewed in reference 40. The gelations of DAP, DAIP, and diallyl terephthalate (DATP) near 25% conversion are little affected by conditions and are much higher than predicted.

5.1. DAP Copolymerization. The diallyl phthalates copolymerize readily with monomers bearing strong electron-attracting groups attached to the ethylenic group. These include maleic anhydride, maleate and fumarate esters, and unsaturated polyesters. For example, maleic anhydride copolymerizes with DAP or DAIP in the presence of free-radical initiators at practical rates at ca 50°C; rates are higher than those of the copolymerizations. Additions of styrene, methyl methacrylate, acrylic esters, or acrylonitrile reduce rates of reaction in a linear manner (see Fig. 2). Vinyl chloride, vinyl acetate, or alkenes impede polymerization even more; products are low in comonomer units. Some conjugated comonomers are believed to retard less because they lead to less degradative chain transfer.

The Q and e values of the allyl group in DAP have been estimated as 0.029 and 0.04, respectively, suggesting that DAP acts as a fairly typical unconjugated, bifunctional monomer (42). Cyclization affects copolymerization, since cyclized radicals are less reactive in chain propagation. Thus DAP is less reactive in copolymerization than DAIP or DATP where cyclization is sterically hindered. Particular comonomers affect cyclization, chain transfer, and residual unsaturation in the copolymer products. Diallyl tetrachloro- and tetrabromophthalates are low in reactivity.

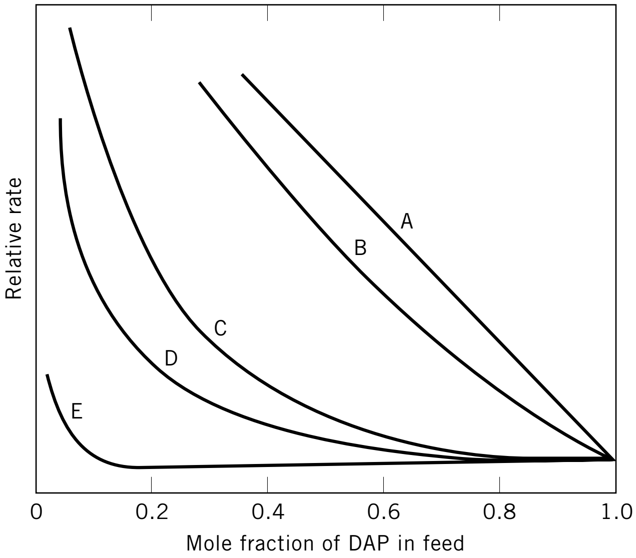


Fig. 2. Relationship between relative rate and monomer composition in the copolymerization of DAP with vinyl monomers: A, styrene or methyl methacrylate; B, methyl acrylate or acrylonitrile; C, vinyl chloride; D, vinyl acetate, and E, ethylene (41).

Diallyl phthalate copolymerizes at 80°C with peroxide catalyst and small amounts of long chain vinyl monomers including vinyl laurate, dioctyl fumarate, lauryl methacrylate, and stearyl methacrylate (43). The products show increased elongations but reduced tensile strengths.

In copolymerization with unsaturated polyesters in fiber-reinforced thermosetting high impact materials, DAP offers advantages over styrene. Glass roving can be immersed in a solution of unsaturated polyester–DAP containing dicumyl peroxide (44). A resin, $CaCO_3$, and lubricant are added and the moldings are cured by heating. A solution of DAP prepolymer, benzoyl peroxide, and polyester (from maleic anhydride, phthalic acid, and propylene glycol) in acetone–toluene solution can be impregnated into a nonwoven glass fabric (45), which is cured in decorative panels by heating under pressure. In electronic moldings, polyester, DAP, peroxide, glass fibers, and alumina hydrate are molded by heating at 140°C under pressure (46). In compositions for carbon fiber-reinforced fishing rods DAP is cured with a polyester to give flexural strength as high as 713 MPa (103,000 psi) (47). Prepregs containing DAP, polyester, and mica filler have been applied to electrical coils (48), and other prepregs, containing less DAP, used for decorative panels (49).

Other examples of DAP copolymerizations of industrial interest include copolymerization with MMA in emulsion (50) and for light focusing rods (51); with vinylnaphthalene for lenses (52); with epoxy acrylates and glass fibers (53); epoxy acrylates and coatings (54); with diacetone acrylamide (55); with aliphatic diepoxide compounds (56); triallyl cyanurate in lacquers for printed circuits (57); and DAIP with MMA (58).

5.2. Diallyl Isophthalate. DAIP polymerizes faster than DAP, undergoes less cyclization, and yields cured polymers of better heat resistance, eg, up to ca 200°C. Prepolymer molding materials such as Dapon M, are not sticky. Maleic anhydride accelerates polymerization, whereas vinyl isobutyl ether retards it and delays gelation in castings. Copolymers with maleic anhydride are exceptionally hard and tough and may scratch homopolymer surfaces.

Besides application as heat-resistant molding powders for electronic and other applications, DAIP copolymers have been proposed for optical applications. Lenses of high impact resistance contain 50% DAIP, 20% benzyl methacrylate, and larger amounts of CR-39 (59). A lens of refractive index $n_D = 1.569$ and low dispersion can be cast from phenyl methacrylate, DAIP, and isopropyl peroxide (60). Lenses of better impact properties can be obtained by modifying DAIP with allyl benzoate (61).

Diallyl terephthalate [1026-92-2] is utilized less, but lenses made of copolymers with triallyl cyanurate and methacrylates have been suggested (62). Diallyl tetrabromophthalate and tetrachlorophthalate polymers have been proposed for electronic circuit boards of low flammability (63). They are uv-curable and solder-resistant. Copolymers with unsaturated polyester, vinyl acetate and DAP have been studied (64).

5.3. Telomerization. Polymerization of DAP is accelerated by telogens such as CBr_4, which are more effective chain-transfer agents than the monomer itself (65); gelation is delayed. The telomers are more readily cured in uv than DAP prepolymers. In telomerizations with CCl_4 with peroxide initiator, at a DAP/CCl_4 ratio of 20, the polymer recovered at low conversion has a DP of 12 (66).

5.4. Uses. The largest use of diallyl phthalate thermoset polymers is in moldings and coatings for electronic devices requiring high reliability under long-term adverse environmental conditions. A photocurable diallyl phthalate resin composition for use on printed circuit boards has been developed (67). These devices include electrical connectors and insulators in communication, computer, and aerospace systems. The flow in molding and curing of these prepolymer formulations must be carefully controlled by selection of initiator, monomer or comonomer content, and heating and radiation. Proprietary compositions may contain about equal weights of prepolymer and filler, eg, fine glass fibers or calcium silicate, 10% antimony oxide, 1–2% DAP or DAIP monomer, silane derivative, peroxide, lubricant, and polymerization-control agents. Formulations are designed for injection, compression, and transfer molding.

For best impact strength, glass fibers should be pretreated with a silane derivative. Fillers may include clays, calcium carbonate, silicates, various silicas, glass, and carbon, preferably as short fibers. Small amounts of metallic stearates or long chain organic acids are added as molding lubricants. In addition to antimony oxide, chlorine- and bromine-containing monomers may be added to reduce flammability. For encapsulation of fragile electronic components, prepolymer of lower molecular weight along with more monomer may be used for flow at low mold pressures. Potting with monomer-polymer syrup is normally too slow. Properties of DAP thermoset moldings are given in Table 6.

Diallyl phthalates are used with glass cloth and roving in tubular ducts, radomes, aircraft, and missile parts of high heat resistance. They offer the advantages of low volatility, little odor, and high heat resistance, replacing

Table 6. **Properties of DAP Thermoset Moldings**[a]

Property	ASTM method	Unfilled	Glass-fiber reinforced	Mineral filled
molding temperature, °C		140–190	144–193	133–193
mold shrinkage, cm/cm	D955		0.0005–0.005	0.002–0.007
tensile strength, MPa[b]	D638	27.6	41–76	34–55
flexural strength, MPa[b]	D790	62.0	62–138	55–76
compressive strength, MPa[b]	D695	165	172–241	138–220
elongation, %	D638		3–5	3–5
Izod impact, N per notch[c]	D256A	1.1–1.6	2.1–80	1.6–4.3
hardness, Rockwell	D785	115	E80–87	E61
coefficient of linear expansion, 10^{-6} cm/cm per °C	D696		10–36	10–42
deflection temp under 18.2 MPa, °C	D648	155	166–290	162–290
thermal conductivity, W/(m · K)	C177		0.21–0.62	0.29–1.04
refractive index, n_D^{25}		1.571		
specific gravity	D792		1.70–1.96	1.65–1.85
water absorption[d], 24 h at 25°C, %	D570	0.20	0.12–0.35	0.2–0.5
dielectric strength[d], V/μm	D149		16–18	16–18
dielectric constant at 25°C				
10^3 Hz	3.4	4.4	∼4.8	
10^6 Hz	3.4	4.4	∼4.4	
arc resistance, s	118	125	140	

[a] Ref. 68.

[b] To convert MPa to psi, multiply by 145.

[c] To convert N per notch to lbf/in. per notch, multiply by 0.187.

[d] 3-mm thickness.

styrene with unsaturated polyesters in fiber-reinforced plastic structures. High curing temperatures, however, and high costs limit structures. Glass cloth, textiles, and papers may be impregnated by prepolymer-monomer mixtures in solution along with peroxide initiator and lubricant. Molding and curing gives decorative stain- and heat-resistant overlays for wall panels, tables, and furniture (1).

Favorable rates and yields of DAP prepolymer are obtained by solution polymerization inCCl_4–benzene mixtures (69). Bulk polymerization at 80°C with benzoyl peroxide is advanced to a certain viscosity before addition of ethanol to precipitate the prepolymer that is then dried (70).

Dapon 35 of FMC and a similar Japanese product have been studied by gel permeation chromatography. Hydrogen peroxide acts as a regulator as well as initiator, and gives relatively large fractions of oligomers. In polymerization between 80 and 220°C gelation occurs at 25–45% conversion (71).

Tableware is molded from DAP polymer and prepolymer, cellulose, pigment, dicumyl peroxide, and a silane coupling agent (72). Nontoxic DAP-based polymers have been suggested as being agents of low viscosity and long pot life for glass-reinforced plastics and electroluminescent coatings of high transparency (73). Abrasion-resistant CR-39-DAP copolymer recording disks have low moisture permeability and good heat resistance (74).

Diallyl esters find little application in lenses. However, DAP and DAIP can be polymerized by high energy radiation in lens molds (75). Coatings of silica and alumina by vaporization give antiglare, scratch-resistant lenses.

Table 7. **Properties of Some Diallyl Esters**

Diallyl ester	Molecular formula	CAS Registry Number	$\mathrm{Bp}_{\mathrm{Pa}}$[a]	n_D^{20}	d_4^{20}
oxalate	$C_8H_{10}O_4$	[615-99-6]	$107_{1.9}$	1.4460	1.0081
malonate	$C_9H_{12}O_4$	[1797-75-7]	$119_{1.9}$	1.4489	1.060
succinate	$C_{10}H_{14}O_4$	[925-16-6]	$94_{0.13}$	1.4507	1.056
adipate	$C_{12}H_{18}O_4$	[2998-04-1]	$115_{0.13}$	1.4542	1.023
sebacate	$C_{16}H_{26}O_4$	[3137-00-6]	$164_{0.26}$	1.4550	0.978
tartrate	$C_{10}H_{14}O_6$	[57833-54-2]	$171_{1.3}$	1.187	

[a] To convert Pa to mm Hg, multiply by 0.0075.

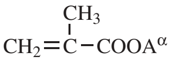
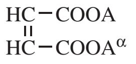
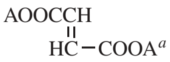
6. Other Diallyl Esters

Tables 7 and 8 give properties of some diallyl esters. Dimethallyl phthalate [5085-00-7] has been copolymerized with vinyl acetate and benzoyl peroxide, and reactivity ratios have been reported (76).

Copolymers of diallyl succinate and unsaturated polyesters cured by x rays provide wear-resistant coatings of MMA dental polymers (77). Copolymers of diallyl itaconate [2767-99-9] with *N*-vinylpyrrolidinone and styrene have been proposed as oxygen-permeable contact lenses (qv) (78). Reactivity ratios have been studied in the copolymerization of diallyl tartrate (79). A lens of a high refractive index ($n_D = 1.63$) and a heat distortion above 280°C has been reported for diallyl 2,6-naphthalene dicarboxylate [51223-57-5] (80). Diallyl chlorendate [3232-62-0] polymerized in the presence of di-*t*-butyl peroxide gives a lens with a refractive index of $n = 1.57$ (81). Hardness as high as Rockwell 150 is obtained by polymerization of triallyl trimellitate [2694-54-4] initiated by benzoyl peroxide (82).

Among the preformed polymers cured by minor additions of allyl ester monomers and catalysts followed by heat or irradiation are PVC cured by diallyl fumarate (83), PVC cured by diallyl sebacate (84), fluoropolymers cured by triallyl trimellitate (85), and ABS copolymers cured by triallyl trimellitate (86).

Table 8. **Properties of Allyl–Vinyl Monomers**

Property	Allyl methacrylate, AMA	Diallyl maleate, DAM	Diallyl fumarate, DAF
structure	 $CH_2{=}\overset{CH_3}{\overset{\vert}{C}}{-}COOA^{\alpha}$	 $\begin{array}{l} HC{-}COOA \\ \Vert \\ HC{-}COOA^{\alpha} \end{array}$	 $\begin{array}{l} AOOCCH \\ \quad\;\;\Vert \\ \quad\;\; HC{-}COOA^{a} \end{array}$
molecular formula	$C_7H_{10}O_2$	$C_{10}H_{12}O_4$	$C_{10}H_{12}O_4$
CAS Registry Number	[96-05-9]	[999-21-3]	[2807-54-7]
boiling point, $°C_{kPa}$[b]	55_4	$112_{0.53}$	$140_{0.40}$
density at 25°C, g/cm^3	0.930	1.070	1.0516
refractive index, n_D^{25}	1.453	1.4664[c]	1.4669
viscosity mPa·s(=cP)	13	4.3	3.0
flash point, open cup, °C		123	74

[a] $A = \text{allyl} = {-}CH_2CH{=}CH_2$

[b] To convert kPa to mm Hg, multiply by 7.5.

[c] At 20°C.

In studies of the polymerization kinetics of triallyl citrate [6299-73-6], the cyclization constant was found to be intermediate between that of diallyl succinate and DAP (86). Copolymerization reactivity ratios with vinyl monomers have been reported (87). At 60°C with benzoyl peroxide as initiator, triallyl citrate retards polymerization of styrene, acrylonitrile, vinyl choloride, and vinyl acetate. Properties of polyfunctional allyl esters are given in Table 7; some of these esters have sharp odors and cause skin irritation.

A series of glycol bis(allyl phthalates) and bis(allyl succinates) and their properties are reported in reference 88. In homopolymerizations, cyclization increases in the order: diallyl aliphatic carboxylates < glycol bis(allyl succinates) < glycol bis(allyl phthalates). Copolymerizations with small amounts of DAP can give thermoset moldings of improved impact (89).

7. Allyl–Vinyl Compounds

Monomers such as allyl methacrylate and diallyl maleate have applications as cross-linking and branching agents selected especially for the different reactivities of their double bonds (91); some physical properties are given in Table 8. These esters are colorless liquids soluble in most organic liquids but little soluble in water; DAM and DAF have pungent odors and are skin irritants.

Addition of dialkyl fumarates to DAP accelerates polymerization; maximum rates are obtained for 1:1 molar feeds (41). Methyl allyl fumarate [74856-71-6] (MAF), $C_8H_{10}O_4$, homopolymerizes much faster than methyl allyl maleate [51304-28-0] (MAM) and gelation occurs at low conversion; more cyclization occurs with MAM. The greater reactivity of the fumarate double bond is shown in copolymerization of MAF with styrene in bulk. The maximum rate of copolymerization occurs from monomer ratios, almost 1:1 molar, but no maximum is observed from MAM and styrene. Styrene hinders cyclization of both MAF and MAM.

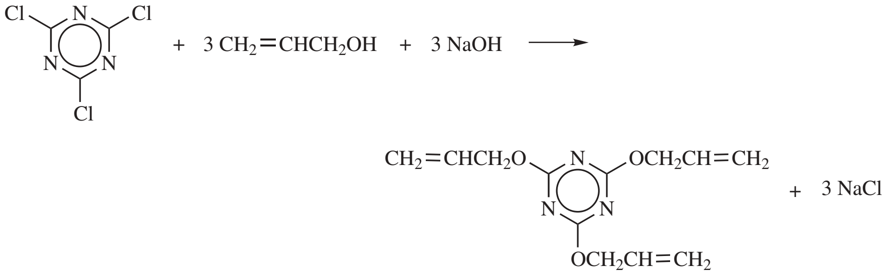
Diallyl fumarate polymerizes much more rapidly than diallyl maleate. Because of its moderate reactivity, DAM is favored as a cross-linking and branching agent with some vinyl-type monomers (1). Cyclization from homopolymerizations in different concentrations in benzene has been investigated (91). Diallyl itaconate and several other polyfunctional allyl–vinyl monomers are available.

7.1. Allyl Methacrylate (AMA).

Of the compounds containing both allyl and vinyl-type double bonds, allyl methacrylate is the most important. The lower reactivity of the allyl group permits controlled, second-stage cross-linking when used in low concentrations. A copolymer with MMA in cured moldings has a heat distortion temperature of 96°C compared to 70°C for MMA homopolymer (92). AMA graft copolymers with acrylate and methacrylate esters blended with PVC and other molding plastics have high impact strength (93). AMA is used as cross-linking agent with methacrylate esters in contact lenses (94). AMA is also used in low concentrations in curable acrylic coatings (95). For cross-linked pressure-sensitive adhesives, a small amount of AMA is used with alkyl acrylates and cured by electron beam irradiation (96). AMA may be added as branching comonomer with acrylic acid for preparing mucilages and thickening agents for aqueous systems (97).

8. Polyfunctional Allyl Nitrogen Monomers

8.1. Triallyl Cyanurate as Cross-linking Agent. Triallyl cyanurate (TAC), 2,4,6-tris(allyloxy)-*s*-triazine [101-37-1], and its isomer triallyl isocyanurate (TAIC) are used as cross-linking agents with comonomers and for aftercuring preformed polymers such as olefin copolymers in electrical insulations. TAC monomer melts at 20–25°C. It is prepared by gradual addition of cyanuric chloride to an excess of allyl alcohol in the presence of aqueous alkali (98).



Properties of TAC and TAIC are given in Table 9.

Crystalline TAC monomer can be stored at room temperature with only slow change, but heating may cause polymerization with violence. In storage, the liquid monomer slowly forms a viscous syrup of prepolymer solution. In homopolymerizations at elevated temperatures with free-radical initiators, two exotherms are observed. An initial release of heat indicates reaction of two allyl groups, a second larger exotherm apparently results from the remaining allyl groups together with rearrangement of the polymer to the more stable isocyanurate structure. Because of brittleness, the homopolymers of TAC and TAIC have had little application.

Triallyl cyanurate is used as a comonomer in small amounts with methacrylate esters and unsaturated polyesters. The addition of 5% or more of TAC to MMA in castings improves heat and solvent resistance as well as thermooxidative stability (99). For optical applications, up to 20% TAC has been suggested. Reactivity ratios for TAC and methacrylate esters have been reported (100).

Small amounts of TAC and TAIC are copolymerized with unsaturated polyesters in glass cloth or fibers in high strength laminates, and electrical sealing and potting applications. In one case, a glass fiber mat impregnated with a

Table 9. **Properties of TAC and TAIC**

Property	TAC	TAIC
molecular formula	$C_{12}H_{15}N_3O_3$	$C_{12}H_{15}N_3O_3$
CAS Registry Number	[101-37-1]	[1025-15-6]
melting point, °C	31	24
boiling point, °C	$140_{67\ \mathrm{Pa}}$[a]	$126_{40\ \mathrm{Pa}}$[a]
density at 30°C, g/cm^3	1.1133	1.1720
refractive index n_D^{25}	1.5049	1.5115

[a] To convert Pa to mm Hg, multiply by 0.0075.

mixture of a maleate polyester, DAP, and TAC was cured with *t*-butyl peroxide at 150°C (101). Solid unsaturated polyesters with 4% TAC have been used in powder coating formulations cured by heating with *t*-butyl perbenzoate and cobalt octanoate (102). Allyl cyanoacrylate modified by TAC has been used in dental adhesives (103).

8.2. Triallyl Cyanurate Cure of Preformed Polymers. TAC and TAIC are often used in small amounts with vinyl-type and condensation polymers for cured plastics, rubber and adhesive products of high strength, and heat and solvent resistance. In some cases, chemical stability is also improved. These effects are the result of grafting at active H atoms as well as penetrating the polymer network. Improvement in strength of PVC by addition of TAC is discussed in reference 104. The modification of PVC by increasing proportions of TAC and diallyl sebacate (DAS) has been studied (105). Up to about 15% TAC, graft polymerization predominates, whereas with higher concentrations polymer networks are observed. DAS is less effective in forming such networks. Both comonomers have a stabilizing effect against loss of HCl under exposure to gamma radiation (106); decomposition products have been studied (107). TAC may act also as sensitizer and stabilizer in electron radiation curing (qv) of PE, PP, and PVC. TAC has been applied to curing PVC elastomers (108).

The use of TAC as a curing agent continues to grow for polyolefins and olefin copolymer plastics and rubbers. Examples include polyethylene (109), chlorosulfonated polyethylene (110), polypropylene (111), ethylene–vinyl acetate (112), ethylene–propylene copolymer (113), acrylonitrile copolymers (114), and methylstyrene polymers (115). In ethylene–propylene copolymer rubber compositions. TAC has been used for injection molding of fenders (116). Unsaturated elastomers, such as EPDM, cross link with TAC by hydrogen abstraction and addition to double bonds in the presence of peroxyketal catalysts (117).

For curing copolymers of tetrafluoroethylene and perfluorovinyl ether, addition of ca 4% TAC has been proposed (118). TFE–propylene copolymers have been cured by TAC and organic peroxide (119). Copolymers of TFE–propylene–vinylidene fluoride are cured with TAC by heating at 200°C.

Nonvinyl polymers cured by TAC include polyamides (120), polyamide–polyurethane blends (121), caprolactone polymers (122), terephthalate polymers (123), epoxy resins (124), and acrylic epoxies (125).

8.3. TAIC as Curing Agent. Triallyl isocyanurate is prepared from an alkali cyanate with allyl chloride. Homopolymers are brittle, intractable, and of little use. A viscous solution of prepolymer first forms under mild polymerization conditions. Addition of alcohol to benzoyl peroxide-catalyzed syrup gives a solid prepolymer of molecular weight 5800 (126). TAIC prepolymer of molecular weight 6000 cures faster than DAP prepolymer (127). TAIC with methacrylic acid in aqueous solution along with azobisisobutyronitrile gives, at first, soluble polymers which cross link on further conversion (128). Zinc chloride accelerates polymerization rates of TAIC (129). Copolymers have been prepared with diallylamine and chloroprene (130).

Small amounts of TAIC together with DAP have been used to cure unsaturated polyesters in glass-reinforced thermosets (131). It has been used with polyfunctional methacrylate esters in anaerobic adhesives (132). TAIC and vinyl acetate are copolymerized in aqueous suspension, and vinyl alcohol copolymer gels are made from the products (133). Electron cure of poly(ethylene terephthalate) moldings containing TAIC improves heat resistance and transparency (134).

Publications on curing polymers with TAIC include TFE–propylene copolymer (135), TFE–propylene–perfluoroallyl ether (136), ethylene–chlorotrifluoroethylene copolymers (137), polyethylene (138), ethylene–vinyl acetate copolymers (139), polybutadienes (140), PVC (141), polyamide (142), polyester (143), poly(ethylene terephthalate) (144), siloxane elastomers (145), maleimide polymers (146), and polyimide esters (147). Compositions containing allyl compounds and processes for forming and curing polymer compositions have been described (148).

8.4. Diallyl Ammonium Polymers. *N,N*-Diallyldimethyl(DADM)ammonium salts are used for the preparation of polyelectrolytes. Polymerization from concentrated water solution can be initiated by *t*-butyl hydroperoxide (149). The polymers are used as flocculating agents, and in water purification (1). The polyelectrolytes are used for aqueous coal flotation (150). Copolymers of DADM ammonium chloride with acrylamide have also been proposed for water purification (151). DADM ammonium polyelectrolyte is used in coatings for copy paper (152). Electrical conductivity of the polyelectrolytes plasticized with poly(ethylene glycol) has been studied (153), and microencapsulation of polyelectrolytes such as DADM ammonium chloride has been reported (154). DADM ammonium compounds can be used as cross-linking agents for temporary gel-blocking in petroleum and natural gas wells (155). Diallyl diammonium polymers have been reported to control snails (156).

Copolymers of diallyldimethylammonium chloride [7398-69-8] with acrylamide have been used in electroconductive coatings (157). Copolymers with acrylamide made in activated aqueous persulfate solution have flocculating activity increasing with molecular weight (158). DADM ammonium chloride can be grafted with cellulose from concentrated aqueous solution; catalysis is by ammonium persulfate (159). Diallyl didodecylammonium bromide [96499-24-0] has been used for preparation of polymerized vesicles (160).

Molded polyamide surfaces can be hardened by grafting with *N,N*-diallylacrylamide [3085-68-5] monomer under exposure to electron beam (161). *N,N*-Diallyltartardiamide [58477-85-3] is a cross-linking agent for acrylamide reversible gels in electrophoresis. Such gels can be dissolved by a dilute periodic acid solution in order to recover protein fractions.

9. Other Allyl Compounds

Although much research has been carried out with allyl ethers there has been only limited commercial use (1). Multifunctional allyl glycidyl ether [106-92-3],

$$CH_2{=}CHCH_2OCH_2\underset{\diagdown\,O\,\diagup}{CH{-}CH_2},$$

a toxic liquid, has been used as an additive to epoxy resins, in copolymers with ethylene oxide and derivatives, and in copolymers with vinyl comonomers. The

Table 10. **Physical Properties of Some Diallyl Ethers**

Ether	Molecular formula	CAS Registry Number	Bp, °C[a]	Sp gr$^{20}{}_{20}$	n^{20}
diallyl ether	$C_6H_{10}O$	[557-40-4]	96	0.805	1.4165
allyl methallyl ether	$C_7H_{12}O$	[14289-96-4]	115		1.4236
1,2-diallyloxyethane	$C_8H_{14}O_2$	[7529-27-3]	$37_{133\ \mathrm{Pa}}$	0.894	1.4340
1,2-dimethallyloxyethane	$C_{10}H_{18}O_2$	[79719-27-0]	$50_{33.2\ \mathrm{Pa}}$	0.8779	1.4383
trimethylolpropane diallyl ether	$C_{12}H_{22}O_3$	[682-09-7]	258	0.957	1.4560
pentaerythritol diallyl ether	$C_{11}H_{20}O_4$	[2590-16-1]	$174_{1.3\mathrm{kPa}}$	1.037	1.4695

[a] To convert Pa to mm Hg, multiply by 0.0075.

second reactive group permits final cross-linking with radiation or heating with peroxides.

A great number of other allyl compounds have been prepared, especially allyl ethers and allyl ether derivatives of carbohydrates and other polymers. They are made by the reaction of hydroxyl groups with allyl chloride in the presence of alkali (1). Polymerizations and copolymerizations are generally slow and incomplete. Products have only limited use in coatings, inks, and specialties. Properties of a few allyl ethers are given in Table 10. An allyl ether-based resin used as a scale inhibitor has been described (162).

These compounds are miscible with most organic solvents. Much research has been directed toward the preparation of air-drying prepolymers or oligomers. Thus allyl groups have been introduced into low molecular weight polyesters, polyurethanes, and formaldehyde condensates (1), but curing rates have been low. Some examples include copolymers of trimethylolpropane diallyl ether with unsaturated polyesters in uv-curable coatings (163). A bis(allyloxy)sulfolane can be used to cross-link unsaturated polyesters in coatings (164). Pentaerythritol triallyl ether [1471-17-6] serves as a curing agent in acrylic photolacquers (165). Diallyl ether reacts with SO_2 to give soluble copolymers containing cyclic structures (166).

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