73. V.M.Volkov, Uspekhi Khim., 31, 1528 (1962) [Russ.Chem. Rev., 730 (1962)].
74. I.P.Romm and E.N.Gur'yanova, Dokl.Akad.Nauk SSSR, 171, 877 (1966).
75. I.P.Romm, E.N.Gur'yanova, I.P.Gol'dshtein, and K.A.Kocheshkov, Dokl.Akad.Nauk SSSR, 172, 618 (1967).
76. I.P.Romm and E.N.Gur'yanova, Teor.Eksper.Khim., 4, 691 (1968).
77. I.P.Romm, E.N.Gur'yanova, and I.P.Gol'dshtein, Zhur. Fiz.Khim., 42, 220 (1968) [Russ.J.Phys.Chem., 113 (1968)].
78. A.I.Kiss, and B.R.Muth, Acta chim.Acad.Sci.Hung., 22, 397 (1960); 24, 231 (1960).
79. A.Mangini and C.Zauli, J.Chem.Soc., 4960 (1956).
80. K.Bowden and E.A.Braude, J.Chem.Soc., 1068 (1952).
81. I.P.Gol'dshtein, E.N.Gur'yanova, N.N.Zemlyanskii O.P.Syutkina, E.M.Panov, and K.A.Kocheshkov, Izv.Akad. Nauk SSSR, Otd.Khim.Nauk, 2201 (1967).

Laboratory for the Synthesis and Structure of Organoelementary Compounds, Karpov Physico-chemical Institute, Moscow

U. D. C. 541.49 : 542.952.6 : 547.254.6

Organomagnesium Compounds and Their Complexes as Polymerisation Initiators

B.L.Erusalimskii, I.G.Krasnosel'skaya, and I.V.Kulevskaya

This the first review devoted specifically to polymerisation processes initiated by organomagnesium compounds. Attention is concentrated mainly on the anionic polymerisation of unsaturated monomers (hydrocarbons, acrylates, nitriles, vinylpyridines, halogeno-derivatives, etc.). The review also includes short sections on the anionic polymerisation of carbonyl derivatives and cyclic monomers, on cationic polymerisation, and on initiating systems of the Ziegler-Natta type. The bibliography contains 215 references.

CONTENTS

I. Introduction	874
II. Anionic polymerisation of unsaturated monomers	874
III. Polymerisation of carbonyl derivatives and cyclic monomers	880
IV. Cationic polymerisation	881
V. Ziegler-Natta initiating systems	881

I. INTRODUCTION

Until quite recently organomagnesium derivatives occupied a very modest position among the organometallic compounds used as initiators for anionic polymerisation. This was due to their relatively low reactivity towards non-polar unsaturated monomers (i.e. hydrocarbons of the vinyl and diene types), on which most of the research on anionic polymerisation was concentrated for a long time. With studies on the anionic polymerisation of polar monomers, organomagnesium initiators have begun to attract substantially more attention, since in these cases they are quite comparable in efficiency with many organic derivatives of the alkali metals. The considerable experimental data which have now accumulated on polymerisations initiated by organomagnesium compounds have not yet been reviewed and we have therefore attempted to fill this gap. Modern ideas on the composition and structure of organomagnesium compounds have been discussed in detail in the recently published reviews by Wakefield[1] and by Ashby[2].

II. ANIONIC POLYMERISATION OF UNSATURATED MONOMERS

Among studies of the polymerisation of anionic systems by organomagnesium compounds and their complexes, investigations on various polar unsaturated monomers are of the greatest interest. These processes are often highly efficient and stereospecific. Non-polar and low-polarity monomers exhibit a very limited tendency to polymerisation in such systems.

1. Hydrocarbons

Gilman[3-5] and Kinney[6] showed that unsaturated hydrocarbons of the ethylene and diene series do not react with organomagnesium compounds under ordinary conditions. Instances of the addition of alkylmagnesium halides to unsaturated hydrocarbons were established by Fuson[7-10] for compounds of the fluorene and fulvene series containing highly reactive double bonds—dibiphenylylene-ethylene, tetraphenylfulvene, etc.

The first results on the polymerisation of unsaturated hydrocarbons in the presence of organomagnesium compounds were obtained by Ziegler[11], who found that solid polymers were formed in C_2H_4–RMgX(or R_2Mg) systems at 100–150°C and pressures from 100 to 1000 atm. Raising the temperature enables several other hydrocarbon monomers to be polymerised with the same initiators. Wang Fo-sung, Dolgoplosk, Erusalimskii, et al.[12-14] have shown that polymerisation of various diene hydrocarbons with initiators of the above type at 90°C and above is feasible, but even under these conditions the rate of polymerisation is low. When isoprene is bulk-polymerised at 90°C with an initiator concentration of about 0.003 M, the rate does not exceed 1% h^{-1}. Still lower rates characterise the polymerisation of butadiene and 2,3-dimethylbutadiene. Kinetic data on the consumption of the initiator have established

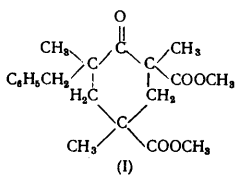
that in the isoprene–$(C_4H_9)_3Mg_2I$ system the rates of initiation and growth are comparable. Thus with an initiator/monomer ratio of 0.01 complete exhaustion of the initiator was observed when 20% of the monomer had been converted. The polyisoprene obtained in the presence of various organomagnesium compounds under these conditions contains 3,4-links as the main structural units (93–99%). The contents of *cis*-1,4-, *trans*-1,4-, and 1,2-links in polybutadiene are 30%, 45%, and 25% respectively (with $(C_4H_9)_3Mg_2I$ as initiator and a polymerisation temperature of 100°C).

Ordinary magnesium alkyls and alkylmagnesium halides are inert towards styrene (at least up to the temperature of its thermal polymerisation). According to Champetier et al.[15] the magnesium–biphenyl–hexametapol [hexamethylphosphoric triamide] system is effective for the polymerisation of styrene and α-methylstyrene.

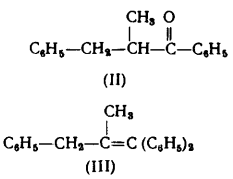
2. Acrylates and Methacrylates

The ability of organomagnesium compounds to initiate the polymerisation of acrylic esters was discovered by Landler[16] in 1949, but systems of this type began to attract significant attention only from the end of the 1950s. Several publications on this question[11,17–28] deal with the effect of the polymerisation conditions on the microstructure of the resulting polymers. Research has also been done[29–41] on the mechanism and the kinetics of the processes involved.

As in other anionic polymerisations of polar monomers, the processes occurring in these systems are complicated by secondary reactions of the initiator with functional groups in the monomer and the polymer chain. According to Goode[29–32] polymerisation in the methyl methacrylate–phenylmagnesium bromide system at 0°C is accompanied by formation of the compounds



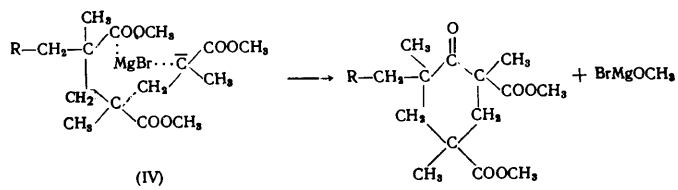
(I)



(II)

(III)

Under the above conditions the relative contents of the polymer and of the compounds (I)–(III) among the reaction products were respectively 96%, 3%, 1%, and 0.1%. Infrared and ultraviolet spectroscopy has established the presence of a large number of short chains in the polymer, the scheme



(IV)

being suggested for their formation.

In a study of the interaction of methyl methacrylate and methyl acrylate with butylmagnesium bromide Tsuruta[33] established that the initiator is consumed mainly in secondary reactions (1,4-addition, interaction with the carbonyl group, metallation with formation of butane)†.

† Similar facts have been established for butyl-lithium, which under similar conditions is consumed predominantly in the formation of butane (55%) and in addition to the carbonyl group (20%)[42].

Studying the kinetics of polymerisation in various organomagnesium halide–methyl methacrylate systems, Watanabe et al.[34–38] and Allen and Moody[39,40] found that the temperature dependence of the rate passes through a maximum, the position of which (the inversion temperature T_i) is determined by the nature of the initiator. In individual cases the reaction orders were also established (Table 1). According to Allen and Moody the inversion phenomenon is due to an increase in the part played by deactivation reactions over a certain temperature range, while the rate of initiation varies little with temperature. Glusker et al.[43–45] have shown that the initiator reacts rapidly with the monomer, but only a small fraction of it forms macromolecules: most of it is consumed in oligomerisation, which is complete after a few minutes, whereas polymerisation lasts under the same conditions for hours. It is suggested that the change which occurs at the inversion temperature in the order of reaction with respect to the monomer (Table 1) represents a change in the way in which the concentration of active centres formed in the initial stage depends on the concentration of the monomer. In this sense the inversion temperature can be regarded as the temperature at which a change occurs in the relative rates of oligomerisation and polymerisation. This ratio in turn determines the fraction of initiator molecules which bring about formation of macromolecules.

Table 1. Kinetics of polymerisation in butylmagnesium bromide–methyl methacrylate systems.

Solvent	Order of reaction with respect to		T, °C	T_i, °C	Ref.
	monomer	initiator			
Toluene	1	2	−50	−25	34, 36
Ether–toluene (1:9)	0.5	—	below T_i	−38.0	40
ditto	2	—	above T_i		40

Table 2. Polymerisation of methyl methacrylate.

Monomer concn., M	Initiator		Solvent	T, °C	Mean rate, % min^{-1}	[η]	Polymer structure	Ref.
	formula	concn., M						
—	MgR_2	—	—	−40	—	—	isotactic	17
1.00	C_6H_5MgBr	0.333	—	−40	2.6	—	—	54
2.93	n-C_4H_9MgBr	0.200	toluene	−50	0.3	0.247	stereoblock	35
2.93	$Mg(n$-$C_4H_9)_2$	0.0005 M	toluene	−78	0.8	2.73	ditto	37
—	Mg-$(C_6H_5)_2CO$	0.04	tetrahydrofuran	−70	0.04	—	,,	27
3.3	C_6H_5MgBr	0.14	ether–toluene	−26	—	—	isotactic	39
5.0	C_6H_5MgBr	0.20	ether–toluene	−40	—	—	stereoblock	39

For systems containing ethyl-, phenyl-, and butyl-magnesium bromides the overall activation energy determined below the inversion temperature was 8 ± 0.3, 10 ± 5, and 13 ± 3 kcal mole^{-1} respectively[40]. In various systems of this type the initial rate of polymerisation has been found to depend on the nature of the radical in the organomagnesium compound. When the process is conducted in a 1 : 9 mixture of diethyl ether and toluene in the presence of various alkylmagnesium bromides, the rate increases in the sequence R = C_2H_5, n-C_3H_7, n-C_4H_9, n-C_6H_{11}, C_6H_5, s-C_4H_9.[39] The mechanism of this phenomenon has not been

Table 3. Polymerisation of derivatives of acrylic and methacrylic acids.

Monomer		Initiator		Solvent	T, °C	Mean rate, % min^{-1}	$[\eta]$	Polymer structure	Ref.
type	concn., M	formula	concn., M						
Methyl thiolmethacrylate	0.05	C_6H_5MgBr	0.001	toluene	0	0.7	0.025	stereoregular	55
Ethyl β-*N*-carbazolylmethacrylate	—	C_6H_5MgBr $(C_2H_5)_2NMgBr$	—	ditto	0	0.01	—	ditto	56
Allyl acrylate	—	C_6H_5MgBr	—	» »	—50	—	1.5	crystalline	57
Menthyl methacrylate	3.3	C_6H_5MgBr	0.1	» »	—15	0.15	0.110	stereoregular	58
Ditto	—	C_6H_5MgBr	—	hydrocarbon	—70	—	—	isotactic	59
Methyl α-phenylacrylate	0.02	C_6H_5MgBr	0.0006	toluene	—78	0.005	0.130	–	60
Methyl α-chloroacrylate	0.025	C_6H_5MgBr	0.0005	ditto	room	0.01	0.309	crystalline	61
Methyl α-chlorothiolacrylate	0.025	C_6H_5MgBr	0.0005	» »	—78	0.04	0.047	ditto	61
s-Butyl methacrylate	—	s-C_4H_9MgBr	—	» »	—40	—	0.055	isotactic	62
α-Methylbenzyl methacrylate	—	C_6H_5MgBr	—	hydrocarbon	—70	—	—	isotactic	59
2-Methyl-2-nitropropyl methacrylate	—	C_6H_5MgBr	—	—	—	—	—	isotactic	63
Trimethylsilyl and benzyl acrylates and methacrylates	—	C_6H_5MgBr	—	—	from −70 to −78	—	—	isotactic	64
2,3-Epoxy- and 2,3-epithio-propyl methacrylate*	—	i-C_4H_9MgBr C_6H_5MgBr $C_6H_{11}MgBr$	—	ether toluene tetrahydro-furan	—78	—	—	stereoregular	65

* Polymerisation occurs only at the double bond.

specially investigated, and the observed differences may be attributed to variation in either the initiation rate constant or the fraction of initiator molecules which form active growth centres. The latter hypothesis is the more plausible.

Watanabe et al.[36] have studied the effect of various complexing agents (KA) on the rate of polymerisation in the methyl methacrylate–butylmagnesium bromide system at [A]/[In] ratios up to unity. Among the large number of compounds used, only pyridine, dioxan, diphenylamine, and diethylamine were found to have an activating effect. It is supposed that new, more active organomagnesium compounds are formed.

The polymerisation of acrylic and methacrylic esters with organomagnesium compounds often occurs stereospecifically. The influence of the polymerisation conditions on the character of the polymers and on the rate of the process can be judged from Tables 2 and 3. The mechanism of the formation of stereoregular polymers, suggested by various authors for systems of this type, is discussed in Reich and Schindler's monograph[46]‡. As for other anionic systems, it is assumed that the decisive stage is formation of a coordination complex of the growing chain and the monomer, which in the case of the ester complexes of organomagnesium compounds would involve displacement of the ester by the monomer. Watanabe[37] explains the role of the nature of alkyl and halogen in the organomagnesium compound by their forming part of a gegenion, to which he assigns the formula $[RMg_2X_2]^+$. Roha[47], examining the known experimental facts in terms of the effect of ionic factors on the structure of the chain, notes that organomagnesium initiators exhibit greater stereospecificity§ than do alkali-metal alkyls, and he attributes this to the relatively less ionic character of organomagnesium compounds. The formation of isotactic polymers of higher molecular weight than the atactic polymers, which is noted in several cases, is explained by Goode[29–32] on the assumption that the deactivating reactions limiting the growing chains take place predominantly when the latter are highly ionic in character, i.e. under conditions which do not ensure formation of isotactic polymers.

Study by nuclear magnetic resonance spectra of the effect of the polymerisation temperature on the structure of polyacrylates formed in the presence of phenylmagnesium bromide and diphenylmagnesium has shown[48–53] that the mode of opening of the double bond is determined at the very start of the reaction. Subsequent variation in temperature has no effect on the structure of the polymer.

3. Nitriles

The ability of organomagnesium compounds to add at the double bond of unsaturated nitriles was first established in 1923 for vinylacetonitrile[66,67]. Investigation of the polymerisation of acrylonitrile and methacrylonitrile originated in a paper by Beamen[68] in 1948, which established that it was possible to obtain polymers of low molecular weight by conducting the process in the presence of butylmagnesium bromide in ethereal medium at temperatures between 20° and −75°C. Acrylonitrile polymers of low molecular weight were also obtained by Terent'ev and Kost[69] and by Askarov et al.[70,71] by the action of several other organomagnesium compounds in ethereal[69,70] and hydrocarbon[71] media. The formation of short chains in all these cases was probably due to an unfavourable ratio of monomer and initiator concentrations. As the work of Erusalimskii, Kulevskaya, et al.[72–78] has established, polymers of molecular weight up to 5×10^5 are formed when polymerisation is conducted in organomagnesium halide–acrylonitrile–hydrocarbon systems at −75°C with the ratio $[M]/[In] \simeq 100$, where [M] is the concentration of monomer and [In] the concentration of initiator¶. Study of the mechanism and kinetics of this process, which has been investigated

‡ Some of the papers which we have cited on the mechanism of the polymerisation of methyl methacrylate are considered in greater detail in this monograph.

§ For example, poly(methyl methacrylate) formed under the influence of phenylmagnesium bromide at −20°C comprises 99% of isotactic sequences[28].

¶ The formation of acrylonitrile polymers of high molecular weight by the use of organomagnesium halides has been reported in a patent[79].

in greatest detail in the acrylonitrile–butylmagnesium chloride–toluene system[74-77], shows that only a small fraction (about 0.01) of the initiator molecules form growing chains. A specific deactivation reaction affects only the initiator, and does not extend to active growth centres, as is indicated by several factors consistent with the development of polymerisation through "live" polymers. These results, together with the finding that the reaction was of the first order with respect to the initiator (for the system containing butylmagnesium chloride) and of the second order with respect to the monomer, while the molecular weight of the polymer was independent of the monomer concentration, led to the following scheme for the process

$$\begin{array}{l} \mathrm{In} + \mathrm{M} \rightleftarrows (\mathrm{In}\cdot\mathrm{M}) + \mathrm{M} \overset{K}{\rightleftarrows} (\mathrm{In}\cdot\mathrm{M}_2) \xrightarrow[k_1]{} \mathrm{M}^* \\ \qquad\qquad\qquad\quad \searrow^{k_3} \\ \qquad\qquad\qquad\quad \text{inactive compounds} \\ \mathrm{M} + \mathrm{M}^*_{n-1} \overset{\text{rapid}}{\rightleftarrows} (\mathrm{M}^*_{n-1}\cdot\mathrm{M}) \xrightarrow[k_2]{\text{slow}} \mathrm{M}^*_n \end{array} \qquad (3)$$

In this scheme the intermediate complexes In.M and In.M_2 are formed, K is the equilibrium constant, k_1, k_2, and k_3 are the rate constants of initiation, growth, and deactivation respectively, and M* is an active centre.

It follows from Eqn. (3) that the proportion of the initiator which forms active centres is determined by the ratio of the rates of initiation and deactivation, i.e. $Kk_1[\mathrm{M}]^2/k_3$. This quantity can also be expressed in terms of the ratio of the experimental molecular weight $\bar{M}_{\mathrm{exp}}$ to the theoretical value $\bar{M}_{\mathrm{th}}$ calculated from [M], [In], and the degree of conversion. Hence

$$\frac{Kk_1}{k_3}[\mathrm{M}]^2 = \frac{M_{\mathrm{exp}}}{\bar{M}_{\mathrm{th}}} \quad .$$

It has been shown[74,77] that a linear relation exists between $\bar{M}_{\mathrm{exp}}/\bar{M}_{\mathrm{th}}$ and $[\mathrm{M}]^2$, which supports the suggested scheme.

The same papers[74,77] record peculiarities of the process depending on the nature of the initiator. In particular, the reaction is of the second order with respect to the initiator and of the first order with respect to the monomer when $(C_4H_9)_3Mg_2I$ is used and (unlike the situation with C_4H_9MgCl and $(C_4H_9)_2Mg$) the polymers formed have a relatively wide molecular-weight distribution. This last feature has been interpreted in terms of the presence of different active centres in equilibrium[80]:

$$\mathrm{RMgI} + \mathrm{R_2Mg} \rightleftarrows \mathrm{R{-}Mg}\overset{\mathrm{R}}{\underset{\mathrm{I}}{\diagdown\diagup}}\mathrm{Mg{-}R} \quad .$$

Consistency of this view with experiment has been confirmed by Bresler et al.[81]

The polymerisation of acrylonitrile in hydrocarbon solution, in contrast to other such processes involving "live" polymers, does not go to completion, owing to the insolubility of polyacrylonitrile in such media and the passage of the growing chains into a solid phase which cannot be penetrated by the monomer. The present of "trapped" live chains in such reaction mixtures can be detected if the system is homogenised by means of a suitable solvent, in particular dimethylformamide[80]. In dimethylformamide medium the process goes extraordinarily rapidly, complete conversion of the monomer being easily achieved†. It is interesting that the rate of polymerisation is substantially increased even in the presence of catalytic quantities of dimethylformamide. Interaction of the latter with organomagnesium halides at −75°C produces coordination complexes, which are less subject to deactivation by interaction with acrylonitrile, and ensure the formation of a larger number (in comparison with RMgX) of active centres[77,78]. This constitutes one of the main reasons for the activating effect of dimethylformamide at $[\mathrm{HCON(CH_3)_2}]/[\mathrm{RMgX}]$ ratios of about unity. Catalytic quantities of dimethyl sulphoxide[78] and hexamethylphosphoramide[82] exert an analogous influence on polymerisation in acrylonitrile–organomagnesium halide–toluene systems. Krasnosel'skaya and Erusalimskii[82] have shown that the acceleration of polymerisation in the presence of complexing agents has various causes. Thus catalytic quantities of hexamethylphosphoramide produce only an increase in the number of active centres: a substantial increase in the yield of polymer is not accompanied in this case by change in molecular weight, compared with results obtained under the same conditions in the absence of hexamethylphosphoramide. Dimethyl sulphoxide and dimethylformamide cause an increase in yield and in the molecular weight of the polymer: both the growth rate constant and the number of active centres increase here (Table 4).

Table 4. Polymerisation in systems comprising 1.5 M acrylonitrile + 0.01 M tributyldimagnesium iodide + a complexing agent in toluene[82] at −75°C for 1 min.

Complexing agent	Conversion, %	Mol. wt., 10^{-3} M	Efficiency of initiation, %
–	11	73	1.3
Hexamethylphosphoramide	65	73	7.7
Dimethylsulphoxide	60	200	2.5
Dimethylformamide	45	160	2.3

Several other papers have discussed the polymerisation of acrylonitrile and methacrylonitrile initiated by organomagnesium compounds as involving the intermediate formation of complexes. Such a conclusion was drawn, for example, by Dawans and Smets[83], who investigated the copolymerisation of acrylonitrile and methacrylonitrile with other monomers under the influence of phenylmagnesium bromide‡, and also by Natta et al.[86], who regard these processes as cases of anionic coordination.

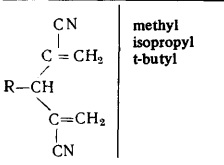
Several papers describe the synthesis of stereoregular polymers of acrylonitrile[87] and methacrylonitrile[86,88-91] under the influence of organomagnesium compounds. In most cases the degree of stereoregularity is estimated from the crystallinity and the solubility of the polymers, but hardly any data are given on their detailed microstructure. This does not apply to work[92-94] in which nuclear magnetic resonance was used to investigate the structure of methacrylonitrile polymers obtained in the presence of various organometallic initiators. The most stereospecific initiators proved to be organomagnesium compounds,

† At −75°C and concentrations of 1.5 M acrylonitrile and 0.005 M butylmagnesium chloride in dimethylformamide medium, polymerisation is complete in a fraction of a minute. In toluene the initial stage of the process (up to 5% conversion) goes at a rate of around 1% min^{-1}.[78,80]

‡ Data on the copolymerisation of acrylonitrile with various monomers in the presence of organomagnesium initiators have been given also in other papers[84,85].

which yielded predominantly isotactic polymers§. According to Natta[86] the stereospecificity of the polymerisation of unsaturated nitriles in the presence of alkylmagnesium halides is due to orientation of the monomer at the stage of coordination of an active centre with the monomer at the nitrogen atom.

Table 5. Polymerisation of α-alkylacrylonitriles and β-alkyl-αγ-dimethyleneglutaronitriles.

Monomer	R	Catalyst	Solvent	Temp., °C	Duration of polymerisation, h	Conversion, %
$CH_2=C(CN)R$	n- propyl	CH_3MgBr	tetrahydrofuran	room	20—70	20
		$Mg(C_2H_5)_2$	toluene	—78		
	isobutyl	CH_3MgBr	tetrahydrofuran	—78	20	10
			toluene			
	neopentyl	CH_3MgBr	tetrahydrofuran	—78	20—70	30
			toluene			
	methyl	CH_3MgBr	toluene	0	4	10
	isopropyl	CH_3MgBr	toluene	0	24	25
	t-butyl	CH_3MgBr	tetrahydrofuran	0	5—25	10
				—78		

The polymerisation of α-alkylacrylonitriles and of β-alkyl-αγ-dimethyleneglutaronitriles under the influence of organomagnesium compounds has been described by Covăcs and Marvel (Table 5).[96] Furukawa et al.[97] have used phenylmagnesium bromide to initiate the polymerisation of *cis*- and *trans*-crotononitrile.

4. Vinylpyridines

The polymerisation of vinylpyridines in the presence of organomagnesium compounds, studied mainly by Natta[98-102], is interesting in connection with the role of various factors in producing the chain structure. In the polymerisation of 2-vinylpyridine in hydrocarbon medium by various metal alkyls, only the magnesium derivatives (RMgX, R_2Mg, R_2NMgX) exhibit high stereospecificity. Nuclear magnetic resonance data indicate that the polymers have an isotactic structure[103-105]. Views on the mechanism of stereoregulation are based on the considerations formulated in discussing the polymerisation of unsaturated nitriles[86] (see subsection 3). In the present case it is postulated that the heteroatom and the double bond of the monomer take part simultaneously in acts of complex formation. This is consistent with differences in the behaviour of 2- and 4-vinylpyridines: stereoregular polymers are formed only in the former case. In Natta's opinion, considerable remoteness of the nitrogen atom from the vinyl group eliminates the possibility that complexes of the growing chain can be formed by means of both donor positions in the monomer, and thereby excludes its rigid orientation in acts of growth. The role of complex formation as a factor determining the microstructure of the polymer is clearly exhibited in the polymerisation of 2-vinylpyridine in the presence of catalytic quantities of Lewis bases, which either hinder or eliminate (depending on their relative basic strength) the stage of complex formation between the growing chain and the monomer (Table 6).

Data are lacking on the kinetics of polymerisation in these systems. The papers cited above indicate only the total conversion of the monomer achieved after a standard time. As Fontanille and Sigwalt[15] remark, polymerisation in the 2-vinylpyridine–biphenyl–magnesium–hexametapol system involves "live" chains and is characterised by a high growth rate constant.

Table 6. Polymerisation of 2-vinylpyridine in anionic systems in toluene at 45°C.[102].

Initiator	Complexing agent (CA)		Yield of polymer in 5 h, %	Crystalline fraction	
	compound	molar ratio [CA]/[In]		content, %	[η] *
$(C_6H_5)_2Mg$	—	—	96	93	0.34
$(C_6H_5)_3MgBr$	—	—	96	85	0.30
C_6H_5MgBr	—	—	92	98	0.49
C_6H_5MgBr	pyridine	2.5	45	0	—
C_6H_5MgBr	diethyl ether	4	80	38	—
C_4H_9Li	—	—	98	0	—
$C_8H_{17}Na$	—	—	85	0	—
$(C_2H_5)_2Be$	—	—	97	**	—
$(C_2H_5)_3Al$	—	—	0	—	—
$[(CH_3)_2N]_2Be$	—	—	40	40	0.27
$[(CH_3)_2N]_3Al$	—	—	15	85	0.35
$LiAlH_4$	—	—	98	82	—

* Determined in dimethylformamide at 30°C.

** Polymer contains 65% of a fraction insoluble in boiling acetone and characterised by low crystallinity.

Some idea of the rate of polymerisation of 2-vinylpyridine with organomagnesium initiators is given by Erusalimskii and Ovsyannikov's results[106] for tributyldimagnesium iodide. At monomer and initiator concentrations of 2.0 M and 0.1 M respectively, quantitative conversion in toluene is reached at −20°C in 10 min. It is shown that effective polymerisation is possible at −50°C. The same paper reports that in hydrocarbon medium 2-methyl-5-vinylpyridine undergoes polymerisation at room temperature.

5. Chlorine-containing Monomers

Organomagnesium compounds have been used for the polymerisation of chlorine-containing monomers—vinyl chloride[107-111], vinylidene chloride[112], chloroprene[14,113-115], and 2,3-dichlorobutadiene[116]—in several researches. Deactivation plays an especially important part with most of these monomers, this being due not only to the great tendency of chlorine atoms to enter into side-reactions with metal alkyls. The low relative activity of these monomers in anionic polymerisation eliminates the possibility of conducting the process at low temperatures; even at room temperature they do not polymerise very rapidly in anionic systems. This makes it impossible to suppress side-reactions by substantially lowering the temperature¶.

§ No data are yet available on the structure of polyacrylonitrile formed in systems involving organomagnesium compounds. A stereoblock isosyndiotactic structure (1 : 1) has been established[95] for the polymer produced in the acrylonitrile–butyl-lithium–toluene system at −78°C.

¶ For example, effective polymerisation can be accomplished in the butyl-lithium–methyl methacrylate system only because the monomer is sufficiently active in the growth reaction at low temperatures. Even at −30°C polymerisation is effectively suppressed by reactions at the carbonyl group.

The polymerisation of vinyl chloride, vinylidene chloride, and chloroprene initiated by organomagnesium compounds is characterised by low consumption of the initiator in forming active centres and cessation of the process at a low degree of conversion. The latter feature, which is shown also by polymerisation of the same monomers in the presence of lithium alkyls[115,117,118], is due to the extension of deactivating reactions to the growing chains. The mechanism of these reactions probably consists in detachment of chlorine from the end of the growing chain by a gegenion:

$$\sim CHCl-CH_2\cdot \quad MgX \rightarrow \sim CH=CH_2 + MgClX$$

This is supported by the data of Guyot and Pham Quang Tho[108-111], who detected vinyl groups in the polymer formed in the vinyl chloride–t-butylmagnesium chloride–tetrahydrofuran system. These workers established the slowness of initiation, which under their conditions lasted for practically the whole time of polymerisation[111], and also the incomplete consumption of the initiator by the initiation reaction: ~ 75% of the initial quantity of initiator was deactivated[110,111]. Polymerisation in this system was found to be formally similar to radical polymerisation (microwave resonance of the polymers constant with time, steady-state occurrence of the reaction). Nevertheless, in view of all the experimental results obtained, the authors do not doubt the anionic character of the polymerisation they were studying.

The occurrence of secondary reactions between the organomagnesium initiator and the chlorine-containing monomer is shown by Erusalimskii and Krasnosel'skaya's investigation[114,115] of polymerisation in the chloroprene–tributyldimagnesium iodide–heptane system. Data on the kinetics of polymerisation, the consumption of the initiator, and the variation in the total concentration of organomagnesium compounds indicate the rapid occurrence of the following parallel reactions

$$M + In \begin{cases} \rightarrow \text{initiation} & < 1\% & (4) \\ \rightarrow \text{elimination of Cl (formation of MgClX)} & 8\% & (5) \\ \rightarrow \text{formation of inactive organomagnesium compounds} & \sim 91\% . & (6) \end{cases}$$

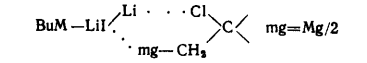
Polymerisation in this system is of the first order with respect to monomer and initiator, and is described by the general equation

$$\frac{[M]_0 - [M]}{[M]_0} = 1 - e^{-k_2/k_3[M^*]_0 (1-e^{-k_3})}\dagger$$

where $[M]_0$ and $[M^*]_0$ are the concentrations of monomer and active centres at zero time, and k_2 and k_3 are the growth and termination rate constants. Values of k_2 and k_3 calculated by means of this equation for 25°C are respectively 0.016 M^{-1} s^{-1} and 1.3×10^{-5} s^{-1}.

A general idea of the effectiveness of the anionic polymerisation of monomers of this type is given by the limiting conversion attainable in several cases (Table 7).

Initiating systems which are considerably more effective towards these monomers are formed by the interaction of certain organomagnesium and organolithium compounds, and have been suggested by Krasnosel'skaya for the polymerisation of chloroprene[112,119-121], vinyl chloride[112,120], and vinylidene chloride[112]. In particular, the interaction of tributyldimagnesium iodide and butyl-lithium in the proportions 1 : 2 in hydrocarbon medium at room temperature yields the heterogeneous system $C_4H_9Li.LiI$ (solid phase)–$2(C_4H_9)_2Mg$ (in solution). The components of the system, which can be easily separated from one another, exhibit enhanced activity towards polymerisation only when present together. Under conditions comparable with those in Table 7 this system brings about up to 90% conversion of chloroprene and up to 50% conversion of vinyl chloride at room temperature. Increased efficiency has been noted also for vinylidene chloride; in this case the limiting conversion was not established. Analogous phenomena are observed when systems formed by the direct interaction of dibutylmagnesium with the complex $C_4H_9Li.LiI$ are used[121]. The hypothetical structure



has been suggested[121] for the active centres.

Table 7. Limiting conversion in the anionic polymerisation of unsaturated chlorine-containing monomers.

Monomer		Initiator		Solvent	Initial rate of polymerisation, % h^{-1}	T, °C	Limiting conversion,		Ref.
compound	concn., M	formula	concn., M				%	reached in, h	
Vinyl chloride	8.0	BuLi	0.09	heptane	3	25	25	15	112
ditto	3.6	Bu^tMgCl $BuMgCl$	0.156	tetrahydrofuran	8	25	~50	25	108, 109
Vinylidene chloride	2.0	Bu_3Mg_2I	0.045	heptane	1	20	18	20	112
		BuLi	0.03	heptane	1	20	4	10	112
ditto	2.0	BuLi	0.10	heptane	1.5	25	7	24	115
Chloroprene	6.0								
ditto	6.0	Bu_3Mg_2I	0.08	heptane	4	40	50	50	115

The mechanism of the process has been examined in greater detail on the closely similar system $C_4H_9Li.LiI$–C_4H_9Li. According to results for the polymerisation of vinyl chloride obtained by Gasan-Zade and Mazurek[112], the enhanced efficiency of the process is due to an increase in the effectiveness of initiation and also a more favourable k_2/k_3 ratio for growth. Both of these constants have lower absolute values than in the polymerisation of vinyl chloride by butyl-lithium.

Dichlorobutadiene differs fundamentally in behaviour from the above monomers. Polymerisation in the $C_4H_4Cl_2$–$(C_4H_9)_3Mg_2I$ system at 20°C takes place at a relatively high rate (around 10% h^{-1} with [M] = 2 M and [In] = 0.025 M), and can be brought to high degrees of conversion[116]. This interesting feature, indicating the exceptionally minor role of termination reactions, can be explained by enhanced reactivity of the monomer (i.e. increase in k_2) or by the absence of labile chlorine atoms (1,2-units) in the polymer chain. In polymers of chloroprene formed by the action of metal alkyls the presence of such units (together with the main structural *trans*-1,4-units) is not excluded[114].

6. Other Monomers and Certain Special Cases

Several other anionic systems involving organomagnesium compounds are worthy of attention. Thus in the

† Reactions (4)–(6) are disregarded here, since they are complete at the very first stage, and the overall rate of polymerisation is low. The value of $[M^*]_0$ is determined from data on the degree of polymerisation, since $\bar{P} = x[M]_0/[M^*]_0$, where x is the conversion.

vinyldiphenylphosphine oxide–organomagnesium halide–toluene system[123] it has been established that termination reactions do not occur (at 25°C). It has been concluded from colorimetric measurements that initiation involves intermediate formation of a monomer–initiator complex, which is then converted into a coloured monomeric anion. An analogous mechanism is assumed for growth (coordination of the phosphine oxide group of the monomer with an active centre).

An interesting case of the use of organomagnesium compounds for synthesising anionic initiators of high molecular weight, suitable for the preparation of graft polymers, has been described by Guber and Egle[124]. Interaction of a styrene–acrylonitrile copolymer with dimethylsilylmethylmagnesium chloride in tetrahydrofuran forms magnesium-substituted imino-groups on the polymer chain:

$$\sim CH_2CH(C_6H_5)-CH_2CH(CN)\sim \xrightarrow{RMgX} \sim CH_2CH(C_6H_5)-CH_2CH(RC{=}NMgX)\sim ,$$

At temperatures of −30°C and below these addition products effectively polymerise acrylonitrile, methyl methacrylate, and 4-vinylpyridine to give the corresponding hybrid polymers.

Grignard reagents have been used by Japanese workers for the migration polymerisation of acrylamide[125–127]. Phenylmagnesium bromide in dioxan showed the highest activity. The peculiar mechanism of this process, leading to the formation of poly-β-alanine, has been studied by Nakayama et al.[126,127]. In particular, when polymerisation is conducted at a high temperature (100°C)‡ in toluene and in pyridine, appreciable differences are observed depending on the nature of the solvent: in pyridine a considerable quantity of dimer is formed, which is barely noticeable in toluene. It has therefore been suggested that polymerisation has a stepwise mechanism in pyridine and a chain mechanism in toluene. The synthesis of block copolymers of acrylamide with acrylonitrile and caprolactam under the influence of alkylmagnesium halides has been reported[128].

Among other monomers which can be polymerised by means of organomagnesium initiators are isopropyl crotonate[129,130], t-butyl crotonate[129–131], methyl atropate[132], isopropenylpyridine[133], and penta-2,4-dienonitrile[134].

III. POLYMERISATION OF CARBONYL DERIVATIVES AND CYCLIC MONOMERS

During recent years organomagnesium compounds have been tested as initiators for the polymerisation of a large number of aldehydes and ketones. Attention has been concentrated mainly on the structure of the polymers formed; in several cases the action of the organomagnesium compounds has been found to be stereospecific (Table 8). Hardly any work has been done specifically on the mechanism of the polymerisation of monomers of this type initiated by organomagnesium compounds. The well known concepts relating to aldehyde–metal alkyl systems, formulated by Natta[136] and by Furukawa[137,138], and generalised by Vogl[154], are entirely applicable to these systems. A case of particular interest is the interaction of but-3-en-2-one and of 3-methylbut-3-en-2-one with butylmagnesium bromide in ethereal solution and in hexane. It was established that polymerisation and secondary reactions—dimerisation of the monomer and formation of butane—take place in parallel[33].

‡ Lowering the temperature for the anionic polymerisation of acrylamide diminishes the role of migration effects. It is possible that polyacrylamide completely free from isomerised units may be synthesised by anionic initiation, but this has not yet been established experimentally.

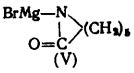
Most of the papers on the polymerisation of various cyclic monomers by the compounds RMgX and R_2Mg are similarly purely descriptive in character. They are concerned predominantly with ethylene and propylene oxides[155–162], with which the process goes efficiently to form polymers of high molecular weight; the oxides of butadiene[157] and of styrene[157], epichlorohydrin[157], and epoxyalkyl ethers[163] have also been mentioned. In the presence of a Grignard reagent trimethylene sulphide yields a crystalline polymer[164]. Organomagnesium compounds initiate the polymerisation of epoxyorganosilanes[165]. Data have been published on the synthesis of copolymers of oxides with other monomers[166], in particular with phthalic anhydride.

Table 8. Polymerisation of aldehydes, ketones, and dimethylketen.

Monomer	Initiator	Solvent	T, °C	Duration	Yield of polymer %	State of polymer	Ref.
HCHO	EtMgBr	Et_2O	−78	—	—	solid	135
CH_3CHO	RMgX	—	−70	—	—	crystalline	136
CH_3CHO	EtMgBr	hexane	−78	20 h	26	ditto	138
$CH_3CH_2CH_2CHO$	Et — and BuMgBr	heptane	−78	—	25—30	"	139
$CH_3CH_2CH_2CHO$	CH_3 — and C_6H_5MgBr	$(CH_3)_2O$	−75	10 min	95—97	"	140
$CH_3CH_2CH_2CHO$	Et_2NMgBr	Et_2O	—	—	40	—	141
CH_2ClCHO	Et_2Mg	toluene	−78	3 days	8	—	142
CH_2=CHCHO	RMgBr	Et_2O, ether hexane,	20—50	5—36 h	10—30	mixture of liquid and solid	143
CH_2=CHCHO	n-C_4H_9MgBr	toluene	room	24 h	30	solid	144
But-3-en-2-one, 1-phenylprop-2-enone, 3-methylbut-3-en-2-one	C_6H_5MgBr; Et_2Mg	in bulk	0	—	—	crystalline	145—147
4,4-Dimethylpent-1-en-3-one	RMgX	tetrahydrofuran	—	—	—	amorphous	148
Acetophenone	C_6H_5MgBr	toluene	−78	3 days	90	solid	149
Dimethylketen	R_2MgX; R_2Mg	toluene, tetrahydrofuran, etc	from 20 to 78	—	20	—	150—153

In most cases the processes can be assumed to have a mechanism of anionic coordination. A possible exception is provided by the initiating systems $RMgX–H_2O$, described by Vandenberg[157], which, by analogy with $R_3Al–H_2O$ systems, can be regarded as cationic. The polymerisation of ethylene and propylene oxides under the influence of R_2Mg has been investigated in rather more detail. According to Kagiya et al.[158–161] this process, in which polymers of high molecular weight are formed in good yield, has a termination reaction. The activation energies for the reactions of growth and termination are found to be 15.8 and 29.2 kcal mole^{-1} respectively.

Organomagnesium compounds, free from ether, are able to initiate the polymerisation of caprolactam[167]. The first act—addition of alkylmagnesium halide to the monomer—takes place even at room temperature, with formation of the compound



(V)

The development of polymerisation requires a substantially higher temperature, 240–250°C. According to the patent literature[168,169] caprolactam is effectively polymerised by the action of organomagnesium compounds in the presence

of certain promoters, e.g. *N*-acetylcaprolactam and *N*-phenylsuccinimide. These agents probably add to the product (V) to form centres which are more active for polymerisation. According to Vofsi et al.[170] the rate constants of reactions of this type are several orders of magnitude larger for substituted than for unsubstituted lactams (Table 9).

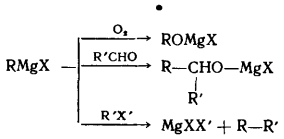
Table 9. Interaction of pyrrolidones with pyrrolidonylmagnesium bromide in tetrahydrofuran at 25°C.[170]

Lactam	Addition rate constant, 10^2 M^{-1} s^{-1}
Pyrrolidone	$3 \cdot 10^{-7}$
N-Methylpyrrolidone	$5 \cdot 10^{-2}$
N-Acetylpyrrolidone	2.8
N-Benzoylpyrrolidone	9.5

Promoter–RMgX systems are used also for initiating the copolymerisation of caprolactam with pyrrolidone[171] and with acrylamide[172]. β-Propiolactone also polymerises in the presence of organomagnesium initiators[173].

IV. CATIONIC POLYMERISATION

Organomagnesium halides, which are Lewis acids, can in principle be regarded as cationic agents. Their ability to initiate cationic polymerisation was discovered with vinyl ethers; here there is no doubt about the mechanism of the process, in view of the inertness of these monomers towards anionic initiators. The first observations in this field were made by Cray[174], who established that various vinyl ethers underwent polymerisation in bulk and in solution in the presence of butylmagnesium bromide at 80°C. It has been assumed that polymerisation is effected by MgX^+, RMg^+, or Mg^{2+} ions, with the monomer acting as cocatalyst. By analogy with other cationic systems it is more probable that catalytic complexes are formed, and produce carbonium ions (if the monomer does actually function as a cocatalyst). However, the concept of the cocatalytic action of vinyl ethers in cationic polymerisation, which was generally accepted until quite recently, requires re-examination in view of results obtained by Eley and Johnson[175], who established that hept-1-en-3-one is inert towards boron trifluoride in hydrocarbon medium provided that the system has been carefully freed from traces of moisture. There is no direct evidence of this kind for organomagnesium initiators, but Iwasaki et al.[176] consider that the presence of an independent cocatalyst is essential in vinyl ether–organomagnesium halide systems. They include among such agents oxygen, aldehydes, metal oxides, and halogenated hydrocarbons. In their opinion reactive compounds can result from the reactions



The cocatalytic action of these agents is confirmed by the results[176]. A positive effect due to oxygen has been noted also by Bruce and Farren[177], but the suggested interpretation of these phenomena cannot be regarded as reliable. In particular, formation of catalytic complexes of the type $R^+[RMgX_2]^-$ cannot be excluded in the presence of alkyl halides. Furthermore, Iwasaki et al.[176] distinguished between use of the $RMgX-O_2$ system and that of alkoxides ROMgX for initiating the polymerisation of vinyl ethers. Only in the former case are polymers of high molecular weight produced. Consequently the active centres which appear when both RMgX and oxygen are present are more complicated in character. As with most other cationic systems, results obtained with maximum exclusion of traces of water would probably be of great interest.

V. ZIEGLER–NATTA INITIATING SYSTEMS

Ziegler's early patents[11] already included the use of organomagnesium compounds among other organometallic components for synthesising new complex catalysts. These compounds have since been used in systems of similar type for the polymerisation of alkenes[13,178–185], acetylene and phenylacetylene[186,187], styrene[13,188–190], and dienes[13,185,191–201]. These systems have not found wide application, obviously owing to their being less stereospecific than catalysts based on aluminium derivatives. In the polymerisation of propene under the influence of $RM-TiCl_3$ catalytic systems, according to Natta[202], organomagnesium compounds result in the formation of polymers having a rather lower isotactic fraction (up to 85%) than do organoaluminium and organoberyllium compounds (90% and 96% respectively). In the polymerisation of diene hydrocarbons a highly stereospecific process is achieved with $RMgX-TiCl_4$(or $TiBr_4$) systems only when certain third components—alkyl iodides[203], hydrogen iodide[204], lithium iodide[205], and others[206–208]—are also present. Under these conditions polybutadiene containing up to 98% of *cis*-1,4-units can be synthesised. In the absence of such additional agents, the greatest homogeneity of chain structure in the polymerisation of dienes under the influence of titanium–magnesium complexes has been found in the isoprene–$(C_4H_9)_3Mg_2I$–$TiCl_4$ system. With an initial ratio of $Mg/Ti = 1.5$, the polyisoprene formed contained 84% of *cis*-1,4-units[13]. *cis*-1,4-Polybutadiene has been obtained in high yield by using the catalytic system $C_6H_5MgX-TiI_4$ ($Mg : Ti \geqslant 2$).[209]

Ziegler–Natta catalysts including magnesium components have been used for the polymerisation of various polar monomers, such as vinyl chloride, acrylonitrile, methyl methacrylate, etc.[11,193,194,210]. The mechanism of the polymerisation of polar monomers initiated by Ziegler–Natta catalysts is a matter of controversy. The most plausible view is the free-radical nature of the process. This was first put forward by Furukawa[211] on the basis of results for the copolymerisation of various pairs of monomers; it has since been confirmed in several kinetic investigations[212,213]§. These conclusions, reached in the study of other systems, can probably be extended to systems involving organomagnesium compounds.

---o0o---

The most interesting aspect of an analysis of the information surveyed in the present Review is to reveal the specific character of organomagnesium compounds distinguishing

§ Milovskaya[214] has discussed a possible mechanism for the generation of free radicals in systems comprising a polar monomer and a Ziegler–Natta catalyst.

them from other organometallic initiators of polymerisation. The data on the polymerisation of isoprene, methacrylonitrile, and 2-vinylpyridine are noteworthy in this connection. In the first case, compounds RMgX and R_2Mg yield polymers constructed almost entirely of 3,4-units (in contrast to the polyisoprene formed by the action of other metal alkyls). In the other two cases a substantially higher stereospecificity of action has been established for these reagents. These characteristics are most probably due to steric factors associated with active centres in the corresponding systems, not to the degree of polarity of the carbon–magnesium bond in the organomagnesium compounds.

Owing to the great sparsity of quantitative data it is difficult to draw rigorous conclusions on the reactivities of different organometallic compounds in polymerisation processes, or to establish the place occupied in this sequence by magnesium derivatives. Nevertheless, there are facts indicating divergence from rules to be expected from general considerations. This applies to differences in the behaviour of lithium and magnesium alkyls towards unsaturated hydrocarbons and halogenated monomers, as is shown especially clearly by a comparison of data on the polymerisation of styrene and of vinyl chloride. Thus the growth rate constants in the polymerisation of styrene in hexane (at 30°C)[215] and of vinyl chloride in heptane (25°C)[117] in the presence of butyl-lithium are respectively 5.0 and 0.0099 $M^{-1}\ s^{-1}$. The reactivity of organomagnesium compounds in these systems is opposite in character: they are inert towards styrene, but cause the polymerisation of vinyl chloride.

Finally, it is worth noting that the lower reactivity in acts of initiation and growth, which is usual for organomagnesium compounds (in comparison with alkali-metal alkyls), is accompanied by a relatively lower tendency to undergo various deactivating reactions. In certain cases this will lead to a relation between the rate constants of the elementary reactions which is more favourable to polymerisation than when alkyl derivatives of the alkali metals are used. This is probably the explanation of the substantially higher conversion limit attainable with organomagnesium initiators, compared with organolithium compounds, in the polymerisation of unsaturated chlorinated monomers.

REFERENCES

1. B.J.Wakefield, Organometall.Chem.Rev., 1, 131 (1966).
2. E.C.Ashby, Quart.Rev., 21, 259 (1967).
3. H.Gilman and H.Crawford, J.Amer.Chem.Soc., 45, 544 (1923).
4. H.Gilman and J.Peterson, J.Amer.Chem.Soc., 48, 423 (1926).
5. H.Gilman and J.McGluphy, Rec.Trav.chim., 47, 418 (1928).
6. C.Kinney and R.Larsen, J.Amer.Chem.Soc., 57, 1054 (1935).
7. R.Fuson, H.Dewald, and R.Gaertner, J.Org.Chem., 16, 21 (1951).
8. R.Fuson and H.Porter, J.Amer.Chem.Soc., 70, 895 (1948).
9. R.Fuson and F.Mumford, J.Org.Chem., 17, 255 (1952).
10. R.Fuson and G.York, J.Org.Chem., 18, 570 (1953).
11. N.G.Gaylord and H.F.Mark, "Linear and Stereoregular Addition Polymers" (Translated into Russian), Inostr.Lit., Moscow, 1962.
12. Wang Fo-sung, B.A.Dolgoplosk, and B.L.Erusalimskii, Vysokomol.Soed., 2, 541 (1960).
13. B.L.Erusalimskii, Wang Fo-sung, and A.P.Kavunenko, J. Polymer Sci., 53, 27 (1961).
14. B.A.Dolgoplosk, B.L.Erusalimskii, A.P.Kavunenko, and A.V.Merkur'eva, Vysokomol.Soed., 4, 1333 (1962).
15. M.Fontanille, P.Sigwalt, and G.Champetier, Compt.rend., 263C, 624 (1966).
16. I.Landler, Rec.Trav.chim., 68, 992 (1949).
17. R.Miller, B.Mills, P.Small, A.Turner-Jones, and D.Goode, Chem.and Ind., 1323 (1958).
18. B.Garrett and W.Goode et al., J.Amer.Chem.Soc., 81, 1007 (1959).
19. B.P. 841388 (1957); J.Appl.Chem.Soc., 11, ii266 (1961).
20. U.S.P. 3100761 (1959).
21. U.S.P. 3222339 (1962).
22. B.P. 927859 (1963); Chem.Abs., 59, 1155c (1963).
23. Jap.P. 12793 (1961); Ref.Zhur.Khim., 17T78P (1963).
24. U.S.P. 3151102 (1958).
25. V.Crescenzi, M.D'Alagni, A.Liquori, L.Picozzi, and M.Savino, Ricerca sci.(Rendiconti), A3, 123 (1963).
26. T.Makimoto, T.Tsuruta, J.Furukawa, et al., J.Chem.Soc. Japan, Ind.Chem.Sect., 65, 279 (1962).
27. T.Tsuruta, T.Makimoto, and J.Nakayama, Makromol. Chem., 90, 12 (1966).
28. K.Matsuzaki, T.Uryu, A.Ishida, T.Ohki, and M.Takeuchi, J.Polymer Sci., 5, A1, 2167 (1967).
29. W.Goode, F.Owens, and W.Myers, J.Polymer Sci., 47, 75 (1960).
30. W.Goode, F.Owens, R.Fellmann, W.Snyder, and J.Moore, J.Polymer Sci., 46, 317 (1960).
31. W.Goode, F.Owens, and W.Myers, Division of Polymer Chemistry of the Amer.Chem.Soc., Polymer Prepr., 1, 79 (1960).
32. F.Owens, W.Myers, and F.Zimmerman, J.Org.Chem., 26, 2288 (1961).
33. J.Jasuda, N.Kawabata, T.Oda, and T.Tsuruta, J.Makromol. Sci., A1, 669 (1967).
34. H.Watanabe, I.Sono, K.Abe, and A.Nishioka, "Mezhdunarodnyi Simpozium po Makromolekulyarnoi Khimii" (International Symposium on Macromolecular Chemistry), Moscow, 1960, Vol.1, p.296.
35. H.Watanabe, J.Chem.Soc.Japan, 82, 362 (1961).
36. A.Nishioka, H.Watanabe, K.Abe, and I.Sono, J.Polymer Sci., 48, 241 (1960).
37. H.Watanabe, J.Chem.Soc.Japan, Ind.Chem.Sect., 65, 1104 (1962).
38. H.Watanabe and A.Nishioka, J.Chem.Soc.Japan, Ind.Chem. Sect., 65, 976 (1962).
39. P.Allen and A.Moody, Makromol.Chem., 81, 234 (1965).
40. P.Allen and A.Moody, Makromol.Chem., 83, 220 (1965).
41. N.Kawabata and J.Furukawa, J.Chem.Soc.Japan, Ind. Chem.Sect., 70, 1423 (1967).
42. N.Kawabata and T.Tsuruta, Makromol.Chem., 86, 231 (1965).
43. D.Glusker, I.Lysloff, and E.Stiles, J.Polymer Sci., 49, 315 (1961).
44. D.Glusker, E.Stiles, and B.Yoncoskie, J.Polymer Sci., 49, 297 (1961).
45. S.Krause, L.Defonso, and D.Glusker, J.Polymer Sci., A3, 1617 (1965).
46. L.Reich and A.Schindler, "Polymerisation by Organometallic Compounds", New York, 1966, pp.579–585.
47. M.Roha, Adv.Polymer Sci., 4, 953 (1965).
48. C.Schuerch, W.Fowells, A.Yamada, F.Bovey, F.Hood, and E.Anderson, J.Amer.Chem.Soc., 86, 4481 (1964).
49. T.Yoshino and K.Kuno, J.Amer.Chem.Soc., 87, 4404 (1965).
50. T.Yoshino and J.Komiyama, J.Amer.Chem.Soc., 88, 176 (1966).
51. W.Fowells, C.Schuerch, F.Bovey, and F.Hood, J.Amer. Chem.Soc., 89, 1396 (1967).
52. T.Yoshino, J.Komiyama, and H.Kenjo, J.Polymer Sci., B4, 991 (1966).

53. T.Yoshino, J.Komiyama, and H.Iwanaga, J.Amer.Chem. Soc., 89, 6925 (1967).
54. G.Champetier, O.Merat-Ghasnavi, and P.Sigwalt, Compt. rend., 250, 3836 (1960).
55. I.Nakayama, T.Tsuruta, and J.Furukawa, Makromol. Chem., 53, 197 (1962).
56. G.Natta, P.Longi, and E.Pellino, Makromol.Chem., 71, 212 (1964).
57. M.Donat and M.Farina, Makromol.Chem., 60, 233 (1963).
58. H.Sobue, K.Matsuzaki, and S.Nakano, J.Polymer Sci., 2A, 3339 (1964).
59. Kang-Jen Lin, J.Lignowski, and R.Ullman, Makromol. Chem., 105, 18 (1967).
60. K.Chikanshi and T.Tsuruta, Makromol.Chem., 81, 198 (1965).
61. K.Chikanshi, T.Tsuruta, and J.Furukawa, Makromol.Chem., 80, 158 (1964).
62. K.Matsuzaki, T.Okamoto, A.Ishida, and H.Sobue, J.Polymer Sci., A-2, 1105 (1964).
63. D.Gray, C.Smith, and F.Bonomo, Sci.Tech.Aerospace Rept., 2, 1776 (1964); Chem.Abs., 62, 2831e (1965).
64. T.Tsuruta, J.Takuma, and J.Furukawa, J.Chem.Soc.Japan, Ind.Chem.Sect., 66, 92 (1963).
65. Y.Iwakura, F.Toda, and T.Ito, J.Polymer Sci., B5, 29 (1967).
66. P.Bruylants and J.Gevaert, Bull.Soc.chim.belges., 32, 317 (1923).
67. P.Bruylants and L.Mathus, Bull.Soc.chim.belges., 35, 239 (1929).
68. R.Beamen, J.Amer.Chem.Soc., 70, 3115 (1948).
69. A.P.Terent'ev and A.N.Kost, Vestnik Moskov.Univ., Ser. Fiz.-mat., 5, 41 (1950).
70. S.D.Savranskaya, M.A.Askarov, and T.Kh.Azizkhanov, Fiz.Khim.Prirodn.Sintetich.Polimerov (Akad.Nauk Uzbek. SSR, Tashkent), 1, 183 (1962).
71. S.D.Savranskaya, M.A.Askarov, and T.Kh.Azizkhanov, Uzbek.Khim.Zhur., No.2, 37 (1965).
72. B.L.Erusalimskii, I.V.Kulevskaya, L.M.Pyrkov, and S.Ya.Frenkel', USSR P. 166491 (1963); Byull.Izobr., No.22 (1964).
73. B.L.Erusalimskii and I.V.Kulevskaya, Vysokomol.Soed., 7, 184 (1965).
74. B.L.Erusalimskii, I.V.Kulevskaya, and V.V.Mazurek, International Symposium on Macromolecular Chemistry, Prague, 1965, Preprint 126; J.Polymer Sci., C16, 1355 (1967).
75. B.L.Erusalimskii, I.V.Kulevskaya, S.K.Kamalov, and S.Ya.Frenkel', USSR P. 179925 (1965); Byull.Izobr., No.6 (1966).
76. B.L.Erusalimskii and I.V.Kulevskaya, Vysokomol.Soed., 7, 2180 (1955).
77. I.V.Kulevskaya, B.L.Erusalimskii, and V.V.Mazurek, Vysokomol.Soed., 8, 876 (1966).
78. I.V.Kulevskaya, B.L.Erusalimskii, and V.M.Alekseev, 9A, 107 (1967).
79. Jap.P. 13445 (1961); Chem.Abs., 56, 472 (1962).
80. I.V.Kulevskaya, Candidate's Thesis, Institute of Macromolecular Compounds of the USSR Academy of Sciences, Leningrad, 1966.
81. S.E.Bresler, B.L.Erusalimskii, and I.V.Kulevskaya, J.Polymer Sci., 6, A1, No.8 (1968).
82. B.L.Erusalimskii, Plaste und Kautschuk, 15, No.11 (1968).
83. F.Dawans and G.Smets, Makromol.Chem., 59, 163 (1963).
84. N.Zutty and F.Welch, J.Polymer Sci., 43, 445 (1960).
85. S.D.Savranskaya, L.V.Kravtsova, and M.A.Askarov, Uzbek.Khim.Zhur., No.6, 25 (1966).
86. G.Natta and G.Dall'Asta, Chimica e Industria, 46, 1429 (1964).
87. B.P. 934469 (1963); Organomet.Comp., No.9 (1963).
88. Y.Joh, T.Ioshihara, I.Kotake, F.Ide, and K.Nakatsuka, J.Polymer Sci., 3B, 933 (1965).
89. Y.Joh, T.Ioshihara, I.Kotake, F.Ide, and K.Nakatsuka, J.Polymer Sci., 4B, 673 (1966).
90. Y.Joh, Y.Kotake, T.Yoshikara, F.Ide, and K.Nakatsuka, J.Polymer Sci., 5, A1, 605 (1967).
91. Y.Joh, T.Yoshikara, Y.Kotake, Y.Imai, and S.Kurihara, J.Polymer Sci., 5, A1, 2503 (1967).
92. A.Segre, F.Ciampelli, and G.Dall'Asta, J.Polymer Sci., 4B, 633 (1966).
93. Y.Kotake, T.Yoshikara, H.Sato, N.Yamada, and Y.Joh, J.Polymer Sci., 5B, 163 (1967).
94. T.Yashikara, Y.Kotake, and Y.Joh, J.Polymer Sci., 5B, 459 (1967).
95. K.Matsuzaki, T.Uryu, M.Okada, K.Ishigura, T.Ohki, and M.Takeuchi, J.Polymer Sci., 4B, 487 (1966).
96. J.Covács and C.Marvel, J.Polymer Sci., 5, A1, 563 (1967).
97. Y.Kobuke and J.Furukawa, J.Polymer Sci., 5, A1, 2701 (1967).
98. German P. 1114638 (1961); Chem.Abs., 57, 1076d (1962).
99. G.Natta, Chimica e Industria, 42, 11 (1960).
100. G.Natta, J.Polymer Sci., 48, 219 (1960).
101. G.Natta, G.Mazzanti, G.Dall'Asta, and P.Longi, Makromol. Chem., 37, 160 (1960).
102. G.Natta, G.Mazzanti, P.Longi, G.Dall'Asta, and F.Bernardini, J.Polymer Sci., 51, 487 (1961).
103. G.Geuskens, J.Lubikulu, and C.David, Polymer, 7, 63 (1966).
104. K.Matsuzaki and T.Sugimoto, J.Polymer Sci., 5, A2, 1320 (1967).
105. S.Arichi, Bull.Chem.Soc.Japan, 41, 244 (1968).
106. B.L.Erusalimskii and Yu.N.Ovsyanikov, Vysokomol.Soed., 10B, No.10 (1968).
107. K.Ioshida and T.Morikawa, Sci.and Ind., 27, 804 (1953).
108. A.Guyot and Pham Quang Tho, Compt.rend., 256, 165 (1963).
109. A.Guyot and Pham Quang Tho, J.Polymer Sci., 1, C4, 299 (1964).
110. A.Guyot and Pham Quang Tho, "The Chemistry of Polymer Processes", London, 1966, p.69.
111. A.Guyot, Le De Trung, and R.Riboulet, Comp.rend., 266, 1139 (1968).
112. B.L.Erusalimskii, V.V.Mazurek, I.G.Krasnosel'skaya, and V.G.Gasan-Zade, International Symposium on Macromolecular Chemistry, Tokio, 1966, Preprint, 2.1.14; J.Polymer Sci., C23, 215 (1968).
113. B.L.Erusalimskii, A.V.Merkur'eva, and N.P.Baikova, Vysokomol.Soed., 4, 798 (1961).
114. I.G.Krasnosel'skaya, and B.L.Erusalimskii, Vysokomol. Soed., 6, 1937 (1964).
115. I.G.Krasnosel'skaya, B.L.Erusalimskii, and V.V.Mazurek, Vysokomol.Soed., 9A, 2130 (1967).
116. B.L.Erusalimskii, I.S.Lishanskii, and I.G.Krasnosel'skaya, Vysokomol.Soed., 9B, 6 (1967).
117. V.G.Gasan-Zade, V.V.Mazurek, and V.P.Sklizkova, Vysokomol.Soed., 10A, 479 (1968).
118. A.Konishi, Bull.Chem.Soc.Japan, 35, 197 (1962).
119. B.L.Erusalimskii and I.G.Krasnosel'skaya, USSR P. 181293; Byull.Izobr., No.9 (1966).
120. B.L.Erusalimskii, I.G.Krasnosel'skaya, V.V.Mazurek, and V.G.Gasan-Zade, Dokl.Akad.Nauk SSSR, 169, 114 (1966).
121. I.G.Krasnosel'skaya and B.L.Erusalimskii, Vysokomol. Soed., 9A, 836 (1967).
122. V.G.Gasan-Zade, Candidate's Thesis, Institute of Macromolecular Compounds of the USSR Academy of Sciences, Leningrad, 1966.

123. H.Allcock and R.Kugel, J.Polymer Sci., 1A, 3627 (1963).
124. G.Guber and G.Egle, Makromol.Chem., 62, 196 (1963).
125. N.Ogata, J.Polymer Sci., 46, 271 (1960).
126. H.Nakayama, T.Higashimura, and S.Okamura, Chem. High Polymers (Japan), 23, 537 (1966).
127. H.Nakayama, T.Higashimura, and S.Okamura, Chem. High Polymers (Japan), 24, 42 (1967).
128. K.Ito, Ken-ichi Baba, and Y.Yamashita, J.Chem.Soc. Japan, Ind.Chem.Sect., 68, 703 (1965).
129. B.P. 928157 (1963); Chem.Abs., 59, 5286c (1963).
130. R.Graham, J.Moore, and J.Powell, J.Appl.Polymer Sci., 11, 1797 (1967).
131. M.Miller and J.Skogman, J.Polymer Sci., 2A, 4551 (1964).
132. H.Hopff, H.Lüssi and L.Borla, Makromol.Chem., 81, 268 (1965).
133. East German P. 28494 (1961); Ref.Zhur.Khim., 11S243P (1966).
134. U.Gianini, M.Campini, and A.Cassata, Makromol.Chem., 61, 246 (1963).
135. W.Kern, Chem.-Ztg, 88, 623 (1964).
136. G.Natta, G.Mazzanti, P.Corradini, P.Chini, and I.W.Bassi, Atti Acad.naz.Lincei, Rend.Classe Sci.fis.mat.nat., 28, No.1, 8 (1960).
137. J.Furukawa, T.Saegusa, H.Fujij, A.Kawasaki, H.Imai, and Y.Fujij, Makromol.Chem., 37, 149 (1960).
138. J.Furukawa, T.Saegusa, and H.Fujij, Makromol.Chem., 44–46, 398 (1960).
139. H.Sobue and H.Kubota, J.Polymer Sci., 1C, 147 (1963).
140. O.Vogl, J.Polymer Sci., 2A, 4607 (1964).
141. Italian P. 626551 (1961); Chem.Abs., 57, P3628b (1962).
142. T.Iwata, G.Wasai, T.Saegusa, and J.Furukawa, Makromol. Chem., 77, 229 (1964).
143. M.F.Shostakovskii, V.I.Belyaev, Z.A.Okladnikova, L.V.Vasil'eva, and E.V.Serebrennikova, Izv.Sibirsk.Otd. Akad.Nauk SSSR, Ser.Khim.Nauk, 1, 88 (1965).
144. R.C.Schulz and W.Passman, Makromol.Chem., 60, 139 (1963).
145. R.Fujio, T.Tsuruta, and J.Furukawa, J.Chem.Soc.Japan, Ind.Chem.Sect., 66, 365 (1963).
146. T.Tsuruta, R.Fujio, and J.Furukawa, Makromol.Chem., 80, 172 (1964).
147. Sh.Iwatsuki, Y.Yamashita, and Y.Schii, J.Chem.Soc. Japan, Ind.Chem.Sect., 66, 1162 (1963).
148. Hsin-Te Feng, Nan-Fei Ch'iu, and Te-Chang Chiang, K'o Hsueh T'ung Pao (Scientia), No.5, 51 (1963).
149. T.Tsunetsugu, K.Arimoto, T.Fueno, and J.Furukawa, Makromol.Chem., 112, 210 (1968).
150. Y.Yamashita and S.Nunomoto, Makromol.Chem., 58, 244 (1962).
151. Y.Yamashita and S.Nunomoto, J.Chem.Soc.Japan, Ind. Chem.Sect., 66, 467 (1963).
152. Y.Yamashita, S.Miura, and M.Nakamura, Makromol. Chem., 68, 31 (1963).
153. K.Yoshida and Y.Yamashita, Makromol.Chem., 100, 175 (1967).
154. O.Vogl and W.M.D.Bryant, J.Polymer Sci., 2A, 4633 (1964).
155. J.Furukawa, T.Tsuruta, T.Saegusa, R.Sakata, G.Kakogawa, A.Kawasaki, and I.Harada, J.Chem.Soc.Japan, Ind. Chem.Sect., 62, 1269 (1959).
156. R.Sakata, T.Tsuruta, T.Saegusa, and J.Furukawa, J.Chem.Soc.Japan, Ind.Chem.Sect., 63, 1817 (1960).
157. E.J.Vandenberg, J.Polymer Sci., 47, 486 (1960).
158. T.Kagiya, T.Shimidzu, T.Sano, and K.Fukui, J.Chem.Soc. Japan, Ind.Chem.Sect., 66, 1148 (1963).
159. T.Kagiya, M.Natta, T.Sano, and T.Shimidzu, J.Chem.Soc. Japan, Ind.Chem.Sect., 66, 1152 (1963).
160. T.Kagiya, T.Shimidzu, T.Sano, M.Natta, and K.Fukui, Kyoto Daigaku Nippon Kagaku Seni Kenkyusho Koenshu, 20, 30 (1963).
161. T.Kagiya, T.Sano, T.Shimidzu, and K.Fukui, J.Chem.Soc. Japan, Ind.Chem.Sect., 66, 1896 (1963).
162. T.Tsuruta, S.Inoue, and Y.Yokota, Makromol.Chem., 103, 164 (1967).
163. U.S.P. 3024219 (1962); Chem.Abs., 56, P15674h (1962).
164. C.C.Price, and E.A.Blair, J.Polymer Sci., 5, A1, 171 (1967).
165. T.Tsuruta, S.Inoue, and H.Koenuma, Makromol.Chem., 112, 58 (1968).
166. T.Tsuruta, K.Matsumara, and S.Inoue, Makromol.Chem., 75, 211 (1964).
167. W.Griehl and S.Schaaf, Makromol.Chem., 32, 170 (1959).
168. U.S.P. 3018273 (1962); Chem.Abs., 57, P3637e (1962).
169. B.P. 995384 (1965); Chem.Abs., 63, 7171e (1965).
170. S.Barzakay, M.Levy, and D.Vofsi, J.Polymer Sci., A1, 4, 2211 (1966).
171. S.Bar-Zakay, M.Levy, and D.Vofsi, J.Polymer Sci., A1, 5, 965 (1967).
172. Belgian P. 647513 (1964); Chem.Abs., 63, 10128a (1965).
173. Jap.P. 24289 (1964); Chem.Abs., 62, 9311h (1965).
174. R.Cray, J.Polymer Sci., 44, 264 (1960).
175. D.Eley and A.Johnson, J.Chem.Soc., 2238 (1964).
176. K.Iwasaki, H.Fukutani, Y.Tsuchida, and S.Nakano, J. Polymer Sci., A-1, 2371 (1963).
177. J.M.Bruce and D.W.Farren, Polymer, 4, 407 (1963).
178. L.M.Romanov, B.A.Dolgoplosk, B.L.Erusalimskii, and V.Ya.Bogomol'nyi, Dokl.Akad.Nauk SSSR, 115, 731 (1957).
179. L.M.Lanovskaya, N.V.Makmudova, A.R.Gantmakher, and S.S.Medvedev, Vysokomol.Soed., 7, 741 (1965).
180. B.P. 944928 (1963); Chem.Abs., 60, P9381d (1964).
181. U.S.P. 895417 (1962); Chem.Abs., 57, P8743i (1962).
182. U.S.P. 3031440 (1962); Chem.Abs., 58, P5992c (1963).
183. U.S.P. 3190822 (1963); Chem.Abs., 60, P5662f (1964).
184. U.S.P. 2953531 (1960); Chem.Abs., 55, P6042d (1961).
185. U.S.P. 3078262 (1963); Chem.Abs., 58, P11482f (1963).
186. G.Champetier and M.Martynoff, Compt.rend., 252, 633 (1961).
187. G.Champetier, M.Martynoff, and N.Lefèvre, Bull.Soc. chim.France, 2083 (1961).
188. P.E.Allen and J.F.Harrod, Makromol.Chem., 32, 153 (1959).
189. P.E.Allen and D.Gill, Makromol.Chem., 71, 33 (1964).
190. Belgian P. 560503 (1957); Chem.Abs., 54, P1923d (1960).
191. J.Furukawa et al., J.Chem.Soc.Japan, Ind.Chem.Sect., 61, 1353 (1958).
192. B.P. 946906 (1964); Chem.Abs., 60, P10906c (1964).
193. N.G.Gaylord, J.Kössler, M.Stolka, and J.Vodehnal, J.Amer.Chem.Soc., 85, 641 (1963).
194. N.G.Gaylord, J.Kössler, M.Stolka, and J.Vodehnal, J.Polymer Sci., 2A, 3969 (1964).
195. G.Delheye anf F.Dawans, Makromol.Chem., 98, 164 (1966).
196. Belgian P. 614106 (1962); Chem.Abs., 57, P13948b (1962).
197. B.P. 953089 (1964); Chem.Abs., 61, P4572e (1964).
198. Canadian P. 671670 (1963); Chem.Abs., 60, P4319c (1964).
199. Belgian P. 633487 (1963); Chem.Abs., 61, P4573b (1964).
200. Canadian P. 716173 (1965); Chem.Abs., 63, P15076g (1965).
201. Jap.P. 15662 (1965); Chem.Abs., 63, P18422d (1965).
202. G.Natta, G.Mazzanti and P.Longi, Chimie e Industria, 40, 183 (1958).
203. B.P. 985876 (1965); Chem.Abs., 62, P16487a (1965).
204. B.P. 990451 (1965); Chem.Abs., 63, P15076c (1965).
205. B.P. 984499 (1965); Chem.Abs., 62, P14912d (1965).
206. Belgian P. 646578 (1964); Chem.Abs., 63, P8590b (1965).
207. U.S.P. 3172881 (1965); Chem.Abs., 62, P14912a (1965).
208. B.P. 995064 (1965); Chem.Abs., 63, P7189h (1965).
209. J.Yamaji, J.Chem.Soc.Japan, Ind.Chem.Sect., 70, 1049 (1967).

210. H.Mark, Rev.gen.Caoutchove, 38, 349 (1961).
211. S.Inoue, T.Tsuruta, and J.Furukawa, Makromol.Chem., 49, 13 (1961).
212. Y.Giannini and S.Ceska, Chimica e Industria, 44, 371 (1962).
213. G.P.Budanova and V.V.Mazurek, Chem.High Polymers (Japan), 24, 91 (1967).
214. E.B.Milovskaya, "Tezisy Dokladov XIII Nauchnoi Konferentsii IVS Akad.Nauk SSSR" (Abstracts of Papers at the Thirteenth Scientific Conference of the Institute of Macromolecular Compounds of the USSR Academy of Sciences, Leningrad, 1966, p.26.
215. M.Morton and I.Fetters, J.Polymer Sci., A2, 3311 (1964).

Institute of Macromolecular Compounds, USSR Academy of Sciences, Leningrad

U. D. C. 542.952.6 : 543.226

Dependence of Thermal Stability of Polymers on Their Chemical Structure

V.V.Korshak and S.V.Vinogradova

It is shown, on the basis of a large amount of experimental work, how the thermal stability of polymers depends on the strength of the bonds between the atoms forming the macromolecule, on the structure of the chain unit in the macromolecule, and also on the structure of the polymer molecule itself as a whole. Especially detailed attention is given to the effect on thermal stability of such structural features of the chain unit as the presence of side-chains, halogen atoms, and other elements (boron, silicon, phosphorus, various metals), the positions and number of these substituents, and also groups of aromatic character, including benzene rings and various heterocycles. Those structural features which tend to increase the thermal stability of polymers are elucidated.
An important place in the review is occupied by examining the dependence of thermal stability on such structural aspects of the macromolecule itself as the regularity in the arrangement of monomer units along its chain, the isomerism of substitution in the aromatic ring, the presence of branching and cross-linking, copolymerisation, and also the nature of end-groups, etc. A list of 100 references is given.

CONTENTS

I. Introduction 885
II. Strength of bonds between atoms in the macromolecule 886
III. Dependence of thermal stability on structure of chain unit 887
IV. Dependence of thermal stability on structure of macromolecule 901
1. Dependence of thermal stability on regularity of structure of macromolecule 901
2. Effect of isomerism of substitution in the aromatic ring 901
3. Effect of lateral groups and branching 901
4. Dependence of thermal stability on degree of cross-linking of polymer 902
5. Effect of copolymerisation 904
6. Effect of other structural features on thermal stability 904

I. INTRODUCTION

The most important problem of polymer chemistry is to establish the relation between the properties of polymers and their structure. Only when this is known is it possible to solve consciously and successfully the problems involved in preparing polymers having required properties which have been specified in advance.

Although relatively little experimental work has yet been done on the relations between the structure and the properties of polymers, it is already possible, on the basis of known data, to establish certain relations of this type. The main method for finding links between the structure and the properties of polymers is to study and compare the behaviour of series of polymers of analogous structure[1].

We shall not deal here with one extremely important aspect of this problem—the influence of the physical structure of polymers on their properties—which has been determined by the work of Kargin[2]. He has shown, on the basis of a large number of experimental results, that the physical structure of a polymer affects not only its strength but also several of its chemical reactions.

Without being concerned with the whole problem of the relation between structure and properties, we shall examine only its purely chemical aspect. The aim of the present review is to show quite clearly the relations which have now been elucidated between the chemical structure and the thermal stability of polymers, these being of interest in particular in connection with the problem of producing the heat-resistant materials which are so necessary for modern technology.

Let us first define the concepts of heat-resistance and thermal stability, with which we shall often be dealing. *Heat-resistance* we shall take to mean the limiting temperature at which a given polymer is able to maintain a particular mechanical strength. *Thermal stability* will imply the limiting temperature which a given polymer can withstand without chemical change. Above this temperature the polymer begins to undergo chemical breakdown, in most cases accompanied by loss of mechanical strength.

We shall not be concerned here with problems associated with the thermal breakdown of polymers under the simultaneous influence of high temperatures and chemical reagents such as oxygen, water, etc., i.e. the oxidative thermal degradation and the hydrolytic cleavage of polymers.