Translated from *Uspekhi Khimii*, 50, 1141-1167 (1981) U.D.C. 546.4:66.095.264

Alkaline-earth Metals and Compounds as Initiators of the Anionic Polymerisation of Unsaturated Monomers

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Data on the catalytic activity and stereospecificity of alkaline-earth metals in the polymerisation and copolymerisation of unsaturated monomers are summarised, and the nature of the active centres is examined togeher with the kinetics and the mechanism of these processes. The principal methods of preparing initiators for anionic polymerisation that contain compounds of these metals are outlined, and the most probable immediate prospects for practical application of the compounds in polymerisation processes are noted. A list of 175 references is included.

CONTENTS

I. Introduction 601
II. Principal methods for the preparation of polymerisation initiators based on compounds of alkaline-earth metals 601
III. Catalytic activity and stereospecificity of alkaline-earth metals in polymerisation processes 603
IV. Kinetics and mechanism of polymerisation in systems with bivalent gegenions 607

I. INTRODUCTION

The first publications on the ability of organolithium compounds to initiate the formation of *cis*-1,4-polyisoprene, similar in structure and properties to natural rubber[1,2], and the series of papers by Szwarc began at about the same time, which first directed attention to several unusual and interesting properties of living polymers[3-5], led to a sharp growth of interest in anionic polymerisation. During the past two decades great progress has been made both in the theory of processes initiated by alkali metals and in their practical realisation, thanks to which they now find widespread industrial application in the manufacture of various synthetic polymer materials[6]. Research on processes involving alkaline-earth metals has hitherto developed far more slowly, which is largely due to difficulties in the preparation of appropriate polymerisation initiators.

The first systematic studies in this field[7,8] were made with organocalcium compounds, which were more accessible at that time; but subsequently attention was focussed mainly on barium compounds, which exhibited interesting catalytic properties in the polymerisation and copolymerisation of diene monomers[9-12]. Sufficient information has now been obtained for the possible formulation of several general rules in this independent new field in the theory of anionic polymerisation and for identification of the most promising practical aspects.

The present Review is devoted to the polymerisation of unsaturated polymers initiated by calcium, strontium, barium, and their compounds. Magnesium compounds are included only where necessary for comparison and for citing fundamentally novel results not covered by previous reviews[13,14].

The Review begins with an outline of methods for preparing the chief polymerisation initiators containing compounds of alkaline-earth metals that are used at the present time, since most of this information has been obtained recently and has not appeared in the well known monographs on the preparation of organometallic compounds[15,16].

II. PRINCIPAL METHODS FOR THE PREPARATION OF POLYMERISATION INITIATORS BASED ON COMPOUNDS OF ALKALINE-EARTH METALS

Organometallic compounds are usually formed considerably more readily in the presence of electron-donor solvents, whereas the presence even of catalytic quantities of polar compounds is in many cases sufficient to change appreciably the character of anionic polymerisation processes and also the structure and properties of the resulting polymers[17-19]. Therefore chemists investigating polymerisation tend to prepare the initiator in the solvent in which subsequent polymerisation is to be conducted. Workers studying the polymerisation of diene monomers display a special interest in hydrocarbon solvents, which show the greatest practical promise with respect both to the properties of the resulting polymers and to technical and economic factors.

1. Electron Transfer to Hydrocarbons

Alkaline-earth metals are considerably less active than alkali metals in reactions involving electron transfer to aromatic compounds. Only in polar solvents of high solvating power such as hexamethylphosphorotriamide do they form compounds comparatively readily with biphenyl, naphthalene, anthracene, 1,1-diphenylethylene, and similar compounds[20-22]. In reactions of this type calcium is considerably less active than are magnesium and barium[22,23], which as with alkali metals[18,24] is due to competition between two main factors governing the activity of metals in these processes—the tendency to donate electrons and the gain in energy of solvation of the cation—which vary in opposite directions within a given group.

In ethereal solvents only the higher fused hydrocarbons (naphthacene, perylene), among aromatic compounds, react with alkaline-earth metals, forming sparingly soluble radical-anions and dianions that are inert towards polymerisation[23,25].

The addition of barium to non-polymerising 1,1-disubstituted vinylated aromatic compounds—1,1-diphenylethylene or α-methylstyrene—proceeds considerably more readily[10,26-28]. The products are probably metal salts of dianions—of the dimer of diphenylethylene $ba^{+}C(C_6H_5)_2.CH_2.CH_2.C(C_6H_5)_2C^{-}ba^{+}$ (where ba is an equivalent of barium) or an oligomer of α-methylstyrene—like the well studied alkali-metal compounds[10]. Formation of the corresponding barium derivatives of oligomeric dianions of styrene (degree of polymerisation 2–5) has also been reported recently[29], but in this case special measures are necessary to prevent homopolymerisation of styrene.

Formation of all these products involves recombination of primary monomeric radical-anions[18], which is responsible for the difunctionality of the product and also increases their yield significantly, despite the relatively low electron affinity of the initial hydrocarbons.

It has recently been reported[30] that depending on the conditions the action of barium on α-methylstyrene in oxolan yields either dianions of the above type or products having only one active end. As single-ended products had never previously been observed in such systems and their formation is difficult to understand, it is not yet clear whether their appearance is a specific feature of barium or whether it is due to experimental error.

Bis-1,1,4,4-tetraphenylbutylbarium has been characterised by spectroscopic and conductivity methods[31-33]. Together with its α-methylstyrene analogue it is now probably the simplest (with regard to preparation) and most often used organobarium polymerisation initiator. Similar compounds have been obtained with strontium[34,35]; in the cases of calcium and magnesium, reaction with 1,1-diphenylethylene in ethereal media is insignificant if it occurs at all[23,26].

The reaction of alkaline-earth metals with hexa-arylethanes is apparently of the same type; it occurs readily in oxolan at room temperature and yields bistriarylmethyl derivatives of the metals[36,37]. Addition products of calcium, strontium, and barium with benzophenone (ketyls) have also been obtained in oxolan[38,39]; they initiate the polymerisation of acrylates[39], but are apparently inactive in the polymerisation of hydrocarbon monomers[40].

It has recently been shown[174] that in aromatic hydrocarbons at 50–80 °C hexaphenylethane reacts with metallic barium and strontium to form the corresponding bistriphenylmethyl derivatives, which are soluble in the reaction medium. This is the first known example of the synthesis of completely substituted compounds of alkaline-earth metals in the absence of solvating agents.

2. Reaction with Halogenohydrocarbons

Organic derivatives of alkaline-earth metals were first obtained in this way—phenylcalcium iodide in 1905,[41] phenylbarium iodide in 1927 [42]—but after it was early established that difficulties were involved in synthesis and that the products were unpromising in preparative chemistry compared with Grignard reagents, interest in this reaction died away for a long time, and was renewed only in the 1960s [43] (the history and the present-day achievements of this method have been covered quite fully in Ref. 44). Quite a number of publications have now appeared on the preparation of compounds of type RCaX (in which X is most often iodine, more rarely bromine or chlorine) in oxolan or diethyl ether[45-50]. If the metal used is especially pure, the reaction can be conducted even in a hydrocarbon medium[51] (though insoluble products are then formed, which hinders their further application). Compounds of strontium[36,52-54] and of barium[36,52,53,55] have been obtained by this method in ethereal media. With these two metals the preparation could not be effected in a hydrocarbon medium, but compounds of calcium, strontium, and barium have been obtained by cocondensation of metal and halogenoalkane vapours on a cooled surface in the absence of a solvent[53].

The substances obtained by this reaction are mixtures of completely and incompletely substituted compounds (R_2M + RMX), whose composition depends both on the nature of the alkyl halide and on the reaction conditions[8,50,56]. On the whole this method, though the principal route to lithium initiators, has not yet found appreciable extension to the synthesis of polymers in the case of alkaline-earth metals.

3. Dimetal Compounds

Alkaline-earth metals on reaction with excess of diethylzinc in benzene[57] fairly readily form dimetal complexes of general formula $MZn(C_2H_5)_4$. Such compounds were used by Furukawa et al. for the polymerisation of certain polar monomers[58,59], but they were relatively inactive owing to their insolubility and their complicated composition. At the beginning of the 1970s interest was renewed in organometallic derivatives containing both barium and zinc, as they exhibited interesting catalytic properties in the polymerisation and copolymerisation of dienes[9,11,12,60]. Methods were found for obtaining hydrocarbon-soluble initiators, which could be readily separated from excess of metal and other impurities by conducting the preparation in the presence of 1,1-diphenylethylene[61] or by replacing diethylzinc with dibutylzinc[12,62] (in the latter case there are grounds for supposing that the initiator is formed in diethyl ether[63]). Opportunities for the wider application of these compounds apparently depend on the availability of zinc alkyls.

Analogous aluminium complexes of general formula $M(AlR_4)_2$ have recently attracted attention. They are formed from the trialkylaluminium and the alkaline-earth metal[61,64] or an alkoxide thereof[65,66]. They are readily soluble in benzene and effect the polymerisation of hydrocarbon monomers, although considerably less active than zinc complexes[61].

4. Other Methods

Completely substituted organic derivatives of calcium, strontium, and barium are readily formed in oxolan from the corresponding compounds of mercury[67-70] and also (under more severe conditions) of lead[71] and tin[72]. Organomercuric synthetic reactions and the properties of the compounds isolated—including infrared, ultraviolet, and nuclear magnetic resonance spectra of several compounds—have been described most fully in patents of the Dow Chemical Co.[68]; compounds containing radicals with conjugated bonds (allyl, phenyl, benzyl, indenyl, etc.) can be obtained more readily.

Hydrocarbons containing a mobile hydrogen atom—such as fluorene, triphenylmethane, indene, cyclopentadiene, phenylacetylene—have been metallated by the action of alkaline-earth metals in strongly solvating media (liquid ammonia[73,74], hexamethylphosphorotriamide[75], 1,1-dimethyl ethylene[75], methylamine[76]). Fluorenylstrontium[77,78] and fluorenylbarium[78-81] have been obtained also by the metallation of fluorene with 1,1,4,4-tetraphenylbutyl derivatives of the metals in oxolan. However, compounds containing mobile, readily substituted hydrogen (fluorene, cyclopentadiene, etc.) form stable carbanions, which are relatively inactive in the polymerisation of hydrocarbon monomers[18,82,83].

Cumenylstrontium and cumenylbarium can be obtained[84] by cleaving cumenyl methyl ether with dispersion of the metals in oxolan.

Exchange reactions have recently been observed between barium alkoxides and organomagnesium (and organolithium) compounds[85-87], similar to those between lithium alkyls and sodium (and potassium) alkoxides[88]. The products apparently contain varying proportions of symmetrical and unsymmetrical compounds R_2Ba and RBaOR', with a significant influence on their catalytic properties[86]. Various systems of this type have been described in the patent literature[89-91]. Numerous multicomponent systems, representing various combinations of the above variants, have also been suggested (e.g. calcium–anthracene–trialkylaluminium[92], barium or strontium acetylacetonate–trialkylaluminium–alkyl–lithium[93], barium alkoxide–lithium alkoxide–trialkylaluminium[94]).

Thus the preparation of organic derivatives of alkaline-earth metals in the presence of highly polar solvents such as hexamethylphosphorotriamide presents no difficulty, but the products hardly differ in catalytic properties from the more readily available alkali-metal compounds. In ethereal solvents (oxolan, dimethyl ether) compounds having two active ends, such as bistetraphenylbutyl-barium and -strontium, are most simply obtained. The most reliable method for obtaining compounds that are completely substituted with hydrocarbon radicals having one active end is apparently reaction with mercury compounds or with hexaphenylethane.

In hydrocarbon media completely substituted compounds (bistriphenylmethyl-barium and -strontium) have been obtained only recently, as mentioned above. Several workers[9,95-97] have therefore used initiators obtained in ethereal media by removing the electron donor under more or less severe conditions. With such a method, of course, doubt always remains whether the solvent has been completely removed. The possibility of almost complete removal of oxolan has until now been confirmed analytically only for barium compounds[98].

Furthermore, as many workers have shown[51-53,68,87], the lower alkyl compounds of alkaline-earth metals are thermally unstable at room temperature, and also decompose under the influence of oxolan and other ethereal solvents. Dibenzylbarium in oxolan also undergoes gradual deactivation and isomerisation[70]. On the other hand, compounds having branched carbanions of the di- and tri-phenylmethyl type are completely stable both in hydrocarbon and in ethereal media[32]. Therefore the introduction of 1,1-diphenylethylene (sometimes α-methylstyrene) into the reaction system is often a useful method for improving the stability and the solubility of the resulting organometallic compounds[69,85,97].

III. CATALYTIC ACTIVITY AND STEREOSPECIFICITY OF ALKALINE-EARTH METALS IN POLYMERISATION PROCESSES

1. General Behaviour

The first investigations on polymerisation involving calcium, strontium, and barium used the free metals as initiators[99-105], but in most cases the results showed considerable scatter. Satisfactory reproducibility was subsequently obtained with respect to the structure of the polymers and the composition of copolymers[10,106,107], but recently almost all studies have been made under homogeneous conditions, as a consequence of the progress made in preparing compounds of these metals.

By now most monomers capable of anionic polymerisation—unsaturated compounds containing conjugated double bonds or polar substituents, such as dienes, styrene, methyl methacrylate—have been subjected to polymerisation initiated by alkaline-earth metals and their compounds. Acrylonitrile and vinyl chloride have been polymerised by the action of a dispersion of barium[100] (under homogeneous conditions, the latter could not be polymerised by an organobarium initiator[108]).

Monomers having polar side-groups are readily polymerised by the action of magnesium compounds[13,14]. Reaction of hydrocarbon monomers requires either the presence of such strong solvating agents as hexamethylphosphorotriamide[13,21,109,110] or magnesium alkoxides of certain ether–alcohols, e.g. methylcellulose or oxolan-2-ylmethanol[111,112], or (slowly) heating to 80–100 °C.[113,114]

It is interesting that metallic magnesium, which is fairly active in electron-transfer processes, reacts comparatively readily in ethereal solvents with butadiene[115-117], isoprene[118], and also with styrene and several other unsaturated compounds[119]. Since the organomagnesium compounds thus formed do not polymerise these monomers, the reaction ceases at the stage of the primary oligomeric products, and can be used to obtain concentrated solutions of double-ended organomagnesium compounds.

In the early work, concerned mainly with the polymerisation and copolymerisation of methyl methacrylate under the influence of dispersions of alkaline-earth metals, doubts were expressed concerning the mechanism of these processes: in particular it was suggested that not only an anionic but also a radical process took place[106,120-122]. The chief arguments supporting this hypothesis were the presence of a certain quantity of styrene and its copolymer with methyl methacrylate and also the difference in the general rules of stereoregulation from those found previously for reactions with alkali metals. A relevant fact here is that it has been shown many times with alkali metals that the styrene–methyl methacrylate pair cannot be used to establish the mechanism of heterogeneous processes, since in this case polymerisation is initiated predominantly on the styrene as a consequence of its considerably stronger adsorption on the metal surface[18,123]. At the present time no doubt arises about the anionic mechanism of polymerisation processes initiated by alkaline-earth metals, and the differences (sometimes very substantial) observed from processes with alkali metals reflect differences in the properties of active centres with uni- and bi-valent gegenions.

2. Stereospecificity of Alkaline-earth Metals

(a) Diene monomers

The most complete and reliable information has been obtained for the polymerisation of butadiene. The laws thus found (Table 1) differ in many respects from those established previously for alkali metals.

Hydrocarbon medium. Firstly it is evident that in hydrocarbon media metals of Group II possess a considerably greater ability than the corresponding metals of Group I to cause the 1,4-addition of butadiene units. Moreover, the total content of 1,4-units in butadiene polymers formed by the action of any alkaline-earth metal approaches those obtained in the presence of lithium, which has hitherto occupied an exceptional position among initiators of anionic polymerisation. In its ability to form a *cis*-1,4-butadiene structure barium surpasses all other initiators based on non-transition metals, including lithium (at very low concentrations of active centres ($\sim 10^{-5}$ M) the content of *cis*-1,4-units in lithium-polybutadiene obtained in an aliphatic solvent may reach 80–85%[128]). When the temperature is raised to

95 °C however, the content of *cis*-1,4-butadiene units in polymers obtained by using barium falls to 42% (with a constant content of 1,2-units[129]); for comparison the content of *cis*-1,4-units when polymerisation is effected by using lithium remains almost unchanged between −20 and 196 °C.[130]

Table 1. Structure of butadiene polymers formed at room temperature by means of initiators based on metals in Groups I and II.

Initiator	Content of monomer units, %			Ref.
	cis-1,4	*trans*-1,4	1,2	
hydrocarbon medium				
RLi	43	50	7	[17]
Na	23	45	32	[17]
K	16	49	35	[17]
Rb	7	31	62	[124]
Cs	6	35	59	[124]
R_2Mg—RMgI *	26—32	45—49	23—25	[114]
R_2Ca—RCaI **	18—39	48—72	7—13	[95]
$CaZnR_4$	13	77	10	[12]
$Ca(AlR_4)_2$	15	80	5	[61]
R_2Sr **	27	64	9	[34]
$SrZnR_4$	20	70	10	[12]
Ba	75—80	9—13	11	[10]
R_2Ba	60—70	20—30	10	[32]
$BaZnR_4$ ***	18	76	6	[61]
$Ba(AlR_4)_2$	8	91	1	[61]
$Ba(OR)_2$+RLi	15—30	60—80	5—10	[86, 90, 125]
$Ba(OR)_2$+R_2Mg	15—30	60—80	5—10	[86, 90, 125]
oxolan				
RLi	7	7	86	[126]
RNa	5	16	79	[126]
RK, RCs	6—8	30—51	61—64	[126]
Mg	6****	39****	55****	[23]
R_2Ca—RCaI	12	17	71	[95]
R_2Sr	16	47	37	[34]
R_2Ba	28	50	22	[10]
hexamethylphosphorotriamide				
Li, Na, K	2—4	19—22	74—77	[109]
R_2Mg	4	16	80	[127]
Mg, Ca, Ba	4—7	19—22	74—77	[109]

*Temperature 90—100 °C.
**Initiator obtained in oxolan or ether with subsequent removal of solvent by distillation.
***Concentration of initiator ~3 mM.
****Oligomer.

The stronger coordinating power of alkaline-earth than of alkali metals is undoubtedly due to the presence of the double charge on the gegenions and hence to their increased acceptability for similar ionic radii. However, the enhanced ability of barium to form *cis*-1,4-polybutadiene, though noted some time ago[10,22] (and its ability to form isotactic poly(methyl methacrylate) was noted still earlier[120]), has not yet been rigorously explained.

Several publications (mainly patents) have recently appeared on the formation of polybutadiene in which the *trans*-1,4-structure predominates[86,89-91,125], under the influence of various initiators containing alkoxides or other oxygen-containing compounds of barium and alkyl derivatives of lithium or magnesium, between which exchange reactions undoubtedly occur. Since both lithium compounds and fully substituted barium alkyls are *cis*-regulating initiators for the polymerisation of butadiene, it is highly probable that unsymmetrical barium compounds of the type RBaOR′ are responsible for appearance of the *trans*-1,4-structure[86,87]. Investigation of such unsymmetrical compounds is of considerable general interest, since the possibility of introducing modifying groups directly into an active centre, which opens up wide prospects for controlling its catalytic properties, is evidently the most important fundamental feature of the systems that is absent in the case of univalent gegenions.

Table 2. Structure of isoprene polymers formed at room temperature by using initiators based on metals in Groups I and II.

Initiator	Content of monomer units, %				Ref.
	cis-1,4	*trans*-1,4	3,4	1,2	
hydrocarbon medium					
RLi	84—96	0—15	5—9	0	[131]
Na	0—4	12—46	51—77	6—11	[131]
K, Rb, Cs	0—20	40—55	32—40	7—9	[131]
R_2Mg—RMgI *	—	—	>95	—	[113]
Ca	72	0	28	0	[132]
R_2Ca—RCaI **	56	23	21	0	[7]
$CaZnR_4$ ***	12	73	15	0	[132]
Sr	46—56	0—12	35—44	0	[99, 103, 105]
R_2Sr **	38	24	37	1	[34]
$SrZnR_4$ ***	32	56	11	0	[132]
Ba	23—71	0—56	20—30	0	[99, 103, 105]
R_2Ba **	56	7	37	0	[133]
$BaZnR_4$ ***	34	53	12	0	[132]
oxolan					
RLi	0	0	74	26	[134]
R_2Ca—RCaI ****	0	69	31	0	[7]
Sr	53	12	27	8	[103]
R_2Sr	23	22	51	4	[34]
Ba	44	24	20	11	[103]
hexamethylphosphorotriamide					
RLi	0	4	58	38	[127]
R_2Mg	0	8	57	35	[127]
R_2Ca	0	0	55	45	[135]

*Temperature 90 °C.
**Initiator obtained in oxolan or ether with subsequent removal of solvent by distillation.
***Concentration of initiator ~3 mM.
****Polymerisation in diethyl ether.

Structural data on polyisoprene (Table 2) give no clear picture owing to their great scatter, at least partly due to the complexity of analysing the structure of this polymer. Alkaline-earth metals vary little in stereospecificity towards the polymerisation of isoprene. Comparison of corresponding metals in Groups I and II definitely reveals considerably higher contents of *cis*-1,4-units for the latter, although, in contrast to the polymerisation of butadiene, none of the alkaline-earth metals reaches the high level of stereospecificity characteristic of lithium compounds.

Influence of electron donors. Increase in the atomic weight of the metal whether in Group I or II produces a regular decrease in the proportion of 1,2-units when butadiene is polymerised in oxolan (Table 1), which is fully consistent with the corresponding decrease in the tendency of the cations to undergo solvation[17,136]. Even in this case, however, heavy alkaline-earth metals (strontium and barium) differ from their neighbours in Group I in a sharp increase in the content of 1,4-units. From solvents of ethereal type only strongly solvating multidentate agents (1,1-dimethylethylene, 3,6,9-trioxaundecane) give on polymerisation with a barium gegenion

the predominance of 1,2-units characteristic of anionic polymerisation[10,32,129]. In the highly polar hexamethylphosphorotriamide all metals in Groups I and II give polymers of almost the same structure. In general the structure of polyisoprene obeys the same laws; in any case there is a clear tendency for a greater proportion of 1,4-units with alkaline-earth metals when polymerisation occurs in oxolan.

The slight tendency of alkaline-earth metal cations to be solvated is well supported by other investigations. Thus in the polymerisation of butadiene with bistetraphenylbutylbarium introduction of oxolan up to a fiftyfold excess with respect to barium has hardly any effect on the structure of the polymer[98]; with larger quantities of oxolan a gradual transition of *cis*- into *trans*-1,4-units begins, but change in the proportion of 1,2-units is observed only when the oxolan content of the solution exceeds 10 vol.%.[32,129] With lithium initiators, on the other hand, a sharp increase in the proportion of 1,2-units has already begun with equimolecular proportions of oxolan and lithium[137], and in the presence of 1 vol.% of oxolan the resulting polymer has almost the same structure as in pure oxolan[17].

Polymerisation by dimetal complexes. Mixed compounds with zinc or aluminium alkyls form butadiene and isoprene polymers in which *trans*-1,4-structures predominate, independently of the nature of the alkaline-earth metal (Tables 1 and 2). Barium–aluminium complexes are distinguished by especially high stereospecificity: with respect to the total content of 1,4-butadiene units they are comparable with the most stereospecific catalysts based on transition metals. Barium–zinc alkyls are comparable with other organobarium initiators according to the overall rate of polymerisation[61,97]. The activity of barium–aluminium initiators is low[61], but the French Michelin firm has recently proposed in a series of patents several methods for enhancing their activity (with hardly any loss of stereospecificity)—by introducing electron donors[138], lithium alkoxides[139], or lithium alkyls[140].

Table 1 clearly reveals considerable structural differences between polybutadienes formed on compounds of alkaline-earth metals and on dimetal complexes, which are especially large with barium; hence the whole of the complex is directly involved in formation of the growing chain. In this respect alkaline-earth metals differ significantly from alkali metals, for which it has definitely been established that the introduction of diethylzinc or triethylaluminium affects only the overall rate of polymerisation, not the structure of the polymers (it is assumed that in this case complexes of the type $LiZnR_3$ or $LiAlR_4$ are inactive, while polymerisation occurs only on the uncomplexed portion of the initiator[2,61,132,141,142]). Thus systems based on alkaline-earth metals are sensitive not only to electron-donor agents but also to electron acceptors. This opens up new possibilities for controlling the stereospecificity of anionic initiators that are unknown for alkali metals.

Processes initiated by metal–zinc alkyls are characterised by an appreciable dependence of polymer structure on initiator concentration. Lowering the concentration of a barium–zinc alkyl from 3–5 m*N* to 0.1 m*N* increases the content of *cis*-1,4-butadiene units from 18–21% to 55–60% with a corresponding decrease in the proportion of *trans*-1,4-units (the 1,2-structure being constant), which is due to dissociation of the complex with separation of the free barium alkyl[61]. On the other hand, the polymerisation of isoprene by means of alkylzinc complexes of calcium, strontium, and barium in benzene (though in a different concentration range, 100–1 mM) exhibited the opposite relation: decrease in initiator concentration was accompanied by transition of *cis*- into *trans*-1,4-units[132].

(b) Acrylic monomers

Considerably less attention has been paid to this group of monomers than to dienes. Tetra-alkyls of zinc with calcium, strontium, and barium cause the formation of crystalline polymers of isotactic structure from iso-, s-, and t-butyl acrylates and methacrylates in toluene or ether[59]. In the polymerisation of methyl methacrylate in toluene, as in that of dienes, the variation in the stereoregulating action differs with metals in Groups I and II: the highest contents of isotactic structure are observed with the lightest alkali metal (lithium, up to 80%[143]) and with the heaviest alkaline-earth metal (barium 71%[120]). In oxolan, polymers having a predominantly syndiotactic structure are formed with all alkaline-earth metals[120].

Polymers of methyl methacrylate obtained by the action of dispersions of alkaline-earth metals in the presence of styrene (which does not enter the polymer chain) are enriched with the isotactic structure compared with those formed from the pure monomer[106]. Thus polymerisation by means of calcium in toluene increases the content of the iso-triad from 42% to 67%. It is assumed[106] that the structure of the polymer obtained in the presence of styrene characterises the actual anionic process, whereas in its absence the polymer is enriched with the syndiotactic structure owing to partial superposition of a radical process (another possible explanation will be given in Section IV).

Table 3. Composition of copolymers and copolymerisation constants r_1, r_2 in the presence of alkaline-earth metals.

Monomers		Initiator	Medium	M', mole %, in		r_1	r_2	Ref.
M	M'			initial mixture	copolymer			
Butadiene	styrene	RLi	benzene	50	9	12.5	0.1	[17]
Butadiene	styrene	Ca	toluene	—	—	6.7	0.01	[107]
Butadiene	styrene	RCaI	benzene	—	—	10	0.04	[95]
Butadiene	styrene	$CaZnR_4$	toluene	30	5	—	—	[12]
Butadiene	styrene	Sr	toluene	—	—	3.4	0.12	[107]
Butadiene	styrene	$SrZnR_4$	toluene	30	8	—	—	[12]
Butadiene	styrene	BaR_2	toluene	—	—	1.6	0.4	[107]
Butadiene	styrene	$BaZnR_4$	benzene	25	23	1.1	0.8	[96]
Butadiene	styrene	$ZaBnR_4$	benzene	30	22	1.3	0.7	[145]
Butadiene	styrene	$Ba(AlR_4)_2$	benzene	45	18	—	—	[145]
Butadiene	styrene	RLi	oxolan	50	85	0.2	8.0	[17]
Butadiene	styrene	RCaI	oxolan	—	—	0.6	1.7	[95]
Butadiene	styrene	BaR_2	oxolan	50	86	0.13	8.5	[96]
Butadiene	isoprene	RLi	toluene	50	29.5	—	—	[17]
Butadiene	isoprene	Ca	toluene	—	—	3.5	0.14	[107]
Butadiene	isoprene	Sr	toluene	—	—	4.3	0.3	[107]
Butadiene	isoprene	Ba	toluene	—	—	3.6	0.25	[107]
Butadiene	isoprene	BaR_2	benzene	50	31	2.0	0.3	[133]
Butadiene	isoprene	BaR_2	oxolan	50	20	3.0	0.1	[133]
Isoprene	styrene	RLi	toluene	50	12	9.5	0.25	[17]
Isoprene	styrene	Ca	toluene	—	—	4.5	0.07	[107]
Isoprene	styrene	RCaI	benzene	—	—	7.6	0.14	[95]
Isoprene	styrene	RCaI	oxolan	—	—	0.08	12	[95]
Isoprene	styrene	Sr	toluene	—	—	1.2	0.4	[107]
Isoprene	styrene	Ba	toluene	—	—	0.4	2.6	[107]
Butadiene	α-methylstyrene	BaR_2	benzene	56	0	—	—	[133]
Butadiene	α-methylstyrene	BaR_2	oxolan	54	10	—	—	[133]
Styrene	methyl methacrylate	BaR_2	benzene	50	100	—	—	[108]
Styrene	methyl methacrylate	BaR_2	oxolan	50	100	—	—	[108]

3. Copolymerisation

(a) Composition of copolymers

The copolymerisation of butadiene with styrene has been the most intensely studied, since copolymers having a random distribution of monomer units in the polymer chain provide

one of the main forms of high-volume general-purpose synthetic rubbers, and great interest has recently arisen in the search for catalysts ensuring the production of these rubbers under industrial conditions of solution polymerisation[6].

Table 3 shows that in oxolan, as with alkali metals, styrene is a considerably more reactive monomer than is butadiene. In the presence of initiators based on calcium and strontium in a hydrocarbon medium, as with lithium compounds, the copolymers are considerably enriched in butadiene. Yet butadiene–styrene copolymerisation constants are closely similar in most barium systems. It is interesting that this property is maintained in such structurally different compounds as barium alkyls and barium–zinc tetra-alkyls, despite the difference in their stereoregulating action. It is significant that the resulting copolymers contain considerably fewer 1,2-units than in radical polymerisation (10% on BaR_2 and 5% on $BaZnR_4$ compared with 20% in a radical polymer[6]) and are unlike modified lithium systems[144] in not containing microblocks.

Thus barium compounds are the only individual type effecting the formation of butadiene–styrene copolymers having a random distribution of monomer units in the chain with a low content of vinyl groups (sodium initiators also give similar copolymerisation constants, but with a content of vinyl groups exceeding 30% [17]). Depending on the type of initiator, copolymers can be obtained containing predominantly either *cis*-1,4-units (barium alkyls) or *trans*-1,4-units (barium–zinc alkyls or barium–aluminium alkyls with modifying additives). According to information in the patent literature both types of copolymers are suitable as rubbers.

Other copolymerisation systems have been investigated less thoroughly, and differences in behaviour between alkaline-earth and alkali metals are not so substantial (Table 3). Copolymerisation of styrene with methyl methacrylate on an organobarium initiator has confirmed that a homopolymer of the latter monomer is actually formed under homogeneous conditions, although with heterogeneous initiation by dispersions of alkaline-earth metals a certain quantity of styrene enters the copolymer[11,122] (the reasons for this have been discussed in detail above).

Thus in oxolan the relative reactivities of the monomers increase in the sequence

α-methylstyrene ≪ isoprene < butadiene < styrene ≪ methyl methacrylate

characteristic of anionic polymerisation. On calcium and strontium initiators in a hydrocarbon medium the activity varies in the sequence

styrene < isoprene < butadiene

as with lithium. A somewhat different dependence is observed on a barium initiator:

α-methylstyrene ≪ isoprene < butadiene ≅ styrene ≪ methyl methacrylate

(b) Structure of copolymers

It is usually supposed (explicitly or implicitly) that in anionic copolymerisation, as in the radical process, the presence of the second monomer M′ does not affect the addition of the monomer unit M, i.e. that the structure of M units is the same in the copolymer as in the homopolymer obtained under the same conditions. Only recently has it appeared that styrene influences the structure of diene units in copolymers formed by the action of lithium initiators[146,147]. However, the interaction of monomers in anionic processes has been most fully investigated on barium initiators, where it is apparently general in character (for coordination polymerisation involving transition metals this phenomenon was known considerably earlier[148]).

Table 4. Structure of butadiene part of copolymer with styrene obtained by using bis-1,1,4,4-tetraphenylbutylbarium[96,133].

Styrene in copolymer, mole %	Monomer units, %			Styrene in copolymer, mole %	Monomer units, %	
	cis-1,4	*trans*-1,4	1,2		1,2	1,4
	benzene				oxolan	
0	63	25	12	0	22	78
14	62	27	11	16	26	74
20	57	29	14	34	49	51
25	52	34	14	47	45	55
37	50	40	10	66	51	49
45	36	54	10	84	51	49
69	34	54	12	93	61	39

In the copolymerisation of butadiene with styrene by means of bistetraphenylbutylbarium in benzene (Table 4) increase in the styrene content of the copolymer is accompanied by a gradual conversion of *cis*- into *trans*-1,4-units while the content of 1,2-units remains unchanged (a high content of the *cis*-1,4-structure is maintained in the composition range of practical interest for the production of rubbers, i.e. at styrene contents up to 15 mole %). In oxolan the introduction of styrene produces a sharp increase in the content of 1,2-units (Table 4). Similarly, increase in the content of butadiene in its copolymer with isoprene (polymerisation in benzene) is accompanied by increase in the content of *trans*-1,4-units (up to 43% at a butadiene content of 69 mole %) with a corresponding decrease in the proportion of *cis*-1,4-units, the structure of the butadiene portion changing little[133]. Thus according to their influence on the structure of the diene units these monomers can be arranged in the sequence isoprene < butadiene < styrene, in which each successive member affects the structure of the preceding member, bringing it closer to that characteristic of systems with alkali metals[133].

Discussion of possible reasons for this phenomenon[32,133] shows that solvation of the gegenion by the second monomer M′ plays no decisive part. It is supposed that the main factor in copolymerisation in benzene is the decrease, with increased polarity of the bond with the terminal monomer unit in the above sequence, in the ability of the gegenion to *cis*-orient the monomer unit that is added on. (It is noteworthy that, in copolymerisation by means of a *trans*-orienting organobarium–zinc initiator, the structure of the butadiene units corresponds to that of the homopolymer throughout the composition range[145].) Thus in this process entry of M′ into the chain apparently changes the structure of the following M unit. When copolymerisation occurs in oxolan, introduction of M′ probably changes the structure of the preceding M unit (styrene adds with equal probability to α- and γ-carbon atoms of a terminal allyl unit, whereas butadiene adds predominantly to the α-atom[133]).

Thus the main features of alkaline-earth metals are higher coordinating power, lower sensitivity to electron donors, sensitivity to organometallic electron-accepting complexing agents, and the possibility of introducing modifying groups directly into the gegenion. The last two factors extend significantly the possibilities for controlling the catalytic

activity of these compounds, in definite measure assimilating them to systems based on transition metals. It is sufficient to state that barium initiators represent the first (and only) case in anionic polymerisation in which it is possible to obtain on the same metal butadiene polymers in which any of the possible structures predominates—*cis*-1,4 (BaR_2 in a hydrocarbon medium), *trans*-1,4- (barium–aluminium or barium alkoxide systems), or 1,2-structures (BaR_2 in the presence of 1,1-dimethylethylene or hexamethylphosphorotriamide).

In regard to immediate prospects for practical application a leading position is occupied without doubt by organobarium initiators for the copolymerisation of butadiene with styrene. There are grounds for supposing that, with respect both to the properties of the resulting rubbers and to the general characteristics of the industrial process, barium initiators are fully compatible with lithium initiators, while still inferior to them in economy and simplicity of production.

According to the Phillips Petroleum Col. partly crystalline *trans*-1,4-polybutadiene formed by means of barium alkoxide initiators is also an interesting material with valuable new technical properties[149].

IV. KINETICS AND MECHANISM OF POLYMERISATION IN SYSTEMS WITH BIVALENT GEGENIONS

1. Structure of Active Centres—Physicochemical Investigations

A most characteristic feature of anionic polymerisation is the existence of active centres in diverse forms—molecules having a polarised bond, their association complexes, ion-pairs varying in degree of solvation, free ions, ion-triplets, etc.—differing in their reactivity and stereospecificity[17-19]. (As a distinction from free ions the remaining forms of active centres are sometimes described in general as "combined with a gegenion".) This is fully applicable also to alkaline-earth metals, with which, however, certain complications in terminology arise (thus an electrically neutral species of type (R^-, M^{2+}, R^-) must obviously be termed an ion-pair, although it contains three ions, while the charged species (R_3^{3-}, M^{2+}) is a triplet, etc.). Furthermore, novel forms of active centres appear, that are non-existent or not specially significant in processes with alkali metals.

We must first note the peculiar structure of live polymers having carbanions at both ends of the macromolecule. Early papers on the preparation of a double-ended initiator, bis-tetraphenylbutylbarium[10,26], had already mentioned that from stoichiometric considerations this compound could not exist in a linear monomeric form. Subsequent investigation by various physicochemical methods of this initiator and the double-ended live polymers of styrene and butadiene formed in its presence showed[31,32] that in electron-donor solvents (oxoland, dimethyl ether) these compounds form macrocyclic aggregates, whose presence is responsible for several anomalies in the properties of the systems and also several peculiarities in the polymerisation processes occurring in them. In particular the electrical conductivity of the systems is significantly smaller than that of their single-ended analogues, since the primary dissociation products of macrocycles are non-conducting zwitterions, while the variation of the conductivity with concentration does not correspond to Ostwald's dilution law for weak electrolytes.

It is important to emphasise that, in contrast to other cases of the association of active centres (e.g. lithium compounds in a hydrocarbon medium), in which entry into the association complex changes significantly the character of the metal–carbon bond, in the present case the union of several species to form a single aggregate produces no appreciable change in the nature of the individual active centres in comparison with their single-ended analogues. Formation of similar cyclic aggregates has been established also for products of the action of magnesium on 2-vinylpyridine[150] and on isoprene in oxolan[118]. The latter work has confirmed the previously observed[31,32] decrease in number of fragments in the ring with increase in the length and hence flexibility of individual fragments.

A novel form of active centres, not present in alkali-metal systems, is provided also by "unsymmetrical" ion-pairs, i.e. species of the type (R^-, M^{2+}, R^{2-}), which play an important part in several processes, but as yet have hardly been studied by physicochemical methods.

Table 5. Wavelengths λ_{max} (nm) in absorption spectra of model compounds $R.C(C_6H_5)_2^-M^+$.

Cation	Solvent		Ref.
	benzene	oxolan	
Lithium	420	490	[151]
Sodium	460	480	[151, 153]
Magnesium	—	<330; 490*	[154]
Magnesium	—	298**	[155]
Calcium	460	520	[154]
Strontium	470	470	[154]
Strontium	—	465	[35]
Barium	445	445	[154]
Barium	—	448	[33]

*Below −60 °C.
**Diphenylmethylmagnesium bromide in diethyl ether.

One of the main factors determining the reactivity and the stereospecificity of active centres is the degree of polarisation of the bond between the growing end of the chain and the gegenion. If is often estimated from the electronic absorption spectra of model compounds containing carbanions of the 1,1-diphenylalkyl type[17,151,152]. Spectral data (Table 5) together with results on the structure of butadiene polymers (Table 1) show that the correlation between λ_{max} and the character of polymerisation (the shorter the wavelength λ_{max}, i.e. the less polar the bond, the greater the proportion of the coordination process leading in particular to increase in the content of 1,4-diene structures), established for alkali-metals[17,136], is maintained for alkaline-earth metals.

According to the λ_{max} wavelength in oxolan the polarity of the metal–carbon bond in the series of alkaline-earth metals (apart from magnesium, which is inactive in polymerisation), as in the series of alkali metals[17,136], decreases as the ionic radius increases, with a corresponding diminution in the proportion of 1,2-units in the butadiene polymers, which is well explained by the weakening role of solvation effects in the same sequence. For a 1,1-diphenylalkylbarium in oxolan λ_{max} lies ar appreciably shorter wavelengths compared not only with other compounds in the same solvent but even with the diphenylalkylsodium in benzene. Hence a polybutadiene obtained by the action of barium compounds in oxolan contains more 1,4-units than do polymers obtained with alkali metals (other than lithium) in a hydrocarbon medium. This indicates unusually low polarity of the bond in a barium active centre.

In a hydrocarbon medium alkali and alkaline-earth metals show opposite variations: whereas among the alkali metals the polarity of the metal–carbon bond increases with the ionic radius of the metal, the polarity diminishes on passing from calcium to barium (the λ_{max} given in Table 5 for a 1,1-diphenylalkylstrontium in benzene may be too high[154] owing to incomplete removal of the oxolan used in the preparation). A possible explanation of such divergence is the early view[17] that the polarity of a metal–carbon bond (in a given carbanion) should increase with decrease in the electron-accepting properties of the metal. Calculation showed[156] that the electron affinity (a measure of electron-accepting properties) falls with increase in atomic number in the series of alkali metals, but increases in the alkaline-earth metals, owing to the difference in type of hybridisation of the lowest vacant orbitals—*s* in alkali metals and *sd* in alkaline-earth metals.

Table 6. Conductivity data for systems containing alkaline-earth metals in oxolan.

Metal	Temp., °C	K_{diss}, M	Ref.
	fluorenyl		
Sodium	20	$7.5\cdot10^{-7}$	[78]
Caesium	25	$1.4\cdot10^{-7}$	[157]
Strontium	20	$1.7\cdot10^{-7}$	[78]
Barium	20	$5.3\cdot10^{-9}$	[78]
	tetraphenylborate		
Sodium	25	$8.5\cdot10^{-5}$	[158]
Caesium	25	$1.87\cdot10^{-5}$	[158]
Barium	25	$3.6\cdot10^{-5}$	[31]
Barium	20	$1.65\cdot10^{-5}$	[159]
	triphenylmethyl		
Sodium	25	$7.6\cdot10^{-6}$	[160]
Barium	25	$3.6\cdot10^{-7}$	[31]
	benzyl (styryl)		
Sodium	25	$1.5\cdot10^{-7}$	[18]
Caesium	25	$2.8\cdot10^{-9}$	[18]
Barium	20	$1.1\cdot10^{-10}$	[159]
Barium	25	$4.1\cdot10^{-11}$	[161]

Valuable information on the state of active centres in solvating media is given also by conductivity measurements (Table 6). In ethereal solvents (oxolan, dimethyl ether) barium compounds at concentrations up to 10 μM undergo only the first stage of dissociation[31,32,69], without formation of free Ba^{2+} ions (the values of K_{diss} in Table 6 relate to this stage):

$$BaR_2 \overset{K_{diss}}{\rightleftarrows} [BaR]^+ + R^- \quad . \qquad (1)$$

Compounds containing a barium–carbon bond have considerably lower conductivities than those of alkali metals, in particular for the caesium analogue of the barium compound. This also indicates the low polarity of this bond.

2. Principal Kinetic Laws

The few kinetic investigations have already covered a fairly wide range of polymerisation systems. In most cases initiation stages are rapid, and termination reactions are absent. It is therefore supposed that, where not specially stipulated, the measured rate of polymerisation is the rate of chain growth, as in most research with alkali metals. Published kinetic data are summarised in Table 7.

First order of chain growth with respect to the monomer has been established in all cases without exception. Since the order of reaction with respect to the initiator differs in different systems, the reaction velocity is usually characterised by the experimental first-order rate constant

$$k' = -\frac{1}{M}\cdot\frac{dM}{dt},$$

where M is the concentration of the monomer. The growth constant k_{gr} cited in several papers is calculated: $k_{gr} = k'/c_0$, where c_0 is the concentration of growing chains. This constant acquires real meaning only when chain growth is first order with respect to active centres.

Table 7. Kinetic characteristics of chain growth in polymerisation by using compounds of alkaline-earth metals (not indicated over the concentration range of active centres c_0 = 1–10 mM).

Monomer	Initiator	Order with respect to indicator	T, °C	10^3c_0, mM	$10^3k'$, s^{-1}	k_{gr}, $M^{-1}s^{-1}$	E_{gr}, kJ mole^{-1}
		oxolan					
Styrene	dibenzylcalcium	0	−30	—	5.5	—	—
Styrene	dibenzylstrontium[166,175]	0	20	—	36	—	—
Styrene	dibenzylbarium[161]	0	30	—	1.0	0.33	35
Styrene	bistriphenylmethylbarium[163]	1	30	—	—	0.019	54
Butadiene	dibenzylstrontium[164]	1	30	—	—	$1.5\cdot10^{-3}$	56
Butadiene	dibenzylbarium[161]	1	30	—	—	$8\cdot10^{-3}$	57
Butadiene	bistriphenylmethylbarium[163]	1	30	—	—	$1\cdot10^{-2}$	56
2-Vinylpyridine	oligovinylpyridine magnesium*[150]	variable	20	0.04	2.8	70	
			20	0.06	2.7	45	
		$0<n<1$	20	0.24	5.5	23	
			20	0.9	10.8	12	
MMA	difluorenylbarium[165]	1	−70	—	—	11.5	20
		benzene					
Styrene	bistriphenylpropylbarium[97]	1	30	—	—	0.39	35
Butadiene	bistriphenylpropylbarium[97]	1/3	30	0.24	0.015	—	—
			30	12	0.083	—	67

*Difunctional initiator.

(a) Electron-donor media

Styrene. The most peculiar behaviour has been revealed in the polymerisation of styrene in oxolan. The most important feature is the existence of completely different kinetics for barium initiators of three different types.

The first type—a single-ended initiator with rapid initiation (dibenzylbarium)—has been studied simultaneously by two groups of investigators[69,159,161], who have obtained almost identical results. The measured rate of polymerisation (and hence the rate of chain growth) is independent of the concentration of active centres, so that the usual calculated quantity k_{gr} increases with dilution in inverse proportion to the initiator concentration. Such an unusual law could be explained[69,161] on the principal (established earlier for alkali metals[18]) that free carbanions play a decisive part in the anionic polymerisation of styrene, by introducing the hypothetical formation of more complicated species, "ion-triplets", by coordination of an additional styryl carbanion with the barium cation, which though weakly solvated has a

strong electrostatic field:

$$R^- + BaR_2 \overset{K_{tr}}{\rightleftarrows} [BaR_3]^- \quad (2)$$

On the postulates that equilibrium (2) is displaced to the right and that the total concentration of charged species is small (as follows from the low conductivity of the system—Table 6) calculation by means of Eqns.(1) and (2) yields the kinetic formula

$$k' = -\frac{1}{M}\cdot\frac{dM}{dt} = k_-\cdot c_- = k_-(K_{diss}/K_{tr})^{1/2} \quad (3)$$

consistent with experimental results (k_- is the growth rate constant on free anions and c_- the concentration of free styryl anions).

With the same postulates the suggested scheme predicts that the equivalent conductance of the system shall be independent of c_0. Such behaviour, which is also unusual for solutions of weak electrolytes and is due to the "asymmetry" of formation of the ion-triplets (as stated above, only the negative triplet of type BaR_3^- is formed, not the positive $Ba_2R_3^+$), has been confirmed experimentally for live barium–polystyrene[69] and for dibenzylbarium[161]). The combination of kinetic and conductivity data has permitted calculation of the dissociation constant K_{diss} (Table 6), which from the above discussion evidently cannot be obtained directly from conductivity measurements. (Ion-triplets are not formed in compounds of barium with branched carbanions such as di- and tri-phenylmethane, and the conductivity depends on the concentration[31].)

Recent preliminary reports indicate (Table 7) that this scheme is followed also by the polymerisation of styrene in oxolan under the influence of corresponding calcium and strontium initiators. The overall rate of polymerisation increases from barium through strontium to calcium (apparently owing to the accompanying increase in the dissociation constant K_{diss} and hence in the concentration of free ions[166]). This recalls the situation presented by the alkali metals, when the increase in rate of polymerisation of styrene accompanying each passage from a lower to a higher member is associated with successive increase in K_{diss}, not with change in reactivity of individual species[18].

An initiator of the second type—double-ended with rapid initiation—was historically the first organobarium subject (a barium salt of an oligomeric dianion of α-methylstyrene) of kinetic investigation[167]. Zero order with respect to the initiator was observed for the first time[167], but this was given an untenable explanation (formation of inactive association complexes of active centres), which has subsequently been criticised[69,70,150,161]. Only after the above results had been obtained for the simpler system with dibenzylbarium did it become clear that the zero order with respect to active centres has the same causes here as in the preceding case, i.e. formation of ion-triplets with free ions is kinetically decisive, and views developed subsequently by various authors[70,162] have in the main shown mutual agreement.

The most significant kinetic feature of the polymerisation of styrene with double-ended initiators, which is directly connected with the above formation of macrocyclic aggregates, is that the observed growth constant increases with length of the polymer chain, with consequent autocatalysis despite rapid completion of the initiation stage[10,161,163,168]. Thus at 20 °C the constant k' (in 10^{-3} s^{-1}) increases from 0.25 to 2.0 as the degree of polymerisation rises from 50 to 800.[162] During the polymerisation of styrene (and also of butadiene) in the presence of bistetraphenylbutylbarium the conductivity of the system increases steadily[31,32], which agrees well with the theoretically predicted increase in the constant for the dissociation of cyclic ion-pairs into free ions as the ring becomes larger[18,169]. In conformity with Eqn.(3) increase in K_{diss} leads to increase in the overall rate of polymerisation of styrene.

Only the number of growing chains in the macroring remains obscure. Viscosimetric data[31,32] show that a ring contains 5–7 polystyrene chains halfway through the process, and 3–4 chains at the end. On the other hand, closure of an intramolecular ring from one chain has been assumed, although a fall in viscosity on deactivation was also observed[162], corresponding to a mean degree of association of 1.5–4 (closure of a monomolecular ring should have led to an increase in viscosity). Apparently the most serious (and only) argument in support of a monomolecular ring is the same workers' observation[170] of non-random spontaneous deactivation of solutions of oligomeric styrylbarium dianions in oxolan on reaction with the solvent. Deactivation of one live end caused rapid deactivation of the other, which could be explained only if the two ends were attached to the same gegenion. We remark merely that actual formation of macrorings is sufficient, independently of their size, for the above interpretation of the dependence of rate of growth on chain length.

Finally, a third, completely different type of behaviour is observed on using the relatively inactive (single-ended) initiator bistriphenylmethylbarium[70,163], when the process is autocatalytic, as is usual for reactions having a slow initiation stage. The rate of chain growth (for a given concentration of growing chains) is less than one-tenth of the rate with dibenzylbarium (Table 7) and, most significantly, depends on the concentration of active centres. The non-zero reaction order is qualitatively evident from the very fact that the rate increases with number of growing chains. Mathematical treatment by several methods[70,163] has established that chain growth is first order with respect to active centres.

It is still more surprising that the resulting polymers have comparatively low molecular weight ($\bar{M}_n \cong 10000$ at 30 °C), lower by factors of 20–40 and more than the calculated value, and an extremely wide molecular-weight distribution ($\bar{M}_w/\bar{M}_n \cong 2$, whereas with live polymers slow initiation is able to raise this ratio to at most 1.3–1.4 [16]). Detailed analysis of the results indicated the occurrence of chain transfer to the monomer (probably by transfer of a hydride ion)[163]. This is perhaps the most unexpected fact, since hitherto the anionic polymerisation of styrene has been regarded as the most typical example of the formation of live polymers.

The distinguishing behavioural features of this system can be understood on the basis that, owing to the extremely low rate of initiation ($k_{in} = 2.2\times10^{-6}$ M^{-1} s^{-1} at 30 °C), most of the active centres have the structure of the unsymmetrical ion-pair ($C_6H_5.CH:CH-Ba-C(C_6H_5)_3$: i.e. they contain a triphenylmethyl group attached to the gegenion. Such active centres will dissociate preferentially at the considerably more polar $(C_6H_5)_3C-Ba$ bond (Table 6): dissociation at the $C_6H_5.CH:CH-Ba$ bond is suppressed by the presence of $[(C_6H_5)_3C-Ba]^+$ cations formed by dissociation of unchanged initiator $[(C_6H_5)_3C]_2Ba$, a strong electrolyte. As a consequence the content of $C_6H_5.CH:CH^-$ ions is much lower than in the previous cases, and the contribution by ion-pairs becomes predominant, which well explains both the general decrease in rate of chain growth and the appearance of first order with respect to active centres. Addition of styrene to a bulky active centre containing four phenyl groups around a cation apparently meets considerable difficulties, which greatly increase the probability of chain transfer but also influence significantly copolymerisation processes (for greater detail see below).

Thus in the polymerisation of styrene on barium initiators in oxolan the nature of the hydrocarbon moiety of the initiator has a significant influence on fundamental aspects of chain growth and on the nature of the resulting polymers.

Other monomers. The polymerisation of butadiene in oxolan under the influence of dibenzylbarium[161] and of dibenzylstrontium[164] is first order with respect to the initiator. Hence, as with alkali metals[171], the decisive role in steps of chain growth belongs not to free ions but to forms of active centres "combined with a gegenion". Together with the above data on the structure of the polymers and the spectra of model compounds this led to the conclusion that the active centres of chain growth in the polymerisation of butadiene by means of barium[161] and probably strontium[164] are molecules having a polarised metal–carbon bond. Live polymers of butadiene, formed under the influence of double-ended bistetraphenylbutylbarium, exhibit the same peculiarities of conductivity and viscosity behaviour, associated with the formation of macrocyclic aggregates, as do styrene systems[31]. Since free ions have no decisive role in the polymerisation of butadiene, it is clear that variation in the dissociation constant does not affect the kinetics[161]. When polymerisation occurs under the influence of bistriphenylmethylbarium an induction period is observed, as in the case of styrene, that is due to slow initiation ($k_{in} = 1.1 \times 10^{-5}$ M^{-1} s^{-1} at 30 °C)[163]. Chain growth is first order with respect to active centres, with growth constants closely similar to those obtained with dibenzylbarium (Table 7). Hence butadiene adds at about the same rate to the two types of active centres—"symmetrical" ($CH_2:CH.CH:CH-Ba-CH:CH.CH:CH_2$) and "unsymmetrical" [$CH_2:CH.CH:CH-Ba-C(C_6H_5)_3$].

Comparison of published data shows that the rate of polymerisation of butadiene in oxolan is greatest with barium, the highest alkaline-earth metal[161]; the process is slower with strontium[164], and perhaps still slower with calcium[95]. This corresponds with the variation found with alkali metals[126], but the overall rates are considerably lower than with the latter.

A pattern similar to that with butadiene is observed[165] in the polymerisation of methyl methacrylate in oxolan by means of a barium compound at −70 °C (under these conditions a live polymer is formed; at higher temperatures intramolecular chain termination takes place with involvement of ether side-groups). The reaction is first order with respect to the initiator on both single- and double-ended initiators (difluorenyl- and bistetraphenylbutyl-barium), and occurs at the same rate. Hence, as in the polymerisation of butadiene, it takes place on "combined with a gegenion" active centres (in the present case on ion-pairs[165]).

A more complicated dependence is obtained in the polymerisation of 2-vinylpyridine under the influence of a double-ended magnesium initiator[150]. The concentration dependence of the observed chain-growth constant is described by an equation of the type $k_{gr} = a + bc_0^{-1}$ (or $k' = ac_0 + b$). The same scheme is adopted as for the polymerisation of styrene with dibenzylbarium (allowing for the formation of ion-triplets), but in this case not only free ions but other species (ion-pairs or -triplets) take part in chain growth, their contribution to the total rate of polymerisation being proportional to the initiator concentration. Viscosimetric data indicate the formation of macrocyclic aggregates in the double-ended system, but polymerisation occurs[150] without autocatalysis. Unfortunately the kinetics of polymerisation with a single-ended initiator was not examined[150].

It is interesting that, when a relatively inactive initiator (dibenzylmagnesium) is used, spectral and viscosimetric data indicate formation of unsymmetrical active centres of type $NC_5H_4.CH:CH.Mg.CH_2.C_6H_5$, which differ in properties from $NC_5H_4.CH:CH.Mg.CH:CH.C_5H_4N$ centres[150].

(b) Hydrocarbon medium

The kinetics of the polymerisation of butadiene and styrene in benzene have been investigated[97] in the presence of bis-1,1,3-triphenylpropylbarium, which had been obtained in oxolan and then distilled with chromatographic control of completeness of removal. The order of chain growth with respect to the initiator concentration in the polymerisation of butadiene is close to one-third, which indicates the association of active centres usual in anionic polymerisation in hydrocarbon media, in this case formation of trimeric complexes. The polymerisation of styrene, on the other hand, is first order with respect to the initiator, and hence polystyrylbarium active centres are unassociated even in benzene. Association of polybutadienylbarium active centres and non-association of polystyrylbarium have been confirmed by viscosimetric data[97]. In the polymerisation of butadiene in benzene by means of double-ended bistetraphenylbutylbarium, when association should lead to the formation of a kind of three-dimensional network, "gelation" of the solution was already observed at low degrees of conversion of the monomer, but the solution again became mobile on deactivation[129].

According to the above results styrene is polymerised more rapidly than butadiene by barium compounds in benzene. In the presence of a mixed calcium initiator $R_2Ca-RCaI$, on the other hand, rates of homopolymerisation correspond to the sequence butadiene > isoprene > styrene[95] (the rates of polymerisation of both butadiene and styrene were lower here than with a barium initiator). The activation energy of the polymerisation of butadiene by means of this initiator is 87 kJ $mole^{-1}$.[8]

Overall rates of polymerisation of butadiene and styrene by means of barium compounds in benzene are closely similar to rates observed with lithium initiators[172]. Since, however, both polystyryl- and probably also polybutadienyl-lithium active centres are considerably more strongly associated than are barium centres, the relatively high rate of polymerisation on barium initiators is clearly due to a greater effective concentration of active centres, not to their reactivity.

One of the most characteristic features of anionic polymerisation with alkali metals is the sharp increase in its overall rate on passing from hydrocarbon to electron-donor solvents. With barium initiators, however, Table 7 shows that over the usual concentration range (10–1 mN) transfer from benzene to oxolan produces no appreciable increase in total rate of polymerisation. Since in the polymerisation of butadiene in benzene chain growth involves only a small fraction of unassociated active centres, whereas polymerisation of styrene in oxolan occurs predominantly on free ions with an insignificant contribution by ion-pairs, it is obvious that the reactivity of "combined with a gegenion" forms of polybutadienyl- and polystyryl-barium active centres is higher in benzene than in oxolan[97]. In the polymerisation of styrene under the influence of "butylcalcium iodide"[95], on the other hand, transfer from benzene to oxolan causes a sharp increase in total rate (by several orders of magnitude), as with alkali metals.

3. Mechanism of Copolymerisation

The influence of the hydrocarbon part of the initiator on the character of the processes initiated, which is specific to

alkaline-earth metals and has been reported in the preceding subsection, is just as clearly evident in copolymerisation. The main features of the copolymerisation of butadiene with styrene by means of bistriphenylmethylbarium in oxolan differ significantly[173] from those of copolymerisation initiated by other barium compounds (Section III). Whereas with dibenzylbarium styrene is considerably more active than butadiene (Table 3), in the presence of the former initiator the activities of the monomers level out ($r_1 = r_2 = 1.0$).

Estimation of the rates of indibidual primary steps (by comparing copolymerisation constants with homopolymerisation rate constants of the same monomers) showed that in the presence of bistriphenylmethylbarium the rates of both styrene-addition steps (to its own and to a butadiene active centre) fall by more than 90%, whereas the rates of addition of butadiene to both growing chains remain almost unchanged[173] (this work[173] was done before it became clear that transfer from one initiator to another causes a complete change in the mechanism of individual primary steps; this result can therefore be regarded merely as a qualitative indication of an appreciable decrease in reactivity of styrene as a consequence of the presence of a triphenylmethyl group in the active centre). Such presence influences also the structure of the copolymers[173]. Whereas in copolymerisation by means of "ordinary" barium initiators increase in the styrene content is accompanied by enrichment of the butadiene part with 1,2-units (Table 6), in the presence of bistriphenylmethylbarium introduction of up to 60% of styrene into the copolymer does not affect the structure of the butadiene units. (All the above applies to copolymers obtained in the initial stages: with high conversions, when "symmetrical" active centres begin to appear, a non-uniform copolymer is formed, enriched with styrene and 1,2-butadiene units[173].)

Effects due to interaction of groups in an active centre may obviously be still more widely evident in copolymerisation than in homopolymerisation, since growing chains with different kinds of terminal units can here act as "perturbing" groups. Interpretation of the results is, of course, considerably complicated thereby, but a broad field is opened up for research. Thus investigation of the influence of styrene on the structure of butadiene units in copolymers formed under the influence of barium compounds has revealed[32,96,133] that calculations based on simple models regarding growing chains as isolated will not give a quantitative description of the results. Thus the structure of the resulting monomer unit obviously depends not only on the structure of "its" growing chain but also on the nature of the terminal unit of the adjacent chain combined with the same gegenion.

Results obtained[106] on the structure of poly(methyl methacrylate) formed in the presence of styrene are relevant here. The explanation given (a competing radical process) is open to doubt (Section III). An alternative explanation of this effect may be that, as mentioned earlier, styrene is preferentially involved in initiation when a mixture with methyl methacrylate is in contact with a heterogeneous initiator[18,123], so that subsequent polymerisation of the methacrylate takes place on "unsymmetrical" centres of the type $C_6H_5.CH:CH-Ca-CH:C(CH_3).COOCH_3$.

Such effects due to interaction between two different groups attached to the same gegenion undoubtedly play an important part in homo- and co-polymerisation initiated by compounds of alkaline-earth metals (as also in the chemistry of these compounds in general). Unfortunately the almost complete absence of quantitative experimental data does not permit even qualitative prediction of the direction of this influence. As yet only the single observation can be cited[159] that the dissociation constant of the unsymmetrical styrene–phenylborate salt $C_6H_5.CH:CH.Ba.B(C_6H_5)_4 \rightleftharpoons [C_6H_5.CH:CH.Ba]^+ + B(C_6H_5)_4^-$ in oxolan is roughly double that of symmetrical barium tetraphenylborate. Thus in this case introduction of a less polar group (styryl) causes additional polarisation of the bond with the more polar group.

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The results discussed above confirm the validity and usefulness of many fundamental principles of the theory of anionic polymerisation developed for alkali metals, but also reveal several fundamentally novel forms of behaviour not observed previously. The behavioural features of alkaline-earth metals can be divided (more or less arbitrarily) into two groups. Such phenomena as the presence of unsymmetrical active centres or the formation of live macrorings in double-ended systems are due to the actual bivalency of the gegenion; they should, of course, occur to some extent in processes with all Group II metals. Other phenomena—e.g. low polarity of the metal–carbon bond, enhanced coordinating power in the polymerisation of butadiene, low sensitivity to electron donors, less tendency to association in a hydrocarbon medium, etc.—are connected mainly with the specific electronic structure of actual gegenions, and are usually most strongly developed with the heavier metals (barium and strontium).

Discovery and investigation of all these novel phenomena will both broaden significantly our general theoretical ideas on anionic polymerisation and open up new prospects for their practical application. Although possible uses of alkaline-earth metals in polymerisation are more or less determined (conclusion to Section III), at least for the immediate future, theoretical aspects of this field are only beginning to be worked out. There is every reason to expect that further research will not only prove fruitful in developing the new field—polymerisation by means of alkaline-earth metals—but will also help to shed new light on many phenomena in the "old" field (polymerisation on alkali metals), as has already been observed more than once in the theory of anionic polymerisation, with expansion of the range of materials investigated.

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