U.D.C. 541.6:541.361.1

Polymerisation of Allyl Compounds

V.I.Volodina, A.I.Tarasov, and S.S.Spasskii

The review deals with the advances in the theory of the formation of allyl polymers and their practical applications. Until recently there was only limited interest in allyl polymers because with the usual free-radical initiation allyl compounds polymerise with difficulty and yield polymers with a low molecular weight. The principal cause of the formation of low-molecular-weight polymers is degradative chain transfer to the monomer, as a result of which the kinetic chain is terminated. A property of the degradative chain transfer is the constancy of dM/dP, i.e. a linear relation between the amount of peroxide decomposed and the amount of monomer polymerised. In addition to degradative chain transfer, a characteristic feature of allyl monomers is effective chain transfer, which depends on the structure of the monomer.

The polymerisation of diallyl compounds has a cyclolinear mechanism, which leads to the formation of macromolecules with alternating cyclic and linear units.

The behaviour of allyl monomers in copolymerisation reactions is determined by their low reactivity compared with that of the majority of vinyl monomers. The chemical structure of allyl monomers does not as a rule have a significant influence on their reactivity.

In recent years polymers based on allyl monomers have found many applications in engineering. Copolymerisation with other monomers and polymers yielded materials with high mechanical strength, thermal and chemical stability, and good insulating and adhesive properties. They are used as fibres, films, coatings, optical glasses, binders for reinforced plastics, etc.

The bibliography includes 386 references.

CONTENTS

I. Introduction	140
II. Allyl polymerisation	140
III. Polymerisation of various classes of allyl compounds	144

I. INTRODUCTION

Allyl polymers are obtained by the polymerisation and copolymerisation of allyl compounds, which are characterised by the presence of the allyl group $CH_2=CH-CH_2$. The name of these compounds arises from the fact that they are the principal component of the essential oil of garlic–diallyl sulphide.

In recent years there has been increased interest in allyl resins because of their exceptional physical and electrical properties. They have found extensive application in electronic and electrical engineering industries (insulators, connecting sleeves, gas-tight seals, etc.)[1]. The diallyl phthalate and diallyl isophthalate pre-polymers are thermosetting resins with thermal and chemical stability and exceptional insulating properties; articles made from them are characterised by their dimensional stability[2].

Reinforced materials based on these resins exhibit stability of mechanical strength in prolonged use over a wide range of temperatures and humidities[3].

There is a considerable promise of development for phosphorus-containing allyl polymers, which are used as fire-resistant materials[4].

Allyl monomers are used in coatings and copolymers based on them are used to improve the thermal stability and the resistance to wear of certain materials.

The above wide range of the applications of allyl polymers accounts for the interest in them. However, the extensive data and practical experience accumulated in recent years have not been reflected in Soviet reviews or monographs. Abroad there have also been very few such publications[1,5,6].

II. ALLYL POLYMERISATION

All known methods of initiation are used in the polymerisation of allyl compounds. However, the effectiveness of the initiating agents is not the same. In the presence of free-radical initiators, allyl compounds polymerise with difficulty and give polymers in low yields and with low molecular weights[7]. This applies to a lesser extent to diallyl compounds, which form three-dimensional structures even at relatively low conversions.

Ionic catalysts are more effective. In their presence certain allyl compounds form polymers with very high molecular weights.

The use of γ-radiation also makes it possible to obtain allyl polymers with high molecular weights. For certain allyl monomers, this is the only method of polymerisation.

1. Radical Polymerisation

The same elementary steps are characteristic of the free-radical polymerisation of allyl and vinyl monomers, but for the former the chain transfer from the growing radical to the monomer leads not only to the termination of the growing radical but also to the cessation of the chain reaction. Bartlett, Gaylord, Eirich, Walling, and others[4,8-28] have investigated the mechanism and kinetics of the radical polymerisation of allyl compounds.

In the radical polymerisation of allyl monomers, benzoyl peroxide is most often used as an initiator. Gaylord, Nozaki, and others[23-25] showed that the decomposition of benzoyl peroxide in allyl alcohol, allyl bromide, and allyl esters is a first-order reaction, the rate constant of which

increases with the initial concentration of the peroxide. The rate of decomposition of benzoyl peroxide in allyl esters is not the same, decreasing in the sequence allyl trimethylacetate > allyl propionate > allyl acetate > allyl ethyl carbonate.

In the initiation of the polymerisation of allyl acetate with benzoyl peroxide there is a possibility of the formation of two types of radicals, which are incapable of chain propagation because they are stabilised by conjugation [13]:

$$R^{\cdot} + CH_2{=}CHCH_2OCOCH_3 \rightarrow RH + \begin{matrix} CH_2{=}CH\dot{C}HOCOCH_3 \\ \updownarrow \\ \dot{C}H_2CH{=}CHOCOCH_3 \end{matrix},$$

$$R^{\cdot} + CH_2{=}CHCH_2OCOCH_3 \rightarrow RH + \begin{matrix} O \\ \| \\ CH_2{=}CHCH_2O\dot{C}{-}\dot{C}H_2 \\ \updownarrow \\ CH_2{=}\dot{C}HCH_2OC{=}CH_2 \\ | \\ O^{\cdot} \end{matrix}.$$

On this basis, Bartlett and Altschul [13] proposed a mechanism for the radical polymerisation of allyl monomers and found that the ratio of the amount of monomer consumed to the amount of benzoyl peroxide decomposed is constant. This discovery constituted an important milestone in the development of the theory of the radical polymerisation of allyl compounds. Later Gaylord and Eirich [25] gave a more complete polymerisation mechanism, for example with allyl acetate:

$$(C_6H_5COO)_2 \xrightarrow{k_1} 2C_6H_5COO^{\cdot}, \quad (1)$$

$$C_6H_5COO^{\cdot} + CH_2{=}CHCH_2OCOCH_3 \xrightarrow{k_a} C_6H_5COOCH_2\dot{C}HCH_2OCOCH_3, \quad (2)$$

$$C_6H_5COO^{\cdot} + CH_2{=}CHCH_2OCOCH_3 \xrightarrow{k_b} C_6H_5CH_2\dot{C}HCH_2OCOCH_3 + CO_2, \quad (3)$$

$$C_6H_5COO^{\cdot} + CH_2{=}CHCH_2OCOCH_3 \xrightarrow{k_c} C_6H_5COOH + CH_2{=}CH\dot{C}HOCOCH_3\ (r), \quad (4)$$

$$C_6H_5COO^{\cdot} + CH_2{=}CHCH_2OCOCH_3 \xrightarrow{k_d} C_6H_5COOH + CH_2{=}CHCH_2OCO\dot{C}H_2\ (\gamma), \quad (5)$$

$$R_n + CH_2{=}CHCH_2OCOCH_3 \xrightarrow{k_2} R_nCH_2\dot{C}HCH_2OCOCH_3, \quad (6)$$

$$R + CH_2{=}CHCH_2OCOCH_3 \xrightarrow{k_3} RH + CH_2{=}CH\dot{C}HOCOCH_3\ (r), \quad (7)$$

$$R + CH_2{=}CHCH_2OCOCH_3 \xrightarrow{k_4} RH + CH_2{=}CHCH_2OCO\dot{C}H_2, \quad (8)$$

$$r + r \xrightarrow{k_5} r - r, \quad (9)$$

$$\gamma + \gamma \xrightarrow{k_6} \gamma - \gamma, \quad (10)$$

$$r + \gamma \xrightarrow{k_7} r - \gamma. \quad (11)$$

Kinetic analysis of this mechanism led to an expression, which essentially confirms the finding of Bartlett and Altschul:

$$\frac{dM}{dP} = 2\left[1 + \frac{(k_2 + k_3 + k_4)(k_a + k_b)}{k^0(k_3 + k_4)}\right] = \text{const},$$

where $k^0 = k_a + k_b + k_c + k_d$.

In the study of the polymerisation of allyl trimethylacetate the authors of this mechanism observed, and other investigators confirmed [11,14,26,28], that the kinetics of the polymerisation of certain allyl monomers are significantly affected by radical substitution reactions. Therefore, Gaylord and Eirich [25] modified the kinetic mechanism, replacing reactions (5), (8), (10), and (11) by others corresponding to a radical-substitution mechanism:

$$C_6H_5COO^{\cdot} + CH_2{=}CHCH_2OCOC(CH_3)_3 \xrightarrow{k'_d} CH_2{=}CHCH_2OCOC_6H_5 + (CH_3)_3CCOO^{\cdot}, \quad (12)$$

$$R + CH_2{=}CHCH_2OCOC(CH_3)_3 \xrightarrow{k'_4} CH_2{=}CHCH_2R + (CH_3)_3CCOO^{\cdot}, \quad (13)$$

$$(CH_3)_3CCOO^{\cdot} + CH_2{=}CHCH_2OCOC(CH_3)_3 \xrightarrow{k_{4a}} (CH_3)_3CH + CH_2{=}CH\dot{C}HOCOC(CH_3)_3\ (r), \quad (14)$$

$$(CH_3)_3CCOO^{\cdot} + CH_2{=}CHCH_2OCOC(CH_3)_3 \xrightarrow{k_{4b}} CH_2{=}CHCH_2C(CH_3)_3 + CO_2 + (CH_3)_3CCOO^{\cdot}. \quad (15)$$

In the steady state

$$\frac{dM}{dP} = \frac{2}{k^0}\left[(k_a + k_b + k_c) + \frac{(k_2 + k_3)(k_a + k_b)}{k_3 + k'_4} + k^*\right] = \text{const},$$

where

$$k^* = k'_d + \frac{k'_4(k_a + k_b)}{k_3 + k'_4}.$$

Probably both mechanisms of allyl polymerisation can occur independently, since they show significant differences.

The main conclusion which follows from the mechanisms is the constancy of dM/dP, i.e. a linear relation between the amount of benzoyl peroxide consumed and the amount of monomer polymerised. This implies that in the polymerisation of allyl monomers the rates of chain propagation and termination are similar. Such a rate of chain termination can be explained by chain transfer to the monomer, which results in the formation of radicals stabilised by conjugation and incapable of chain propagation. This type of chain transfer is called degradative and the constancy of dM/dP is its characteristic property.

The occurrence of degradative chain transfer was demonstrated experimentally by Bartlett and Tate [19] in the polymerisation of deuterium-substituted allyl acetate $CH_2{=}CHCD_2OCOCH_3$.

When ordinary hydrogen is replaced by deuterium in allyl acetate, the rate of polymerisation increases by a factor between 1.93 and 2.89.

The molecular weight of the deuteriated polymer increases by a factor of 2.38. On the other hand, it is known that the rate of dissociation of hydrogen in a radical substitution reaction is approximately three times higher than for deuterium. On this basis, one may assert that chain termination occurs as a result of the interaction of the growing polymeric radical with the monomer.

Characteristic allyl polymerisation is observed even when the α-methyl group is located in the side-chain of the monomer. Thus isopropenyl acetate polymerised in the presence of benzoyl peroxide gives a polymer with a low molecular weight [22].

As well as degradative chain transfer, the polymerisation of allyl monomers exhibits effective chain transfer where allyl radicals can combine with monomers and thus propagate the chain reaction [10,11,14,15,25,26]. Sakurada and Takahashi [15] proposed a kinetic mechanism taking into account the effective chain transfer and derived an equation for the quantitative determination of the degradative chain transfer allowing for the effective transfer:

$$\frac{k_D}{k_D + k_T} = \frac{2\overline{DP}}{\left[\frac{dM}{dP}\right]_0 + 2},$$

where k_D and k_T are the rate constants for the degradative and effective chain transfer of the growing polymer radical to the allyl monomer and $\overline{DP}$ is the average degree of polymerisation.

The quantity $k_D/(k_D + k_T)$ for allyl esters and ethers decreases in the sequence allyl ethyl ether > allyl carbonate > allyl acetate > allyl propionate > allyl trimethylacetate > allyl laurate > allyl benzoate > allyl chloroacetate.

In the polymerisation of the first three allyl esters about 50% of the chain transfer reactions are effective. The more effective chain transfer in allyl chloride and allyl chloroacetate (65–86%) results from the formation of halogen-containing reactive radicals: $CH_2{=}C\dot{C}HCl$ and $CH_2{=}CHCH_2OCO\dot{C}HCl$. Gaylord [11] observed that the contribution of effective chain transfer reactions in the polymerisation of allyl acetate is only 24%. The explanation is that, of the two resonance structures of the allyl radicals $CH_2{=}C\dot{C}H \rightleftharpoons \dot{C}H_2{-}CH{=}CH_2$ in allyl acetate, the secondary

(left-hand) radical is more stable, while in methylallyl acetate the primary (right-hand) radical of the pair

$$CH_2{=}CH{-}\dot{C}{-} \rightleftarrows \dot{C}H_2{-}CH{=}C\cdot$$
$$\quad\quad\quad

where J is the radiation dose rate, n_0 and n are the numbers of moles of the monomer before irradiation and at time t, and p is the number of moles of the polymer in monomer units.

The variation of the yield of the monomer with the duration of irradiation is linear [35], the initial rate of conversion is therefore equal to the rate of conversion at any other stage. This is possible when $k_p^m = k_d^p$.

The equality of the rate constants for the radiolysis of the monomer and the polymer implies the equality of the radiochemical yields of the corresponding radicals. Thus the rate of conversion can be written in the form

$$\frac{dW}{dt} = 100\,\% \frac{k_d^m k_p}{k_i} J,$$

i.e. the rate of conversion is constant, independent of the yield of the polymer, and directly proportional to the radiation dose rate.

The degree of polymerisation of allyl monomers increases with the yield of the polymer. If the initiating effect is due solely to the hydroxy-radical, then in the initial stage the degree of polymerisation should be equal to the degree of polymerisation of allyl alcohol initiated by hydrogen peroxide (about 5–10). Indeed at 52.5°C k_p/k_t = 10.2 and it is evident from the work of Dolmatov and Polak [36] that the limiting viscosity number hardly changes up to 80% conversion. At this conversion a polymer with an average degree of polymerisation in excess of 340 begins to form. The participation of the oligomer in polymerisation leads to a branched polymer, which is reflected in a low value of the limiting viscosity number and a higher Huggins constant [36].

4. Ionic Polymerisation

Friedel–Krafts and Ziegler–Natta catalysts are used for the ionic polymerisation of allyl compounds [45–61]. The rate of polymerisation by catalysts of this type depends to a considerable degree on the structure of the allyl compound. However, a distinct correlation has not yet been established between the structure and the capacity of allyl polymers for polymerisation.

In the polymerisation of allylbenzene and allylcyclohexane [48] on chromium oxide catalysts it was found that the rate of polymerisation increases when the benzene ring is replaced by the alicyclic cyclohexane ring. The explanation is that the allyl group in allylcyclohexane is adsorbed on the surface of the catalyst with the major plane of the cyclohexane ring oriented parallel to the surface, while in the case of allylbenzene the allyl group is displaced from the surface of the catalyst.

The degree of adsorption of allylbenzene exceeds by a factor of approximately 3 that of allylcyclohexane. Therefore it is possible that the stable adsorption of the benzene ring with displacement of the allyl group from the surface hinders the interaction between the electrons of the double bond of the monomer and the electron orbitals of the catalyst. This may be the cause of the inertness of the chromium oxide catalyst. The polymerisation of allylcyclohexane can be accounted for by the planar disposition of the molecules on the surface of the chromium oxide catalyst.

The polymerisation of allyl ethers of allyl-substituted phenols on Friedel–Krafts catalysts [59–61] involves only the allyl ether group, while the allyl side groups are not polymerised. Therefore initially thermoplastic resins are produced, which are then converted into thermoreactive resins in the presence of benzoyl peroxide as a result of cross-linking via the allyl side groups. Ziegler–Natta catalysts were used in the polymerisation of allyl acrylate, allyl methacrylate, allyl chloride, and allylbenzene [46,47,49,51,52,54].

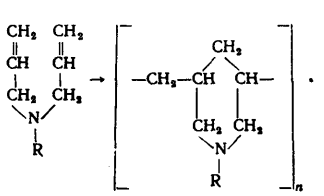
According to D'Alelio et al. [46], the amount of the cationic component $TiCl_4$ in the mixture plays a decisive role in the polymerisation of allylbenzene on these catalysts. The optimum ratio tri-isobutylaluminium : titanium tetrachloride is 1 : 1. With increase of this ratio, the isomerisation of allylbenzene to propenylbenzene predominates. Apart from the ratio $AlR_3 : TiCl_4$, the polarity and the polarisability of the monomer, steric factors, etc. play a significant role in polymerisation on Ziegler–Natta catalysts.

The polymerisation of diallyldimethylsilane and diallylmethylphenylsilane [55] on Ziegler–Natta catalysts in n-heptane yielded solid rubberlike products soluble in benzene at room temperature. The residual degree of unsaturation of these polymers was 12–40%. Polymers obtained with $Al(C_2H_5)_3 : TiCl_4 > 1$ had the lowest degree of unsaturation.

5. Cyclopolymerisation

A characteristic feature of the polymerisation of allyl monomers is a cyclic polymerisation mechanism, investigated for the first time by Butler [62]. Cyclopolymerisation (alternating intra- and inter-molecular polymerisation) occurs with a wide range of monomers when the familiar catalytic systems are used under particular conditions [42,62–79]. Cyclolinear polymers are obtained mainly in the polymerisation of diallyl compounds. This is consistent with Butler's assertion [78] that the main type of chain propagation in the polymerisation of symmetrical 1,6-dienes involves cyclisation, which leads to the formation of a small number of cross links and also residual double bonds. Symmetrical 1,5-dienes polymerise analogously [80]. Butler [63] explains the tendency towards cyclopolymerisation by the fact that the process takes place with a smaller energy expenditure than the intermolecular chain propagation. The lower energy pathway may arise as a result of the electronic interaction between the double bonds of the 1,6-diene or between the reaction centres formed in the interaction between the initiator and the intramolecular double bond.

Matsoyan et al. [66] investigated the capacity of N-substituted tertiary diallylamines and diallylamides for cyclic polymerisation as a function of the nature of the substituent. When polar substituents with electronegative groups are attached to the nitrogen atom of diallylamine, the products are capable of polymerisation in the presence of free-radical initiators with formation of piperidine rings in the main chain:

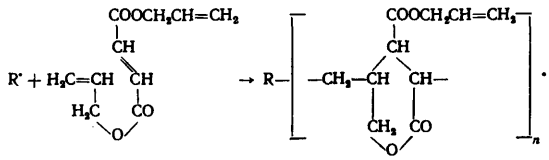


This is associated with the polarisability of allyl groups caused by the displacement of π-electron density of the double bond under the influence of the electron-acceptor substituent.

It is interesting to note that the only substituted diallylamines capable of polarisation are those where the electron-acceptor substituents C=O, C≡N, and SO_2 are linked directly to the nitrogen atom. An increase of the electron-acceptor effect of the substituent favours polymerisation. For example, the effect of substituents in *NN*-diallylamides can be arranged in the following sequence:

$$ClCH_2CO > CH_3CO > CH_3CH_2CO.$$

The studies of Arbuzova and coworkers [81-83] showed that cyclolinear polymers are not obtained solely in the interaction between two allyl groups but also in the interaction between an allyl and a maleate group if their conformation in the molecule is favourable for the formation of five- and six-membered rings:



Cyclisation in the interaction between two allyl groups with formation of ten- or eleven-membered rings is less likely for conformational reasons, for example because of internal steric hindrance to ring closure.

6. Copolymerisation

The nature of the involvement of allyl monomers in copolymerisation depends on their low reactivity compared with the majority of vinyl monomers. Analysis of data on the relative reactivities of monomers in copolymerisation shows that in the vast majority of cases the copolymerisation constants for allyl monomers are zero or significantly less than the constants for vinyl monomers. Because of this allyl monomers enter into the copolymer only as separate units and therefore the copolymer cannot contain more than 50 mole % of the allyl monomer. Only in copolymerisation with relatively inactive vinyl compounds (vinyl acetate, maleic anhydride) do allyl monomers exhibit a fairly high reactivity. In the copolymerisation of diallyl phenylphosphonate with lauryl methacrylate at 140°C the composition of the monomer mixture was found to influence the relative reactivities. In the mixture with 39–92 mole % of lauryl methacrylate (M_1), $r_1 = 6.30 \pm 0.30$ and $r_2 = 0.002 \pm 0.3$, while with 27–46 mole % $r_1 = 3.80 \pm 0.40$ and $r_2 = -0.21 \pm 0.02$. It is suggested that this finding and also the appreciable negative value of r_2 can be explained by the effect of the penultimate unit of the chain on the rate of copolymerisation when the unit consists of the allyl monomer.

The copolymers of allyl monomers with unsaturated compounds are of considerable practical importance. This problem will be discussed in detail below.

In conclusion of this section, the following points should be noted. Judging from the copolymerisation constants, the chemical structure of allyl monomers does not influence their reactivity. However, this finding is probably not uncontroversial. All the investigators who have studied the copolymerisation of allyl and vinyl monomers calculated the constants from differential or integral equations for the composition of the copolymers taking into account only those elementary steps which lead to chain propagation but not to chain termination. For the copolymerisation of vinyl monomers, this assumption is to some degree justified. However, in the copolymerisation of allyl monomers the chain termination rate constant is so large that it is probably comparable with the chain propagation rate constant; for this reason, in the calculation of the ratio of the true chain propagation rate constants it must be taken into account. This problem is not dealt with in the literature and still awaits a solution. Only then will it be possible to assess unambiguously the reactivities of allyl monomers and their dependence on chemical structure.

III. POLYMERISATION OF VARIOUS CLASSES OF ALLYL COMPOUNDS

1. Polymerisation of Allyl Ethers

Allyl ethers $CH_2=CHCH_2OR$ were investigated long before their use in polymer chemistry. In 1944 Nichols and Yanovsky [84,85] observed that, on being kept in air, allyl ethers yield infusible and insoluble resins.

This was the beginning of intense studies on the polymerisation and copolymerisation of allyl ethers and their employment in various branches of industry as adhesives, coatings for wood, glass, metal, and textiles, and as moulded articles with exceptional mechanical strength, resistance to wear, thermal and chemical stability, and resistance to the action of solvents and light.

Allyl ethers derived from polyhydric alcohols are polymerised under the action of oxygen at high temperatures [84, 86-90]. As polymerisation proceeds, the solubility of the polymers in acetone diminishes and their viscosity increases.

Prolonged heating of the polymers in the presence of oxygen leads to insoluble infusible resins. Earlier attempts to polymerise allyl ethers in the presence of 5% benzoyl peroxide were unsuccessful [84]. They began to gel only on addition of 15% of benzoyl peroxide. Later papers [91,92] report the preparation of polymers of allyl ethers initiated by peroxide catalysts. In the solid-phase polymerisation of the diallyl ethers derived from tri-(hydroxymethyl)propane using peroxide initiators, the products are transparent colourless solid thermoreactive resins insoluble in the majority of organic solvents. The capacity of allyl ethers for polymerisation to thermoreactive resins resistant to the action of solvents, oils, and high temperatures, and their compatibility with a large number of resins and plasticisers permit their employment in the manufacture of resins with high rigidity [93-95] and also as decorative coatings [86,96].

Allyl ethers readily copolymerise with other monomers in the presence of benzoyl peroxide. The copolymerisation of allyl ethyl and allyl butyl ethers with vinyl acetate was reported by Sakurada and Takahashi [97]. Copolymers of allyl glycidyl ether and vinyl acetate have been obtained in benzene at 75°C. [98] Allyl trifluoroethyl ether was copolymerised with maleic anhydride at 70°C in the presence of benzoyl peroxide [99]. The triallyl ether of glycerol and other allyl ethers derived from polyhydric alcohols were copolymerised with vinyl chloride in suspension in an autoclave at 51°C. [100]

Britton and Davis [101] copolymerised vinyl chloride with allyl epoxyalkyl and allyl hydroxyalkyl ethers. Losev [102] employed boron trifluoride together with benzoyl peroxide as a catalyst in the copolymerisation of vinyl chloride with diallyl ethers.

Fisher [103] also reported the use of boron trifluoride as an initiator in the copolymerisation of allyl glycidyl ether

with maleic anhydride. The resin formed is then hardened at 110°C for 48–144 h in the presence of benzoyl peroxide. The copolymers may be used as binders for reinforced plastics and as film-forming agents stable up to 260°C. The copolymers of allyl ethers with vinyl acetate, vinyl chloride, vinylidene chloride, styrene, acrylonitrile, butadiene, and acrylic esters have found many applications. The properties of typical copolymers of allyl ethers with other monomers are listed in Table 1.

Table 1. Copolymers of allyl ethers and their properties.

Monomer	Comonomer	Applications of copolymers
Allyloxyethane	Acrilonitrile	Films and fibres with good dyeing properties
Allylpentaerythritol	Acrylonitrile	Thickening agent for non-polar solvents
Allyl glycidyl ether	Vinyl acetate	Surface coatings
Allyl-starch	Styrene	Surface coatings
Diallyl ether of ethylene glycol	Vinyl chloride	Insulation for wires and cables
Triallyl ether of glycerol	Vinyl chloride	Ditto
2-Chloroallyl ether	Methyl methacrylate Butyl methacrylate	Thermosetting coatings for electrical devices, motorcars, and external metallic sheeting
Monoallyl ether of glycerol	Methyl methacrylate Butyl methacrylate	Ditto

Although the copolymerisation of allyl ethers has been as yet inadequately investigated, the use of allyl compounds containing other functional groups (hydroxy-, epoxy-, and ethylene groups) has acquired increasing importance. Even small amounts of allyl ethers added to other monomers considerably improve the physical and mechanical properties of the polymers.

Bifunctional allyl monomers are used for the modification of the existing polymers. They make it possible to obtain copolymers with improved resistance to wear and to the effect of light and solvents.

Valuable polymeric materials have been obtained by the copolymerisation of unsaturated maleate oligoesters with ethers [104–115]. Such compositions harden rapidly in air at room temperature. Light-coloured films with high impact strength, chemical stability, and resistance to wear are obtained. The physical and chemical properties of the copolymers permit their use also in cast compositions, in laminate plastics, and as casting moulds. The copolymers of the unsaturated oligoesters with diallyl phthalate and allyl ethers of glycerol and starch are used [116] as adhesives and binders for emery paper. Allyl ethers of polyhydric alcohols [tri(hydroxymethyl)propane, pentaerythritol, glycerol] react with the unsaturated oligoesters to give copolymers with exceptional water resistance and satisfactory dielectric properties [110,114,115].

Recently much attention has been devoted to unsaturated allyl oligoesters and their copolymers. Unsaturated allyl oligoesters with an allyl bond in the side chain are obtained by the reaction with dibasic acids or their anhydrides of polyhydric alcohols such as allylglycerol and allylglycidol with their hydroxy-groups partly converted into allyl ether groups [117–125].

Such oligoesters are converted into insoluble and infusible polymers by treatment with cobalt naphthenate in the presence of air at room or elevated temperatures [108,111,112,123,125]. However, the homopolymers of allyl oligoesters have not found practical applications.

Sorokin and Gershanova [106] studied the copolymerisation of unsaturated allyl oligoesters with allyl glycidyl ether. They synthesised the oligoesters from allyl glycidyl ether and dibasic acids (maleic, phthalic, and adipic). The copolymerisation was carried out in the presence of redox and peroxide initiators. The authors note that varnish compositions based on the oligoesters obtained from maleic acid and allyl glycidyl ethers harden at room temperature and exhibit fairly satisfactory hardness and degree of solidification. Partial replacement of maleic acid by adipic or phthalic acid in the oligoester lowers the rate of hardening of the varnish compositions.

It has been established by infrared spectroscopy that the copolymerisation involving the double bonds is accompanied by the interaction of the glycidyl groups of the allyl glycidyl ether with the terminal carboxy- or hydroxy-groups of the oligoester.

In their study of mixed allyl-maleic oligoesters, Jenkins et al. [107] showed that an increased content of allyl groups in the oligoester lowers the maximum molecular weight which may be obtained without gelling. This also determines the maximum number of utilisable allyl groups. For the oligoester obtained from propylene glycol, the allyl ether derived from glycerol, and equimolar amounts of maleic and phthalic acids this number is four. When the maleic acid content was less than 25 mole % of the total content of acids, gelling was not observed and it was possible to obtain oligoesters with a high molecular weight.

For polyester varnishes the authors also employed as the allyl component involatile polymerisable compounds of the diallyl ether derived from glycerol and the acetic, adipic, and pyromellitic esters of the diallyl derivative of glycerol.

The copolymerisation of allyl oligoesters with maleic–fumaric oligoesters is described in the publications of Tarasov and coworkers [117–120,126–128] and others [124]. Copolymers with satisfactory physical and mechanical properties have been obtained [117], and may be employed as binders for reinforced plastics. It has been shown [129] that poly(allylglyceryl phthalate-adipate) does not polymerise in the presence of 2% of benzoyl peroxide even at 150°C. The addition of small amounts of the fumaric oligoester (about 10%) leads to the formation of a copolymer even at 80°C. The participation of allyl groups in the copolymerisation reaction has been shown by the fact that the product does not dissolve in organic solvents. Furthermore, bromination of the products of the alkaline hydrolysis of the copolymers reveals the presence of only a fraction of the initial fumaric and allyl double bonds.

2. Polymerisation of Allyl Esters

The allyl esters of mono- and di-carboxylic acids were obtained for the first time in 1885 by Zinin [130] by the double decomposition of the silver salts of aliphatic acids with allyl iodide. Until 1940 there were no data on the use of allyl esters, since allyl alcohol was not readily available. The polymerisation of allyl esters began to acquire practical importance starting with 1941–1942. The allyl esters of carboxylic acids have been used in polymer chemistry in two ways: (1) as monomeric additives to polymers; (2) as partially polymerised thermosetting resins (pre-polymers).

The polymers of allyl esters have found application in those cases where the following properties are necessary: chemical stability, particularly with respect to oxidising agents, exceptionally low dielectric losses, low moisture

absorption, low rate of cross-linking after fusion, resistance to wear, and thermal stability.

The allyl esters of phthalic, isophthalic, maleic, fumaric, succinic, diglycolic, itaconic, acetic, and other acids are most frequently used [131-237].

Allyl esters can be polymerised in the presence of various initiating systems (peroxides, ionic polymerisation catalysts, and under the influence of γ-radiation). Among the most widely used and most important monomers are diallyl phthalate and diallyl isophthalate [131-168]. The kinetics of the polymerisation of diallyl phthalate were investigated by Oiwa, Lalau-Keraly, etc. [154-159,168]. They showed that the residual degree of unsaturation in the polymerisation of diallyl phthalate in the presence of benzoyl peroxide and di-t-butyl peroxide depends very little on the catalyst and temperature but does depend strongly on conversion. With increase of conversion, the residual degree of unsaturation falls.

In the initial stage of the polymerisation of diallyl phthalate in the presence of peroxide initiators about 43% of cyclic structures is formed. The structure of the polymer has been confirmed on the basis of the rate of disappearance of C=C bonds revealed by infrared spectroscopy in the region of 1644 cm^{-1}. [165]

In the polymerisation of diallyl phthalate the duration of the hardening process and the contraction of the polymer are very considerable [132]. For this reason, diallyl phthalate is rarely used for the synthesis of a homopolymer. Instead it serves for the preparation of a pre-polymer which is readily moulded, exhibits satisfactory fluidity, and hardens rapidly [147-153]. Diallyl phthalate and diallyl isophthalate pre-polymers are stable on storage and when employed as compositions with catalysts which decompose at high temperatures. On heating and at high pressures (in casting, in the preparation of laminate materials), they soften, flow, and are cross-linked to give three-dimensional insoluble resins.

Diallyl esters of fumaric and maleic acids are also of interest for a wide variety of engineering applications [81-83, 169-183,229]. The mechanism of the formation of polymers based on mono- and di-allyl esters of maleic acid was investigated by Arbuzova et al. [81-83] They established that in the polymerisation of monoallyl maleate and diallyl maleate five- and six-membered lactone units are formed, and with increase of the polymerisation temperature the content of five-membered rings increases. On the other hand, the polymerisation temperature and the nature of the initiator do not affect the degree of cyclisation. With monoallyl maleate, it is 63-64% and, with diallyl maleate, it is almost 100%. The cyclolinear polymers obtained are converted on further polymerisation in the presence of initiators into three-dimensional polymers, which are very hard and exhibit high thermal stability.

The polymerisation of allyl acrylate and allyl methacrylate has been investigated by Schulz, Kawai, Gindin, and others [51,54,74,184-209]. The polymerisation of allyl acrylate in benzene solution with a radical polymerisation initiator yielded a brittle vitreous polymer soluble in benzene and pyridine. The polymer does not soften on heating and hydrolyses only in molten sodium hydroxide–potassium hydroxide. A study of the structure of the polymer showed that 24.2% of the structural units are linked via acrylic groups, 17.2% are linked via allyl groups, and the remaining 58.6% form lactone groups as a result of cyclopolymerisation [186].

The anionic polymerisation of allyl acrylate gives a product with a low molecular weight, which is isotactic to a fairly high degree. Only acrylic double bonds participated in the linear polymerisation; the allyl bonds were involved only in the cross-linking, which occurred when the polymer was stored in air [51]. Similar results were obtained by Gindin et al. [185] in the polymerisation of allyl acrylate under the influence of benzoyl peroxide and ultraviolet light.

Compared with the acrylate, the polymerisation of allyl methacrylate shows certain characteristic features. When azobisisobutyronitrile is used as an initiator, allyl methacrylate polymerises to a product without rings in the chain, which is insoluble in the usual organic solvents [187]. In the polymerisation of allyl methacrylate under the influence of ultraviolet light, Cohen et al. [236] also showed that the polymerisation is not accompanied by cyclopolymerisation. This can be accounted for by resonance stabilisation of the allyl groups as a result of degradative chain transfer, which leads to the cross-linking of the polymer.

In the anionic polymerisation of allyl methacrylate [54] a linear soluble polymer containing allyl groups as branches from the polymer chain is formed. The linear polymers of allyl methacrylate are classified as "self-reactive", yielding polymers which harden on heating or in the presence of radical initiators. Only the copolymers of allyl methacrylate with other monomers have found applications.

Allyl acetate has been homopolymerised [10,18,210-213], largely in order to investigate the kinetics of allyl polymerisation, as mentioned above. This polymer has not found practical application, since it has low molecular weight and poor mechanical properties.

Polymers based on the diethylene glycol–diallyl carbonate system are produced in the presence of free-radical polymerisation initiators as light-coloured castings with exceptional optical properties, high chemical stability, and resistance to wear [237]. The polymerisation of this monomer is inhibited by air and therefore the castings are obtained between glass plates separated by plastic spacers. The diethylene glycol–diallyl carbonate polymers are produced in the manufacture of optical lenses and glass for spectacles, and as coatings for expensive ultraviolet and infrared glasses [6].

Apart from the applications of the polymers of allyl esters, their copolymers with other monomers and unsaturated oligoesters have found many applications in engineering.

The addition of 0.01–0.3% of diallyl phthalates (*o*-, *m*-, and *p*-isomers) to vinyl chloride makes it possible to prepare a polymeric material with mechanical properties 4–10% better than those of poly(vinyl chloride) itself [141]. Diallyl phthalates are frequently used instead of styrene in mixtures with unsaturated oligo-glycol maleates [142]. Articles with homogeneous surfaces and much smaller contraction can be obtained by casting. Diallyl phthalate imparts mechanical strength and thermal stability to oligoester resins and improves their dielectric properties.

The copolymerisation of diallyl maleate and diallyl fumarate with methyl methacrylate and styrene in the presence of a mercaptan and peroxides yields in pregnating powders [183], which can be moulded under pressure of 7 kg cm^{-2}. The copolymer of diallyl maleate with 0.05–0.3% of vinyl chloride is used as an electrical insulator [180]. The copolymer of diallyl maleate and chlorotrifluoroethylene has good adhesive properties [182].

Diallyl fumarate and diallyl maleate are also used with styrene in compositions containing unsaturated oligoesters, which are employed to prepare reinforced plastics [173]. The addition of diallyl phthalate and diallyl maleate to

poly(vinyl chloride) imparts hardness to the polymeric materials [176].

Allyl acrylates and allyl methacrylates copolymerise with methyl methacrylate, vinyl chloride, acrylonitrile, polyethylene, etc. [196-208]. The copolymerisation of allyl methacrylate (20%) with methyl methacrylate in the presence of benzoyl peroxide yields polymers with higher softening temperatures than that of poly(methyl methacrylate). [200-202]

The copolymers of allyl furylenemethacrylate with styrene, vinyl acetate, acrylonitrile, and methyl methacrylate have been suggested as plasticisers [197].

The copolymers of acrylonitrile, methyl methacrylate, and methacrylamide, modified with allyl methacrylate, exhibit exceptional mechanical properties (for example, a bending resistance of 1849 kg cm^{-2}).

The copolymerisation of allyl acrylate (1–15%) with acrylonitrile gives transparent castings [207]. Allyl acrylate is used as a cross-linking agent in the irradiation of polyethylene and polypropylene [209].

The copolymerisation of allyl acetate with other monomers [6,214-216] has been carried out largely to investigate the mechanism of the copolymerisation and to determine the relative reactivities.

3. Polymerisation of *N*-Allyl Derivatives

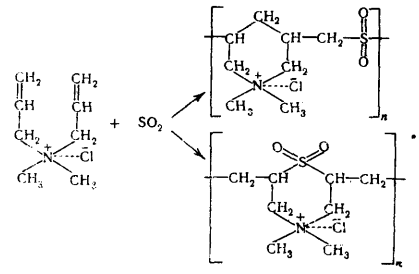
In recent years much attention has been devoted to the study of the polymerisation and copolymerisation of *N*-allyl derivatives (*N*-substituted diallylamines, diallylammonium, salts, *N*-allylamides, *N*-allylimides, triallyl cyanurates, hexa-allylmelamines, etc.)[66,238-289]. The interest in this class of compounds arises from the practical value of the polymers and copolymers of *N*-allyl derivatives (particularly those based on triallyl cyanurate and triallyl isocyanurate).

Butler has shown that the polymerisation of diallylammonium salts in aqueous solutions in the presence of t-butyl hydroperoxide or an azo-initiator leads to the formation of cyclolinear polymers [78,79].

The polymerisation of diallyl- and diallyldimethylammonium bromides [258] yields saturated linear soluble polymers with repeating *N*-substituted piperidinium halide units together with methylene groups.

The ability of diallyl derivatives of quaternary ammonium salts to undergo radical polymerisation is associated with the polarisability of the allyl groups due to the displacement of the π-electron density of the double bond by the electron-accepting nitrogen atom of the ammonium group. In the presence of radical-polymerisation initiators these monomers copolymerise fairly readily with styrene, acrylonitrile, and other monomers.

In the copolymerisation of diallyl-ammonium halides with sulphur dioxide [73], water-soluble cationic polysulphones are formed:



These copolymers do not melt but decompose at 180°C and lose about 40% of their weight at 190°C in 3 h. They are unstable to sodium hydroxide.

The mechanism of the polymerisation of *N*-substituted diallylamines was discussed in detail above [66]. It is noteworthy that the polymerisation of these monomers involves a cyclic mechanism with formation of piperidine rings in the main polymer chain, as in the polymerisation of quaternary diallyl-ammonium salts. Among the cyclic polymerisation products of *N*-substituted diallylamines, *NN*-diallylacetamide, *NN*-diallylbenzamide, *NN*-diallylpropionamide, etc., polyallylcyanamide is of particular interest, being distinguished by low solubility and a high melting point.

Ostroverkhov et al. [238] established that tertiary diallylamines and diallylamides form in the presence of radical initiators polymers with low molecular weights and low softening temperatures which are readily soluble in organic solvents. The low tendency of diallylamides to polymerise can be explained by the vigorous chain termination reaction with participation of the hydrogen atom of the allyl group.

In the presence of anionic and cationic catalysts diallylamides and tertiary diallylamines did not yield polymers either in the solid state or in solution. Allylamines have been recently polymerised by irradiation with cobalt-60 γ-rays. [44] The homopolymers of allylamines and allylamides have not found practical application. It is mainly their copolymers with other monomers and polymers which are used in industry.

The copolymers of triallylamine with acrylic acid have been obtained at 50°C in an atmosphere of nitrogen in the presence of 2% azobisisobutyronitrile. They are excellent thickening agents for latex dyes [242].

The copolymers of diallylamine and acrylonitrile are used as fibres which are more readily dyed than polyacrylonitrile [243].

The copolymers of allylamines with styrene and butadiene have been recommended as hardening agents for epoxy- and ion-exchange resins [239].

Diallylamine introduced into poly(vinyl chloride) in an amount of 0.01–0.3% increases its molecular weight and improves its physical and mechanical properties [230].

Much work has been done on the polymerisation and copolymerisation of triallyl cyanurate, triallyl isocyanurate, and hexa-allylmelamine [248,263-294]. The vitreous polymers obtained in the presence of free-radical polymerisation initiators, are colourless, solid (but brittle), and readily cracked.

Clampitt [265] observed by infrared spectroscopy that in the course of its polymerisation triallyl cyanurate isomerises to triallyl isocyanurate.

Poly(triallyl isocyanurate) has a higher decomposition temperature (377°C) than poly(triallyl cyanurate) (321°C) and higher stability on heating in air and in an atmosphere of nitrogen. Therefore conditions for the hardening of triallyl cyanurate are chosen so that the latter isomerises to triallyl isocyanurate. However, despite their high thermal stabilities, the homopolymers have not found practical application because of their brittleness.

Solid polymeric materials with high thermal stability have been obtained by the copolymerisation of methyl methacrylate (5–50%) with triallyl cyanurate [284,286].

In the presence of peroxide or ionic catalysts allyl derivatives of cyanuric and isocyanuric acids copolymerise with vinyl monomers, dienes, etc. Solid thermostable copolymers insoluble in organic solvents are obtained [282].

The copolymers of triallyl cyanurate, diallyl itaconate, styrene, and methyl methacrylate are used in high-speed

military aviation [287]. Triallyl cyanurates and triallyl isocyanurates are introduced into oligoesters to improve their thermal stability and mechanical properties [291-293]. When triallyl cyanurate (2–5 weight units) is introduced into polyethylene to increase the effectiveness of cross-linking, a copolymer with a high melting point is obtained [277].

The polymerisation and copolymerisation of other *N*-allyl derivatives of heterocycles have been less investigated. Only *N*-allyl-α-pyrrolidinone, *N*-allyl-α-piperidinone, and *N*-allyl-α-caprolactam have been polymerised [290]. These monomers hardly polymerise in the presence of 10% benzoyl peroxide at 60°C over a period of 60–100 h. On addition of not less than 5% of azobisisobutyronitrile, *N*-allyl-α-pyrrolidinone and *N*-allyl-α-caprolactam undergo stepwise polymerisation with formation of low-molecular-weight products and trimers in low yields (10–25%). The polymerisation of *N*-allylsuccinimide and *N*-allylphthalimide, in the solid phase and in solution, under the influence of cobalt-60 γ-radiation was reported recently [261]. The polymerisation products have a low molecular weight; the degree of polymerisation is about 10.

4. Polymerisation of Allyl Monomers with Organic Derivatives of Different Elements as Substituents

This class of compound includes allyl derivatives of silicon, titanium, germanium, tin, phosphorus, sulphur, and other elements [7,42,43,68,291-340]. Polymers based on these compounds have attracted attention because they should exhibit high thermal stability and the phosphorus containing polymers should exhibit self-extinguishing properties. The polymerisation of alkenylsilanes containing one allyl or methylallyl group takes place with difficulty [341]. Mironov and Petrov [342] described the polymerisation of alkylmethylallyl- and allyloxy-silanes on platinised charcoal. Later Korshak et al. [343] established that the polymers based on alkylsilanes have different structures depending on the polymerisation initiator. The polymers obtained in the presence of peroxide catalysts contain Si–H bonds, while those obtained in the presence of platinum catalysts do not.

Lyashenko et al. [43] showed that polymers produced in the presence of benzoyl peroxide at 200°C have structures analogous to those obtained at 100°C in the presence of cobalt-60 γ-radiation. The authors observed that the tendency to polymerise increases with the number of allyl groups in alkenylsilanes. Monoallylsilanes exhibit different activities in polymerisation reactions depending on the nature of other groups linked to the silicon atom. Diethylallylsilane does not polymerise in the presence of benzoyl peroxide over a period of 10 h, ethylallylphenylsilane polymerises to a liquid polymer, while ethyldiallylsilane and triallylsilane give crystalline products, the latter being formed in 30 min.

In the polymerisation of diallylsilanes under the influence of cobalt-60 γ-radiation, Gusel'nikov et al. [42] established that the reaction involves inter- and intra-molecular mechanisms. The cyclolinear polymers formed are soluble in organic solvents.

Using Ziegler–Natta catalysts, Topchiev, Bogomol'nyi, Kolesnikov, and others [68,300-303,308] obtained rubberlike products containing unsaturated groups in the side chains. The dominant units in the polymer chain are silicon-containing rings alternating with methylene groups. The copolymers of allylsilanes with other monomers obtained in the presence of Ziegler–Natta catalysts were found to have a constant melting point and high stability when worked. The hardened copolymers did not dissolve in boiling heptane. They have been used as elastomers [305].

There are only isolated data on the polymerisation of the allyl derivatives of titanium, tin, and germanium [50,308,310,311]. A polymer decomposing without fusion above 400°C was obtained from allyl trimethyl titanate in the presence of boron trifluoride or compounds capable of yielding boron trifluoride [50]. The copolymerisation of allyl derivatives of titanium with vinyl acetate gave water-resistant enamels [311].

The polymerisation of diallyldimethylgermane takes place in the presence of triethylaluminium and titanium tetrachloride with formation of a coloured oil in about 50% yield. The molecular weight of the polymer is 270. It is suggested that in this case the main polymerisation product is a cyclic dimer [308].

The polymerisation of phosphorus-containing allyl monomers and their copolymerisation with other monomers and polymers have been investigated by Kamai, Toy, Berlin, Laible, Kennedy, and others [7,67,238,294,296-298,312-334]. The ability of phosphorus-containing allyl monomers to undergo radical polymerisation as a function of the nature of the substituents has been investigated by Kamai [297] and later by Toy [296] using as an example the allyl esters of phosphonic acid. They showed that steric hindrance, the polarity of the substituents, and the presence or absence of inhibiting groups can greatly modify the polymerisation characteristics of the monomers, their effect diminishing on going from allyl to methylallyl esters.

Table 2. Groups of polymerisable diallyl compounds of the type $R-P(O)(OCH_2CH=CH_2)_2$.

First group		Second group	
R	Taft's constant σ* (Ref.344)	R	Taft's constant σ*
H—	0.49	CH_3 –	0
C_6H_5—	0.60	C_2H_5—	—0.1
$C_6H_5CH_2$—	0.22	n-C_3H_7—	—0.115
C_6H_5—O—	2.38	n-C_4H_9—	—0.13
$(CH_3)_2C=CH$—	—	$(CH_3)_2CH$	—0.38

Monomers can be divided into three groups in relation to their capacity for the formation of polymers. The first group includes monomers which polymerise to a solid vitreous product. These are monomers in which the substituent at the phosphorus atom is an electron acceptor. When the substituents are electron donors, the monomers polymerise either to gels or solid but elastic polymers. These constitute the second group (Table 2). The third group includes monomers which polymerise to a liquid product or do not polymerise at all under the influence of peroxide initiators. These are *NN'*-dimethylallylphenylphosphonamide, diallylthiophenylphosphonamide [*NN*-diallylphosphonothionic diamide ? (Ed. of Translation)], diethyl *N*-allylphosphoramidate, and others. The polymerisation passivity of compounds in the third group is due to the inhibiting effect of sulphur and amide groups in the monomers.

Diallyl *NN*-dimethylphosphoramidate ? (Ed. of Translation)] not only does not polymerise but is actually capable of retarding the polymerisation of other diallyl esters.

The interest in polymers of this class arises from their flame-resistant properties.

Toy and Cooper [296] believe that the phosphorus content in allyl monomers is not the sole factor determining the flame-resistant properties of polymers. The polymers of diallyl phenylphosphonate (13% of phosphorus) and diallyl methylphosphonate (17.6% of phosphorus) are more flame-resistant than the polymer of diallyl phosphite (19.2% of phosphorus). However, the authors do not quote other reasons to account for their flame-resistant properties.

In engineering, applications are found mainly for the copolymers of phosphorus-containing allyl monomers with other monomers and polymers. The copolymerisation of diallyl phenylphosphonate with vinyl acetate and methyl methacrylate yielded a transparent polymer with self-extinguishing properties [323].

Phosphorus-containing allyl monomers are introduced into unsaturated oligoesters to make them flame-resistant. The copolymers based on these components have good mechanical and dielectric properties in addition to being flame-resistant [298,333].

5. Polymerisation of Allyl Alcohol and Allyl Halides

Poly(allyl alcohol) was obtained for the first time by the reduction of poly(n-butyl acrylate) with lithium aluminium hydride in dry tetrahydrofuran [345]. The degree of reduction was more than 95%, the molecular weight was 15 900, and the intrinsic viscosity in dimethyl sulphoxide was 0.436.

Poly(allyl alcohol) of low molecular weight is obtained by the polymerisation of allyl alcohol in the presence of a large amount of benzoyl peroxide [346,347]. Poly(allyl alcohol) with an average degree of polymerisation $\overline{DP} = 20$ is soluble in water, methanol, and other organic solvents. With $\overline{DP} = 200$, the polymer shows limited miscibility in water but is readily soluble in methanol, while with $\overline{DP} = 400$ it is soluble only in a mixture of concentrated hydrochloric acid and methanol in dioxan.

Poly(allyl alcohol) of high molecular weight ($\overline{DP} = 370$) has been obtained by irradiating allyl alcohol with cobalt-60 γ-rays. Allyl alcohol with $\overline{DP} = 10^3-10^4$ can be obtained by radiation-induced polymerisation. Poly(allyl alcohol) is a highly branched polymer with a low intrinsic viscosity. It is thermostable and thermoplastic, can be pressed into sheets on heating, and fibres can be readily formed from its melt. Crystalline poly(allyl alcohol) with a melting point of 210–222°C has been obtained by the polymerisation of allyl alcohol in the presence of boron trifluoride at −78°C in petroleum ether [50].

Practical applications have been found mainly for the copolymers of allyl alcohol with other monomers [348-367]. When allyl alcohol is copolymerised with styrene (15–80%), transparent solid polymers are formed and are used as coatings which are colour-fast on heating [353,368]. The copolymers of allyl alcohol and styrene have been used to prepare films with good adhesive properties, resistance to water, dilute alkalis, methanol, and detergents [354,356,357]. These copolymers can serve as binders for the preparation of articles with fibrous fillers [355]. Filled copolymers of styrene, allyl alcohol, and maleic acid are used as facing plates and other constructional materials [359]. Copolymers of allyl alcohol and acrylonitrile have been used as fibres [362].

The polymers of allyl halides (allyl chloride and allyl bromide) are obtained by polymerisation in the presence of peroxides and Ziegler–Natta catalysts and by γ-irradiation [369-375]. High-molecular-weight compounds are obtained only when the monomers are irradiated with cobalt-60 γ-rays.

Polymerisation of allyl chloride on a Ziegler–Natta catalyst yielded a pale-yellow polymer melting at 70–110°C. It contained double bonds formed as a result of the elimination of HCl from the polymer molecules [370].

Polymers of allyl chloride are also obtained in benzene or toluene in the presence of 0.2–0.5% (relative to the monomer) of metallic aluminium [376].

The polymerisation of allyl iodide under the action of γ-radiation yields mainly dimers [370]. The monomers are used in the polymerisation of ethylene to regulate the molecular weight of the polymer [377,378].

6. Polymerisation of Aromatic Allyl Compounds

Korshak and coworkers have investigated the synthesis, polymerisation, and copolymerisation of allyl-containing polyarylates [379-386]. The formation of allyl-containing polyarylate structures under the influence of heat takes place at a temperature in excess of 230°C with a considerable yield of the three-dimensional product. At the beginning of the reaction the β-polymer forms, which is then converted into the γ-polymer. The polymers obtained under conditions ensuring the maximum degree of cross-linking (267°C, 7 h) have an extensive region of elastic deformations, the upper limit of which occurs at temperatures above 500°C. It has been noted that the deformations diminish with increase in the number of cross-links.

The copolymerisation of allyl-containing polyarylates with various vinyl and allyl monomers reduces the thermal stability of the polyarylates. However, in some cases (diallyl phthalate, styrene, etc.) this happens to only a slight extent. It was found that styrene is a poor cross-linking agent and this is why only a small amount of the cross-linked polymer forms at high concentrations of the polyarylate in styrene solution.

Methyl methacrylate, allyl methacrylate, and ethylene dimethacrylate are effective cross-linking agents for allyl-containing polyarylates.

Some of the copolymers have good mechanical and thermal properties. For example, the copolymer with diallyl phthalate has a bending strength of 1190 kg cm^{-2} which hardly changes after 6 h at 250°C. Copolymers of 2-allylphenol with methyl methacrylate and with ethylene dimethacrylate retain a fairly high strength after heat treatment at 300°C in the presence of air. Furthermore, these copolymers exhibit high heat resistance (above 500°C) and thermal stability.

REFERENCES

1. "Modern Plastics, Encyclopedia issue for 1964", New York, 1963, Vol. 41, No. 1A, p. 140.
2. Brit Plastics, 40, 91 (1967).
3. R. L. Tracey, Brit. Plastics, 39, 40 (1966).
4. H. Starkweather, A. Adikoff, and F. Eirich, Ind. Eng. Chem., 47, 302 (1955).
5. H. Raech, "Allylic Resins and Monomers", Reinhold Publ. Corp., New York, 1965.
6. Encyclopedia of Polymer Technology", New York, 1964, Vol. 1, p. 771.

7. R. C. Laible, Chem. Rev., 58, 807 (1958).
8. I. Sakurada and G. Takahashi, Chem. High Polymers (Tokyo), 14, 156 (1957).
9. S. F. Reed and M. G. Baldwin, J. Polymer Sic., A2, 1355 (1964).
10. M. Litt and F. R. Eirich, J. Polymer Sci., 45, 379 (1960).
11. N. G. Gaylord and F. M. Kujawa, J. Polymer Sci., 41, 495 (1959).
12. N. G. Gaylord and F. R. Eirich, J. Amer. Chem. Soc., 74, 334 (1952).
13. P. D. Bartlett and R. Altschul, J. Amer. Chem. Soc., 67, 816 (1945).
14. N. G. Gaylord, J. Polymer Sci., 22, 71 (1956).
15. I. Sakurada and G. Takahashi, Chem. High Polymers (Tokyo), 11, 266 (1954); Chem. Abs., 50, 601 (1956).
16. A. C. R. Brown and D. G. L. James, Canad. J. Chem., 40, 796 (1962).
17. C. Walling, J. Polymer Sci., 48, 335 (1960).
18. C. Walling and J. Pellon, J. Amer. Chem. Soc., 79, 4782 (1957).
19. P. Bartlett and F. A. Tate, J. Amer. Chem. Soc., 75, 91 (1953).
20. P. Argon, T. Alfrey, J. Bohrer, H. Haas, and H. Wechsler, J. Polymer Sci., 3, 157 (1948).
21. N. G. Gaylord and F. R. Eirich, J. Polymer Sci., 7, 575 (1951).
22. N. G. Gaylord and F. R. Eirich, J. Polymer Sci., 5, 743 (1950).
23. N. G. Gaylord and F. R. Eirich, J. Amer. Chem. Soc., 73, 4981 (1951).
24. K. Nozaki and P. D. Bartlett, J. Amer. Chem. Soc., 68, 1686 (1946).
25. N. G. Gaylord and F. R. Eirich, J. Amer. Chem. Soc., 74, 337 (1952).
26. N. G. Gaylord, M. Katz, and H. F. Mark, J. Polymer Sci., B2, 151 (1964).
27. P. D. Bartlett and R. Altschul, J. Amer. Chem. Soc., 67, 812 (1945).
28. D. G. L. James and G. E. Troughton, J. Polymer Sci., A3, 75 (1965).
29. V. A. Kargin, V. A. Kabanov, and V. P. Zubov, Vysokomol. Soed., 2, 765 (1960).
30. V. P. Zubov, M. B. Loginov, V. B. Golubev, et al., "Materialy Simpoziuma po Makromolekulyarnoi Khimii, Tokio, 1966" (Proceedings of the Symposium on Macromolecular Chemistry, Tokyo, 1966), Vol. 2, p. 56.
31. C. H. Bamford, A. D. Jenkins, and R. Johnston, J. Polymer Sci., 29, 355 (1958).
32. V. F. Kulikova, I. V. Savinova, V. P. Zubov, V. A. Kabanov, L. S. Polak, and V. A. Kargin, Vysokomol. Soed., A9, 299 (1967).
33. M. Imoto, T. Otsu, and B. Yamada, Chem. Abs., 64, 12 793 (1966).
34. M. Imoto, T. Otsu, B. Yamada, and A. Shimizi, Makromol. Chem., 82, 277 (1965).
35. S. A. Dolmatov and L. S. Polak, Kinetika i Kataliz, 6, 797 (1965).
36. S. A. Dolmatov and L. S. Polak, Kinetika i Kataliz, 7, 27 (1966).
37. S. A. Dolmatov and L. S. Polak, Neftekhimiya, 3, 683 (1963).
38. S. A. Dolmatov, Kinetika i Kataliz, 7, 214 (1966).
39. M. S. Matheson and L. M. Dorfman, J. Chem. Phys., 32, 1870 (1960).
40. A. F. Everard, G. A. Swan, and P. S. Timmons, J. Chem. Soc., 918 (1962).
41. W. T. Dixon and R. O. Norman, J. Chem. Soc., 3119 (1963).
42. L. E. Gusel'nikov, N. S. Nametkin, L. S. Polak, and T. I. Chernyshova, Vysokomol. Soed., 6, 2002 (1964).
43. I. N. Lyashenko, N. S. Nametkin, L. S. Polak, A. V. Topchiev, A S. Fel'dman, and T. I. Chernysheva, Vysokomol. Soed., 3, 833 (1961).
44. F. F. Shcherbina and I. P. Fedorova, Vysokomol. Soed., 7, 1549 (1965).
45. G. Hardy, L. Nagy, and F. Cser, Chem. Abs,, 64, 15 994 (1966).
46. G. F. D'Alelio, A. B. Finestone, L. Taft, and T. U. Miranda, J. Polymer Sci., 45, 83 (1960).
47. A. V. Topchiev, V. N. Andronov, and G. I. Chernyi, Neftekhimiya, 3, 725 (1963).
48. A. V. Topchiev, E. A. Mushina, and A. I. Perel'man, Neftekhimiya, 3, 74 (1963).
49. G. Pregaglia and M. Binaghi, J. Polymer Sci., 51, s61 (1961).
50. B. P. 854 207 (1960); Chem. Abs., 55, 11 920 (1961).
51. S. Bywater, P. E. Black, and D. M. Wiles, Canad. J. Chem., 44, 695 (1966).
52. S. Murahashi, S. Nozakura, and H. Hatada, Bull. Chem. Soc. Japan, 34, 631 (1961).
53. A. B. Finestone, G. F. D'Alelio, and C. Brauschweiler, Chem. Abs., 57, 4848 (1962).
54. G. F. D'Alelio and T. R. Hoffend, J. Polymer Sci., Part A-1, 5, 323 (1967).
55. V. Ya. Bogomol'nyi, Vysokomol. Soed., 1, 1469 (1959).
56. H. W. Coover and F. B. Joyner, US P 3 230 208 (1966); Chem. Abs., 64, 14 309 (1966).
57. T. L. Dawson and R. D. Lundberg, J. Polymer Sci., A3, 1801 (1965).
58. J. P. Kennedy, J. Polymer Sci., A2, 5171 (1964).
59. G. B. Butler and F. L. Ingley, J. Amer. Chem. Soc., 73, 1512 (1951).
60. G. B. Butler and J. L. Nash, J. Amer. Chem. Soc., 73, 2538 (1951).
61. S. Nose and K. Satoshige, Japanese P. 15 591 (1960); Chem. Abs., 55, 10 961 (1961).
62. M. D. Barnett and G. B. Butler, J. Org. Chem., 25, 309 (1960).
63. G. B. Butler, Amer. Chem. Soc., Div. Polymer Chem., Preprints, 8, No. 1, 35 (1967).
64. M. Oiwa and Y. Ogata, J. Chem. Soc. Japan, 79, 1506 (1958); Chem. Abs., 54, 4488 (1960).
65. S. G. Matsoyan, G. M. Pogosyan, and G. A. Zhamkochyan, Izv. Akad. Nauk Arm. SSR, Khim. Nauki, 17, 62 (1964).
66. S. G. Matsoyan, G. M. Pogosyan, A. O. Dzhagalyan, and A. V. Mushegyan, Vysokomol. Soed., 5, 854 (1963).
67. K. D. Berlin and G. B. Butler, J. Amer. Chem. Soc., 82, 2712 (1960).
68. C. S. Marvel and R. G. Woolford, J. Org. Chem., 25, 1641 (1960).
69. S. Harada and M. Katayama, Makromol. Chem., 90, 177 (1966).
70. D. P. Brust, Chem. Abs., 64, 9659 (1966).
71. G. B. Butler and M. L. Miles, Polymer Eng. Sci., 6, (1), 71 (1966).
72. L. Trossarelli, M. Guaita, and A. Priola, Makromol. Chem., 100, 147 (1967).
73. S. Harada and K. Arai, Makromol. Chem., 107, 64, 78 (1967).
74. G. B. Butler and M. A. Raymond, J. Polymer Sci., A3, (10), 3413 (1965).

75. T. Holt and W. Simpson, Proc. Roy. Soc., A238, 154 (1956).
76. B. H. Clampitt and A. P. Mueller, J. Polymer Sci., 62, 15 (1962).
77. K. Sultanov, "Sintez i Izuchenie Tsiklicheskoi Polimerizatsii Dienovykh Atsetalei: Divinil-, Allilvinil-, i Diallilatsetalei" (Synthesis and Investigation of the Cyclic Polymerisation of Diene Acetals: Divinyl, Allyl Vinyl, and Diallyl Acetals), Candidate's Thesis, Institute of Macromolecular Compounds, Leningrad, 1963.
78. G. B. Butler and R. J. Angelo, J. Amer. Chem. Soc., 79, 3128 (1957).
79. G. B. Butler, A. Crewshow, and W. L. Miller, J. Amer. Chem. Soc., 80, 3615 (1958).
80. C. S. Marvel and R. D. Vest, J. Amer. Chem. Soc., 79, 5771 (1957).
81. I. A. Arbuzova, S. A. Plotkina, and O. V. Sokolova, Vysokomol. Soed., 4, 843 (1962).
82. I. A. Arbuzova and S. A. Plotkina, Vysokomol. Soed., 6, 662 (1964).
83. I. A. Arbuzova, E. S. Fedorova, S. A. Plotkina, and R. M. Minkova, Vysokomol. Soed., A9, 189 (1967).
84. P. L. Nichols and E. Yanovsky, J. Amer. Chem. Soc., 66, 1625 (1944).
85. P. L. Nichols and E. Yanovsky, J. Amer. Chem. Soc., 67, 46 (1945).
86. P. L. Nichols, R. M. Hamilton, L. T. Smith, and E. Yanovsky, Ind. Eng. Chem., 37, 201 (1945).
87. A. N. Wrigley and E. Yanovsky, J. Amer. Chem. Soc., 70, 2194 (1948).
88. E. A. Talley, M. D. Vale, and E. Yanovsky, J. Amer. Chem. Soc., 67, 2037 (1945).
89. P. L. Nichols, A. N. Wrigley, and E. Yanovsky, J. Amer. Chem. Soc., 68, 2020 (1946).
90. M. Zief and E. Yanovsky, Ind. Eng. Chem., 41, 1697 (1949).
91. B. P. 821 977 (1959); Chem. Abs., 54, 6552 (1960).
92. H. Dannenberg and D. Adelson, US P 2 545 689 (1951); Chem. Abs., 45, 5449 (1951).
93. C. H. Fisher, M. Zief, and R. C. Hockett, US P 2 594 303 (1952); Chem. Abs., 46, 9322 (1952).
94. P. L. Nichols, R. M. Hamilton, L. T. Smith, and E. Yanovsky, Paint. Ind. Mag., 60, 84 (1945).
95. P. L. Nichols and R. M. Hamilton, US P 2 449 816 (1948); Chem. Abs., 43, 2028 (1949).
96. P. L. Nichols and L. T. Smith, US P 2 458 191 (1949); Chem. Abs., 43, 2466 (1949).
97. I. Sakurada and G. Takahashi, Chem. High Polymers (Tokyo), 11, 348 (1954); Chem. Abs., 50, 602 (1956).
98. E. Shokal, P. A. Devlin, and D. L. Winkler, US P 3 040 010 (1962); 20C193 (1964).
99. E. B. Davidson, J. Polymer Sci., B4, 175 (1966).
100. R. H. Martin, US P 3 025 280 (1962); Chem. Abs., 57, 3629 (1962).
101. E. C. Britton and C. W. Davis, US P 2 160 943 (1939); Chem. Abs., 33, 7442 (1939).
102. I. P. Losev and S. M. Zhivukhin, "Trudy 1 i 2 Konferentsii po Vysokomolekularnym Soedineniam" (Transactions of the First and Second Conference on Macromolecular Compounds), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1945, p23.
103. R. F. Fisher, J. Appl. Polymer Sci., 7, 1451 (1963).
104. P. Castan and C. Gandillon, Swiss P. 369 898 (1963); Chem. Abs., 59, 15 445 (1963).
105. French P. 1 320 809 (1963).
106. M. F. Sorokin and E. L. Gershanova, Lakokrasochnye Materialy i Ikh Primenenie, No. 4, 1 (1966).
107. V. F. Jenkins, A. Mott, and R. J. Wicker, J. Oil Colour Chemists' Assoc., 44, 42 (1961).
108. H. Dannenberg, T. F. Bradley, and T. W. Evans, Ind. Eng. Chem., 41, 1709 (1949).
109. T. L. Phillips, Brit. Plastics, 34, 69 (1961).
110. D. E. Cordier, US P 2 623 030 (1952); Chem. Abs., 47, 3613 (1953).
111. H. W. Chatfield, Paint Technol., 26, 17 (1962).
112. H. W. Chatfield, Paint Technol., 26, 13 (1962).
113. W. J. Maker, US P 2 852 487 (1958).
114. T. F. Anderson, US P 2 632 753 (1953); Chem. Abs., 47, 7259 (1953).
115. T. F. Anderson, US P 2 635 089 (1953); Chem. Abs., 47, 6700 (1953).
116. N. P. Robie, US P 2 496 234 (1950); Chem. Abs., 44, 3691 (1950).
117. A. I. Tarasov and M. A. Bulatov, USSR P. 168 876 (13th July, 1962); Byul. Izobret., No. 5 (1965).
118. A. I. Tarasov and M. A. Bulatov, "Trudy Instituta Khimii, Ural'skii Filial AN SSSR" (Transactions of the Institute of Chemistry, The Urals Branch of the USSR Academy of Sciences), Sverdlovsk, 1966, No. 13, p. 123.
119. V. I. Volodina, A. I. Tarasov, and D. I. Kurbatov, Zhur. Anal. Khim., 22, 1438 (1967).
120. A. I. Tarasov, V. I. Volodina, and S. S. Spasski, Zhur. Anal. Khim., 21, 360 (1966).
121. M. F. Sorokin and E. L. Khinchina, Lakokrasochnye Materialy i Ikh Primenenie, No. 5, 15 (1964).
122. M. F. Sorokin and E. L. Khinchina, Lakokrasochnye Materialy i Ikh Primenenie, No. 6, 1 (1964).
123. "α-Allyl Glycerol Ether", Technical Information Bull., M. D.: 109 Shell Chemical Co., New York, December 1958 (quoted after Ref. 3).
124. H. Willersinn, French P. 1 234 630 Cl.co8f, Applied for by Badische-Anilin et Soda-Fabrik, A. G. (applied for 5th September, 1959; published 18th October, 1960).
125. E. L. Kropa and T. F. Bradley, US P 2 280 242 (1942); Chem. Abs., 36, 5289 (1942).
126. A. I. Tarasov, Z. S. Krivoruchkina, and S. S. Spasskii, USSR P. 1 233 902 (16th August, 1965); Byul. Izobret., No. 3 (1969).
127. T. V. Novikova, A. I. Tarasov, O. M. Levitskaya, and R. D. Palishkina, USSR P 176 345 (2nd November 1965); Byul. Izobret., No. 22 (1965).
128. A. I. Tarasov, V. I. Kodolov, and S. S. Spasskii, USSR P 171 554 (14th February, 1964); Byul. Izobret., No. 11 (1965).
129. A. I. Tarasov, M. A. Obolonskaya, V. G. Lundina, and S. S. Spasskii, Plast. Massy, No. 5, 23 (1967).
130. N. N. Zinin, Annalen, 96, 361 (1885).
131. A. Ya. Drinberg, "Tekhnologiya Plenkoobrazuyushchikh Veshchestv" (Technology of Film-forming Substances), Goskhimizdat, Leningrad, 1955, p. 516.
132. H. Raech and J. L. Thomas, Modern Plastics, 38, No. 10, 143 (1961).
133. A. L. Smith, Ind. Eng. Chem., 58,(4), 50 (1966).
134. L. S. Burnett, "Modern Plastics. Encyclopedia Issue for 1963", 1962, Vol. 40, No. 1A, p. 146.
135. F. P. Greenspan, "Modern Plastics. Encyclopedia Issue for 1964", 1963, Vol. 41, No. 1A, p. 140.
136. J. L. Thomas, Insulation, 7, 25 (1961).
137. K. Oda, M. Niki, and K. Takiyama, Japanese P. 544 (1965); Chem. Abs., 64, 16 089 (1966).
138. Belg. P. 545 030 (1956); Chem. Abs., 54, 16 927 (1960).

139. Tsutomiu Akita and Tonoo Nagai, Japanese P. 1793 (1958); Ref. Zhur. Khim., 14S230 (1964).
140. E. Szabóné-Réthy and I. Vancosóné-Szmercsanyi, Magyar kem. lapia, 18, 328 (1963).
141. T. Morikawa and K. Takiguchi, US P 3 012 013 (1959); Chem. Abs., 56, 6185 (1962).
142. H. H. Beacham, J. Litwin, and C. W. Johnston, Plast. Technol., 9, 44 (1963).
143. G. Sarofeen, US P 2 964 501 (1960); Chem. Abs., 55, 10961 (1961).
144. H. L. Gerhart, DBR P. 1 099 174 (1961); Chem. Abs., 55, 26475 (1961).
145. R. Jacquier, French P. 1 254 962 (1960); Chem. Abs., 56, 10320 (1962).
146. S. Kohn and G. Taguet, French P. 1 133 032 (1957); Chem. Abs., 54, 968 (1960).
147. B. P. 863 573 (1961); Chem. Abs., 55, 18179 (1961).
148. C. H. Heiberger and J. Thomas, US P. 3 087 915 (1963);
149. J. Le Prevost and S. Sorepe, French P. 1 259 025 (1960); Chem. Abs., 56, 7513 (1962).
150. P. E. Willard, B. P. 894 239 (1962); Chem. Abs., 57, 8735 (1962).
151. W. Festag, DBR P. 1 131 016 (1962); Chem. Abs., 57, 8739 (1962).
152. W. Festag, DBR P. 1 123 111 (1962); Chem. Abs., 57, 6132 (1962).
153. C. H. Heiberger and J. L. Thomas, B. P. 861 817 (1961); Chem. Abs., 55, 20506 (1961).
154. I. Vancsó-Szmercsányi and J. Paulik, Plaste und Kautschuk, 10, 462 (1963).
155. M. F. Lalau-Keraly, Compt. rend., 250, 2697 (1960).
156. J. Majer, Chem. prumysl., 8, 265 (1958).
157. P. E. Willard, US P. 3 030 341 (1962); Chem. Abs., 58, 3558 (1963).
158. M. F. Lalay-Keraly, Compt. rend., 253, 2975 (1961).
159. K. Wunsch, Plaste und Kautschuk, 10, 8 (1963).
160. T. W. Evans, D. E. Adelson, and L. N. Whitehill, US P. 2 500 607 (1950); Chem. Abs., 44, 4722 (1950).
161. A. Suzuki, Chem. High Polymers (Tokyo), 1072 (1962); Ref. Zhur. Khim., 9S451 (1964).
162. H. Raech, Kunstoff-Rundschau, 11, 69 (1964).
163. H. Mayer, DBR P. 1 104 182 (1961); Chem. Abs., 55, 25371 (1961).
164. Y. Harano, Plast. Age, No. 12, 89 (1964).
165. M. F. Lalau-Keraly, Compt. rend., 249, 1213 (1959).
166. French P. 1 276 039 (1962); Chem. Abs., 57, 6189 (1962).
167. C. W. Johnston, J. L. Thomas, and A. V. Duluis, Mach. Design, 34, 126 (1962).
168. G. Takahashi, Chem. High Polymers (Tokyo), 14, 151 (1957); Chem. Abs., 52, 1660 (1958).
169. J. G. Kuderna and R. H. Snyder, US P. 2 498 084 (1950); Chem. Abs., 44, 4722 (1950).
170. P. O. Towney, US P. 2 546 798 (1951); Chem. Abs., 45, 7379 (1951).
171. A. Ya. Drinberg, B. M. Fundyler, and K. G. Zinger, Symposium, "Khimiya i Fiziko-khimiya Vysokomolekulyarnykh Soedinenii" (Chemistry and Physical Chemistry of High-Molecular-Weight Compounds), Izd. Akad. Nauk SSSR, Moscow, 1952, p. 83.
172. B. S. Bernstein, G. Odian, S. Binder, and A. Benderly, J. Appl. Polymer Sci., 10, 143 (1966).
173. B. P. 858 916 (1961); Chem. Abs., 55, 14 993 (1961).
174. C. H. Alexander, Belg. P. 614 391 (1962); Chem. Abs., 58, 3520 (1963).
175. Dutch P. 102 479 (1962).
176. DBR P. 1 069 314 (1959); Chem. Abs., 55, 9967 (1961).
177. E. Ya. Golysheva, A. R. Fragina, and A. P. Levin, Plast. Massy, No. 1, 7 (1961).
178. US P. 3 012 012 (1961).
179. G. Gatta and G. Benetta, Ital. P. 611 733 (1960); Chem. Abs., 55, 21670 (1961).
180. R. H. Martin, US P. 3 012 011 (1961).
181. S. D. Douglass, US P. 3 008 911 (1961).
182. B. F. Landrum and R. L. Herbst, US P. 2 951 783 (1960); Chem. Abs., 55, 1090 (1961).
183. Ital. P. 630 731 (1961); Chem. Abs., 57, 16 894 (1962).
184. A. A. Berlin, A. K. Dabagova, and E. F. Rodionova, "Sbornik Statei po Obshchei Khimii" (Collected Papers on General Chemistry), Izd. Akad. Nauk SSSR, 1953, Vol. II, p. 1560.
185. L. Gindin, S. Medvedev, and E. Fleshler, Zhur. Obshch. Khim., 19, 1694 (1949).
186. R. C. Schulz, M. Marx, and H. Hartman, Makromol. Chem., 44, 281 (1961).
187. W. Kawai, J. Polymer Sci., Part A-1, 4, 1191 (1966).
188. A. Polis, DBR P. 1 053 786 (1959); Chem. Abs., 55, 9950 (1961).
189. K. Noma, R. Yosomiya, and I. Sakurada, Chem. High Polymers (Tokyo), 22, 166 (1965); Ref. Zhur. Khim., 1, C110 (1966).
190. B. P. 948 718 (1964).
191. M. Donati et al., Makromol. Chem., 60, 233 (1963).
192. M. G. Baldwin and S. F. Reed, J. Polymer Sci., A1, 1919 (1963).
193. D. M. Wiles and S. Brownstein, J. Polymer Sci., B3, 951 (1965).
194. T. Otsu, T. Ito, and M. Imoto, J. Polymer Sci., B3, 113 (1965).
195. M. Oiwa, J. Chem. Soc. Japan, 78, 1403 (1957); Chem. Abs., 52, 8701 (1958).
196. J. L. Lang, US P 3 055 872 (1962); Chem. Abs., 57, 16 891 (1962).
197. K. Thinius and K. Friese, Plaste und Kautschuk, 7, 3 (1960).
198. V. P. Golendeev and I. S. Okronova, "Trudy po Khimii i Tekhnologii, Gor'kii" (Papers on Chemistry and Technology, Gorky), 1964, No. 2, p. 326.
199. C. Schramm and C. B. Miller, US P. 3 062 790 (1962).
200. R. H. Martin, US P. 3 043 814 (1962).
201. Shao-Hsiung Li, Kao Fên Tsu T'ung Hsun, 3, 355 (1959); Chem. Abs., 54, 20287 (1960).
202. Shao-Hsiung Li, Kao Fên Tsu T'ung Hsun, 3, 355 (1959); Ref. Zhur. Khim., 2P32 (1961).
203. B. M. Rutovskii and A. M. Shur, Zhur. Prikl. Khim., 24, 1173 (1951).
204. E. R. Blout and B. E. Ostberg, J. Polymer Sci., 1, 230 (1946).
205. Dutch P. 292 416 (1965); Chem. Abs., 64, 8487 (1966).
206. J. J. Pellon, N. M. Smith, R. L. Kugel, K. J. Valan, and W. M. Thomas, J. Appl. Polymer Sci., 10, 429 (1966).
207. J. J. Pellon, N. M. Smith, R. L. Kugel, and W. M. Thomas, J. Appl. Polymer Sci., 10, 421 (1966).
208. W. Wilson and H. May, B. P. 1 022 563 (1966); Chem. Abs., 64, 19 824 (1966).
209. B. P. 844 231 (1960); Chem. Abs., 55, 5031 (1961).
210. N. H. Chemberlain, Plastics (London), 9, 622 (1945).

211. W. Simpson, J. Soc. Chem. Ind., 65, 107 (1946).
212. B. I. Keda and E. I. Vasil'eva, Izv. Akad. Nauk SSSR, Ser. Khim., 1458 (1966).
213. D. Hill and L. Valentine, J. Polymer Sci., 37, 455 (1959).
214. T. T. Minakova, F. P. Sidel'kovskaya, and M. F. Shostakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1880 (1965).
215. Dutch P. 6 505 969 (1965); Chem. Abs., 64, 12 911 (1966).
216. P. D. Bartlett and K. Nozaki, J. Amer. Chem. Soc., 68, 1495 (1946).
217. R. Sartorius and F. Schuelde, DBR P. 1 033 409 (1958); Chem. Abs., 54, 13 723 (1960).
218. B. N. Rutovskii and N. S. Leznov, Zhur. Prikl. Khim., 22, 1008 (1949).
219. B. N. Rutovskii and N. S. Leznov, Zhur. Prikl. Khim., 22, 887 (1949).
220. Gy. Hardy, L. Nagy, and F. Czer, Magyar Kem. Folyóirat, 72, 112 (1966).
221. D. A. Kardashev, N. S. Leznov, and V. P. Nuzhdina, Khim. Prom., No. 2, 5 (1945).
222. G. F. D'Alelio, US P. 3 074 866 (1963).
223. Wm. S. Reid, B. P. 821 093 (1959); Chem. Abs., 54, 2814 (1960).
224. US P. 3 013 305 (1961).
225. R. H. Martin, US P. 3 025 272 (1962); Chem. Abs., 56, 14 485 (1962).
226. DBR P. 967 485 (1957); Chem. Abs., 54, 13 745 (1960).
227. DBR P. 967 487 (1957); Chem. Abs., 54, 13 746 (1960).
228. J. Kennedy and V. J. Wheeler, Analyt. Chem. Acta, 20, 412 (1959).
229. P. O. Tonwey and J. G. Kuderna, US P. 2 489 099 (1950); Chem. Abs., 44, 4722 (1950).
230. R. H. Martin, US P. 3 043 816 (1962); Chem. Abs., 57, 11 342 (1962).
231. B. P. 1 009 421 (1965); Chem. Abs., 64, 3786 (1966).
232. W. Hodes and R. E. Van Strein, US P. 3 046 258 (1962); Chem. Abs., 58, 1602 (1963).
233. French P. 1 298 513 (1962).
234. Dutch P. 6 500 207 (1965); Chem. Abs., 64, 3854 (1966).
235. R. H. Martin, US P. 3 012 009 (1959); Chem. Abs., 56, 8940 (1962).
236. S. G. Cohen, B. E. Osberg, D. B. Sparrow, and E. R. Blout, J. Polymer Sci., 3, 264 (1948).
237. W. R. Dial, W. E. Bissinger, B. J. De'Witt, and F. Strain, Ind. Eng. Chem., 47, 2447 (1955).
238. V. G. Ostroverkhov, L. A. Brunovskaya, and A. A. Kornienko, Vysokomol. Soed., 6, 925 (1964).
239. P. A. Devlin, US P. 3 057 833 (1962).
240. G. B. Butler, R. J. Angelo, and A. Crawshaw, US P. 2 926 161 (1960); Chem. Abs., 54, 13 743 (1960).
241. J. R. Lovett, US P. 3 062 798 (1962); Chem. Abs., 58, 2515 (1963).
242. D. C. Spaulding, US P. 3 032 538 (1962); Chem. Abs., 57, 3638 (1962).
243. W. H. Schuller and J. A. Price, US P. 3 032 539 (1962); Chem. Abs., 57, 6151 (1962).
244. F. M. Michelotti, J. Polymer Sci., 59, S1 (1962).
245. J. A. Price, US P. 2 883 370 (1959); Chem. Abs., 53, 14 590 (1959).
246. G. V. Gurash and A. P. Meleshevich, Ukrain. Khim. Zhur., 31, 89 (1965).
247. R. H. Martin, US P. 3 012 019 (1961).
248. M. Oiwa and W. Kawai, J. Chem. Soc. Japan, 76, 684 (1955)
249. H. Ishida, Japanese P. 10 093 (1956); Ref. Zhur. Khim., 23, 94 659 (1960).
250. D. S. Trifan and J. J. Hoglen, J. Amer. Chem. Soc., 83, 2021 (1960).
251. G. B. Butler and M. D. Barnett, Chem. Abs., 55, 24 083 (1961).
252. G. B. Butler and T. W. Brooks, J. Makromol. Chem., 1 (2), 231 (1966).
253. Yun Jen, US P. 2 958 673 (1960); Chem. Abs., 55, 6048 (1961).
254. R. H. Martin, US P. 3 012 010 (1961).
255. G. B. Butler and F. L. Ingley, J. Amer. Chem. Soc., 73, 895 (1951).
256. L. Trossarelli, M. Guaita, and A. Priola, Ricerca Sci. Rend., A8(3), 429 (1965).
257. R. H. Martin, US P. 2 996 486 (1961).
258. F. F. Shcherbina, I. P. Fedorova, and A. P. Ivanova, Vysokomol. Soed., A9, 2615 (1967).
259. E. F. Jordan and A. N. Wrigley, J. Polymer Sci., A2, 3909 (1964).
260. E. F. Jordan and A. N. Wrigley, J. Appl. Polymer Sci., 8, 527 (1964).
261. F. F. Shcherbina and I. P. Fedorova, Vysokomol. Soed., A9, 1321 (1967).
262. E. J. Goethals, J. Bombeke, and E. De Witte, Makromol. Chem., 108, 312 (1967).
263. T. C. Frazier, E. D. Little, and B. E. Lloyd, J. Org. Chem., 25, 1944 (1960).
264. R. W. Roth and R. F. Church, J. Polymer Sci., 55, 41 (1961).
265. B. H. Clampitt, D. E. German, and J. R. Gally, J. Polymer Sci., 27, 515 (1958).
266. B. H. Sheehan, A. P. Bentz, and J. C. Petropoulos, J. Appl. Polymer Sci., 6, 47 (1962).
267. J. K. Gillham and A. F. Lewis, Nature, 195, 1199 (1962).
268. R. I. Gruz, A. A. Vansheidt, and E. K. Strakhova, USSR P. 164 677 (1964).
269. L. A. Lundberg, US P. 2 930 776 (1960).
270. H. M. Day and D. G. Patterson, Modern Plastics, 29, N 11, 116 (1952).
271. P. M. Elliott, Modern Plastics, 29, N 11, 113, 185 (1952).
272. H. M. Day and J. G. Affleck, SPE J., 9, No. 2, 22 (1953).
273. W. Cummings and M. Botwick, Ind. Eng. Chem., 47, 1317 (1955).
274. G. F. D'Alelio, US P. 3 056 760 (1962).
275. N. E. Wahl and H. M. Preston, Modern Plastics, 35, No. 2, 153 (1957).
276. C. B. Murphy, J. A. Palm, C. D. Doile, and E. M. Curtiss, J. Polymer Sci., 28, 447, 453 (1958).
277. J. Nakamura, J. Saito, and T. Soda, J. Chem. Soc. Japan, Ind. Chem. Sect., 67, 648 (1964).
278. W. J. Read, Brit. Plastics, 31, 432 (1958).
279. D. E. German, B. H. Clampitt, and J. R. Galli, J. Polymer Sci., 38, 433 (1959).
280. L. A. Lundber, US P. 3 044 913 (1962).
281. L. Schmerling, US P. 3 046 253 (1962); Chem. Abs., 57, 15 374 (1962).
282. Japanese P. 7835 (1960); Chem. Abs., 57, 6128 (1962).
283. French P. Suppl. 67 646 (1958); Chem. Abs., 55, 6033 (1961).
284. J. A. Caton, US P. 3 049 517 (1962).
285. J. F. Jones, US P. 3 066 118 (1962).

286. J. A. Caton, Austral. P. 233 828 (1961).
287. E. E. Parker and Th. L. St. Pierre, Modern Plastics, 38, No. 6, 133 (1961).
288. H. Prieble, B. Falk, and K. Deutsch, Plaste und Kautschuk, 13, 223 (1966).
289. Japanese P. 528 (1965); Chem. Abs., 64, 16 107 (1966).
290. M. F. Shostakovskii, M. P. Sidel'kovskaya, and F. L. Kolodkin, Vysokomol. Soed., 2, 1794 (1960).
291. G. Greber and G. Degler, Makromol. Chem., 52, 174 (1962).
292. G. B. Butler and R. W. Stackman, J. Org. Chem., 25, 1643 (1960).
293. Yun Boken, L. E. Gusel'nikov, N. S. Nametkin, L. S. Polak, and T. I. Chernysheva, Vysokomol. Soed., 8, 557 (1966).
294. K. D. Berlin and G. B. Butler, J. Org. Chem., 25, 2006 (1960).
295. J. A. Price, M. R. Lytton, and B. G. Randy, J. Polymer Sci., 51, 541 (1961).
296. A. D. Toy and R. S. Cooper, J. Amer. Chem. Soc., 76, 2191 (1954).
297. G. Kamai and V. A. Kukhtin, Dokl. Akad. Nauk SSSR, 89, 309 (1953).
298. P. Robitschek and C. T. Bean, US P. 3 131 115 (1964).
299. A. V. Topchiev, N. S. Nametkin, and L. S. Polak, J. Polymer Sci., 58, 1349 (1962).
300. G. Greber and G. Degler, Makromol. Chem., 52, 184 (1962).
301. T. W. Campbell, US P. 2 958 681 (1960); Chem. Abs., 55, 6028 (1961).
302. Y. Iwakura and N. Nakaboyashi, Ming Hsing Lee, Makromol. Chem., 104, 37 (1967).
303. Y. Tsuda, J. Chem. Soc. Japan, Ind. Chem. Sect., 62, 1112 (1959); Chem. Abs., 57, 13 972 (1962).
304. G. Greber and G. Degler, Makromol. Chem., 52, 199 (1962).
305. K. R. Guenther, US P. 3 240 768 (1966); Chem. Abs., 64, 16 106 (1966).
306. E. L. Kropa, US P. 2 388 161 (1945); Chem. Abs., 40, 592 (1946).
307. C. A. MacKenzie and J. B. Rust, US P. 2 438 612 (1948); Chem. Abs., 42, 4795 (1948).
308. G. S. Kolesnikov, S. L. Davydova, and T. I. Ermolaeva, Vysokomol. Soed., 1, 1493 (1959).
309. G. Greber and L. Metzinger, Makromol. Chem., 39, 189 (1960).
310. B. I. Mikhant'ev and S. A. Kretinin, "Trudy Laboratorii Vysokomolekulyarnykh Soedinenii (NII Esteстvennykh Nauk Voronezhskogo Universiteta)" [Transactions of the Laboratory of High-Molecular-Weight Compounds (Natural Sciences Institute at Voronezh University)], 1962, No. 1, p. 34.
311. H. S. Rotherock, US P. 2 258 718 (1941); Chem. Abs., 36, 595 (1942).
312. K. A. Petrov, A. I. Gavrilova, and V. P. Korotkova, Zhur. Obshch. Khim., 32, 915 (1962).
313. M. F. Sorokin and I. Manovich, Vysokomol. Soed., 8, 444 (1966).
314. E. L. Gefter, Plast. Massy, No. 11, 38 (1961).
315. L. P. Raskina, L. N. Turovskaya, and A. A. Berlin, Plast. Massy, No. 12, 7 (1966).
316. S. Hashimoto, I. Furukawa, and T. Yanegawa, J. Chem. Soc. Japan, Ind. Chem. Sect., 64, 1682 (1961); Chem. Abs., 57, 3620 (1962).
317. R. C. Laible, R. M. Esteve, and J. D. Margerum, J. Appl. Polymer. Sci., 1, 376 (1959).
318. J. Kennedy, B. P. 825 767 (1959).
319. I. A. Krivosheeva, A. I. Razumov, B. Ya. Teitel'baum, and T. A. Yagfarova, Symposium, "Karbotsepnye Vysokomolekulyarnye Soedineniya" (High-Molecular-Weight Carbon Chain Compounds), Izd. Akad. Nauk SSSR, Moscow, 1963, p. 160.
320. R. S. Ludington and W. W. Young, US P. 3 009 897 (1961); Chem. Abs., 56, 11 801 (1962).
321. Junji Ogura and Katsumi Matsumoto, Japanese P. 10 644 (1961); Ref. Zhur. Khim., 10, T137 (1963).
322. A. D. Toy, J. Amer. Chem. Soc., 70, 186 (1948).
323. A. D. Toy and L. V. Brown, Ind. Eng. Chem., 40, 2276 (1948).
324. G. E. Walter, I. Hornstein, and C. A. Sheld, US P. 2 660 542 (1953); Chem. Abs., 48, 1700 (1954).
325. J. Kennedy, B. P. 777 248 (1957); Chem. Abs., 51, 15 339 (1957).
326. J. Kennedy, R. V. Davies, H. Small, and B. K. Robinson, J. Appl. Chem. (London), 9, 32 (1959).
327. J. Kennedy, J. Appl. Chem. (London), 9, 26 (1959).
328. J. W. Haworth, B. P. 675 783 (1952); Chem. Abs., 46, 11 778 (1953).
329. K. I. Beynon, J. Polymer Sci., A1, 3343, 3357 (1963).
330. H. D. Anspon, US P. 3 234 192 (1966); Chem. Abs., 64, 11 408 (1966).
331. S. Hashimoto and I. Furukawa, Chem. High Polymers (Tokyo), 21, No. 234, 647 (1964).
332. A. D. F. Toy and K. H. Rattenbury, DBR P. 1 041 251 (1958); Chem. Abs., 55, 3122 (1961).
333. M. E. Mat'kova and S. S. Spasskii, Vysokomol. Soed., 3, 93 (1961).
334. A. D. Toy and K. H. Rattenbury, US P. 2 714 100 (1955); Chem. Abs., 49, 14 380 (1955).
335. V. I. Kodolov, S. I. Alyamovskii, I. V. Podgornaya, and S. S. Spasskii, Symposium, "Elementoorganicheskie Soedineniya, Trudy Instituta Khimii Ural'skogo Filiala AN SSSR" (Organic Derivatives of the Elements. Transactions of the Institute of Chemistry of the Urals Branch of the USSR Academy of Sciences), Sverdlovsk, 1966, No. 13, p. 93.
336. V. I. Kodolov and S. S. Spasskii, USSR P. 162 661 (11th July, 1963); Byul. Izobret., No. 10 (1964).
337. F. P. Sidel'kovskaya, A. A. Avetisyan, and M. F. Shostakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 702 (1965).
338. R. H. Martin, US P. 2 996 484 (1961); Chem. Abs., 55, 27 987 (1961).
339. G. B. Butler and R. W. Stackman, J. Org. Chem., 25, 1643 (1960).
340. Dutch P. 6 506 295 (1965); Chem. Abs., 65, 853 (1966).
341. A. M. Polyakova, V. V. Korshak, A. A. Sakharova, A. D. Petrov, V. F. Mironov, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 979 (1956).
342. V. F. Mironov and A. D. Petrov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 383 (1957).
343. V. V. Korshak, A. M. Polyakova, V. F. Mironov, A. D. Petrov, and V. S. Tambovtseva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1116 (1959).
344. "Spravochnik Khimika" (The Chemists' Handbook), Izd. Khimiya, Moscow–Leningrad, 1964, p. 954.
345. B. G. Randy, Makromol. Chem., 42, 68 (1960).
346. D. E. Adelson and H. F. Gray, US P. 2 555 775 (1951); Chem. Abs., 45, 8270 (1951).
347. Dutch P. 66 784 (1950); Chem. Abs., 45,
348. R. H. Reinhard, US P. 2 891 037 (1959).
349. M. R. Sullivan and F. Hahn, Offic. Dig. J. Paint Technol. Eng., 37, 1279 (1965); Chem. Abs., 64, 2165 (1966).

350. E. C. Chapin, R. H. Reinhard, and W. F. Yates, US P. 2 962 462 (1960); Chem. Abs., **55**, 7924 (1961).
351. G. Gatta and G. Banetta, Belg. P. 612 110 (1962); Chem. Abs., **58**, 1598 (1963).
352. E. C. Shokal and P. A. Devlin, US P. 2 940 946 (1960).
353. E. C. Shokal and P. A. Devlin, DBR P. 1 059 665 (1959); Chem. Abs., **55**, 14 992 (1961).
354. B. P. 960 835 (1964); Chem. Abs., **64**, 3847 (1966).
355. E. C. Chapin, US P. 2 961 423 (1960).
356. J. J. Zonsveld, US P. 3 013 999 (1961); Chem. Abs., **56**, 15 632 (1962).
357. F. J. Hahn, M. Sullivan, and S. Steinhauer, Offic. Dig. J. Paint Technol. Eng., **37**, 1251 (1965).
358. J. M. Gethins and R. J. Longley, US P. 2 995 535 (1958); Chem. Abs., **56**, 3658 (1962).
359. Dutch P. 99 722 (1961).
360. H. Thiele and F. Jentsch, Kolloid. Z., **190**, 99 (1963).
361. Z. Csuros, M. Gara, and I. Gyurkovics, Acta Chim. Acad. Sci. Hung., **29**, 207 (1961).
362. T. Haneda, M. Ishihara, and Y. Yamane, Japanese P. 14 145 (1959); Chem. Abs., **56**, 10 417 (1962).
363. R. C. Nelson, US P. 3 033 828 (1962).
364. G. Klement, J. Galinke, and M. Dohr, DBR P. 1 207 532 (1965); Chem. Abs., **64**, 14 419 (1966).
365. J. R. Stephens, R. E. Van Strein, and R. L. Broadhead, US P. 3 040 000 (1962); Chem. Abs., **57**, 11 339 (1962).
366. E. C. Chapin, US P. 3 036 029 (1962); Chem. Abs., **57**, 7466 (1962).
367. J. G. Abramo and R. H. Reinhard, US P. 2 975 161 (1961); Chem. Abs., **55**, 17 101 (1961).
368. E. C. Shokal and P. A. Devlin, US P. 2 630 430 (1953).
369. P. H. Carnell, US P. 2 533 425 (1950); Chem. Abs., **45**, 2195 (1951).
370. D. Leaver, A. H. McQuillan, W. Miller, and H. W. W. Ehrlich, J. Chem. Soc., 3331 (1962).
371. T. Hata, M. Ishihara, and Y. Yamane, Japanese P. 14 041 (1961); Ref. Zhur. Khim., 65 149 (1964).
372. A. I. Ageev, A. I. Azrielev, and E. S. Roskin, Vysokomol. Soed., **9**, 571 (1967).
373. S. Murahashi, S. Nasakura, and K. Hatada, Bull. Chem. Soc. Japan, **34**, 631 (1961).
374. I. Ito, H. Hayshi, T. Saigusa, and I. Furukawa, Makromol. Chem., **55**, 15 (1962).
375. W. Bauer and F. Götz, German P. 706 510 (1941); Chem. Abs., **36**, 1952 (1942).
376. N. Nabujin and S. Koji [tentative transcription from Russian (Ed. of Translation)], Japanese P. 6 743 (1962); Ref. Zhur. Khim., 19S210 (1964).
377. G. Beinert and J. Parrod, Makromol. Chem., **70**, 61 (1964).
378. W. Heikrich and K. Klaus, Makromol. Chem., **70**, 54 (1964).
379. V. V. Korshak, S. V. Vinogradova, P. M. Valetskii, and M. G. Deborin, Lakokrasochnye Materialy i Ikh Primenenie, No. 1, 3 (1963).
380. S. V. Vinogradova, V. V. Korshak, V. I. Kul'chitskii, B. V. Lokshin, and G. Z. Mirkin, Vysokomol. Soed., A **10**, 1108 (1968).
381. V. V. Korshak, S. V. Vinogradova, M. G. Korchëvei, and V. I. Kul'chitskii, USSR P. 173 936 (1965).
382. V. V. Korshak, S. V. Vinogradova, M. G. Korchëvei, and L. I. Komarova, Vysokomol. Soed., **7**, 457 (1965).
383. S. V. Vinogradova, V. V. Korshak, and M. G. Korchëvei, Vysokomol. Soed., **7**, 1884 (1965).
384. S. V. Vinogradova, V. V. Korshak, and M. G. Korchëvei, Vysokomol. Soed., **7**, 1889 (1965).
385. V. V. Korshak, S. V. Vinogradova, M. G. Korchëvei, and V. I. Kul'chitskii, Vysokomol. Soed., **8**, 109 (1966).
386. V. V. Korshak, S. V. Vinogradova, and V. I. Kul'chitskii, Vysokomol. Soed., **8**, 1080 (1966).

Institute of Chemistry, The Urals Branch of the USSR Academy of Sciences, Sverdlovsk