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ANIONIC POLYMERISATION IN THE PRESENCE OF ALKALI METALS AND THEIR COMPOUNDS

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INTRODUCTION

Anionic polymerisation processes are of considerable interest, since they enable us to synthesise polymers with valuable properties, e.g. polymers of regular structure, such as *cis*- and *trans*-polyisoprene, isotactic polystyrene, isotactic and syndiotactic methyl methacrylate, etc., and also block copolymers.

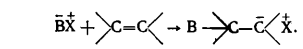
The catalysts for anionic polymerisation are substances of basic, electron-donor character — alkali metals and their amides, various organometallic compounds, complex organometallic compounds, organomagnesium compounds, etc. Anionic polymerisation of very reactive monomers is also brought about by water, alkalis, amines, and alkali-metal carbonates and bicarbonates.

The present review is concerned mainly with polymerisation in the presence of alkali metals and their derivatives.

The monomers most active in anionic polymerisation are compounds containing electronegative substituents attached to a double-bonded carbon atom — vinylidene cyanide, nitroethylene, acrylonitrile, methyl acrylate, methacrylonitrile, methyl methacrylate, etc. The polymerisation takes place by an ionic mechanism of the acid—base type[1], the catalysts or active centres acting as electron donors, and the monomers as electron acceptors.

Under the influence of an anionic catalyst BX an active

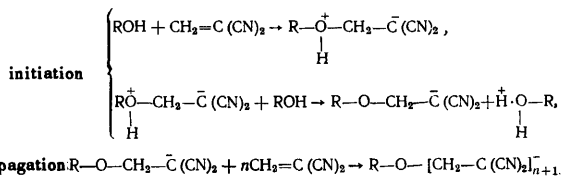
growth centre is formed by the reaction



This active centre is a tervalent negatively charged ion of carbon, a carbanion; in weakly polar media a positive gegenion is always present in the field of the carbanion, forming with it an ion pair.

I. POLYMERISATION BROUGHT ABOUT BY WATER, ALCOHOLS, AND AMINES

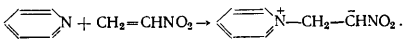
Monomers which are very active in anionic polymerisation — vinylidene cyanide and nitroethylene — polymerise in the cold in the presence of water, alcohols, and amines[2,3,4]. The proposed mechanism of polymerisation is represented by the scheme



Gilbert et al.[5] observed that polymerisation of vinylidene cyanide occurs in the presence of isobutyl vinyl ether, which acts as the base, while the vinylidene cyanide acts as the acid. With these two monomers present together, anionic and cationic polymerisation occurred simultaneously. Polymers of two types separated out, one soluble in benzene and having a high content of isobutyl vinyl ether, formed by cationic polymerisation, and the other insoluble in benzene and with a high content of vinylidene cyanide, formed by an anionic mechanism. On addition of triethanolamine to the system, the cationic polymerisation was suppressed, and no formation of benzene-soluble polymer was observed. Introduction of phosphorus pentoxide into the system inhibited the anionic polymerisation of the vinylidene cyanide.

The polymerisation of nitroethylene in the presence of pyridine in ethyl methyl ketone was studied by Vofsi and Katchalsky[6,7], who found the rate of reaction to be proportional to the concentration of pyridine and to the square of the concentration of monomer. The molecular weight hardly varied with change in the monomer concentration, indicating the occurrence of chain transfer with the monomer, and was independent of the concentration of catalyst.

These workers suggest the following initiation mechanism:



This process has a negative activation energy, -1.5 kcal/mole.

II. POLYMERISATION IN THE PRESENCE OF ALKALI METALS, THEIR AMIDES, AND ORGANIC DERIVATIVES

The polymerisation of unsaturated compounds by means of metallic sodium was observed by Karakau[8] in the case of styrene as long ago as 1878. The possibility of polymerising diene hydrocarbons with alkali metals was first established by Kondakov[9].

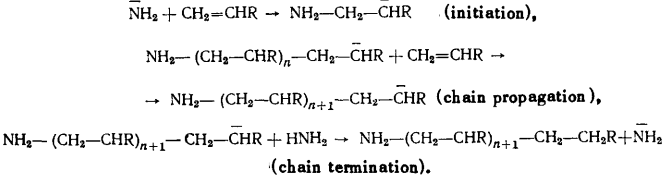
Subsequently Matthews[10] and Harries[11] suggested a method for polymerising diene hydrocarbons with metallic sodium, and Lebedev[12] originated a method for obtaining synthetic rubber from butadiene using metallic sodium as catalyst. Ostromyslenskii[13] showed that unsaturated compounds could be polymerised with organosodium derivatives. Subsequent research on the laws governing these reactions has made it possible to clarify the nature of such processes.

A. Polymerisation in the Presence of Alkali-Metal Amides in Liquid Ammonia

In a study of the polymerisation of various monomers with butylmagnesium bromide and triphenylmethylsodium Beaman[14] found that the resulting copolymer contained groups originally present in the initiator.

The investigations of Sanderson and Hauser[15] and of Higginson and Wooding[16] on the polymerisation of styrene with potassamide in liquid ammonia showed that each polymer molecule contains an NH_2 group. The rate of polymerisation of styrene was proportional to the square of the concentration of monomer and to the concentration of amide ion. The molecular weight of the polymers was independent of the catalyst concentration but was proportional to the concentration of styrene. Molecular weights determined viscosimetrically and cryoscopically were in good agreement with values calculated from analytical results for the nitrogen content on the assumption that every polymer molecule contains a single NH_2 group. On the basis of these results the following mechanism was proposed for the process occurring in the presence of alkali-metal amides in liquid ammonia:

Scheme 1



Thus chain termination occurs by elimination of a proton from an ammonia molecule with regeneration of the catalyst, the amide ion.

From the temperature variation of the rate of polymerisation of styrene and of the molecular weight of the resulting polystyrene, an estimate was made of the activation energies of the individual stages in this process:

$$E = E_i + E_p - E_t + {}^1/_2\,\Delta H \text{ (diss. } KNH_2) = 9 \pm 2 \text{ kcal},$$

where E is the overall activation energy, E_i the activation energy of initiation, E_p that for propagation, and E_t the activation energy of chain termination. It was found that ΔH (diss. KNH_2) = 0 ± 2 kcal/mole and $E_p - E_t$ = = -(4 ± 1) kcal/mole. By subtracting these quantities from the value of E, a value of 13 ± 4 kcal/mole was obtained for the activation energy of initiation E_i.

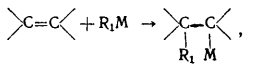
Polymerisation of acrylonitrile, methyl methacrylate, and methacrylonitrile also occurred with alkali-metal amides in liquid ammonia. Butadiene did not polymerise under these conditions, possibly because its solubility in liquid ammonia is low. α-Methylstyrene and diphenylethylene did not polymerise with alkali-metal amides in

liquid ammonia, but reacted with the amide ion with the formation of the corresponding carbanions, the solution becoming red.

These results show that anionic polymerisation in the presence of a proton-donor solvent is accompanied by a chain-terminating reaction. In such systems the molecular weight of the polymers is proportional to the concentration of monomer and is independent of the concentration of catalyst.

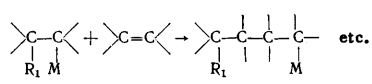
B. Polymerisation in the Presence of Alkali Metals and their Organic Derivatives*

An investigation of the reaction products formed by organometallic compounds with unsaturated molecules led Ziegler and Bähr[17] to the conclusion that the organometallic compound adds on to the double bond as follows:



where M represents an alkali metal.

The polymerisation can be regarded also as a process of successive entry of monomer into the organometallic compound at the R–M bonds by addition of R and M to the double bond of the unsaturated compound:

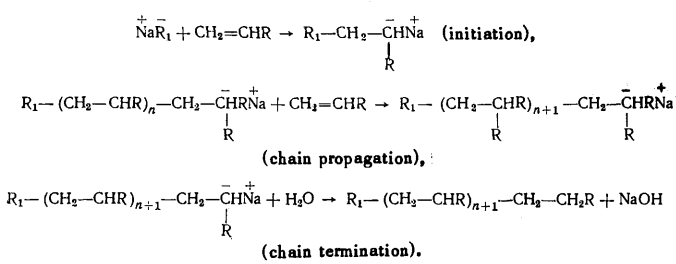


It was shown that an organometallic compound of high molecular weight is formed by such a process.

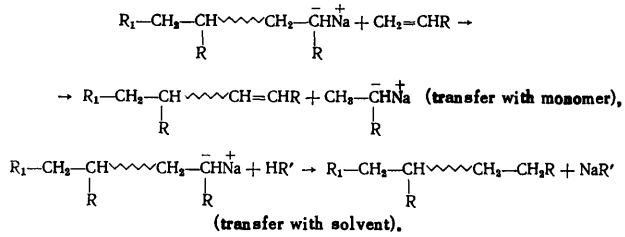
On analysing their own results and those of Schlenk[21], Ziegler and Bähr concluded that polymerisation in the presence of alkali metals occurs in a similar manner, the primary organometallic compound being formed by addition of sodium to the unsaturated molecule. Further investigations showed that the polymerisation of unsaturated compounds with alkali metals and with their organometallic compounds in polar solvents occurs by an anionic mechanism, the active centre under these conditions being the ion pair $\bar{R}\overset{+}{M}$ or a free carbanion.

The individual steps in such a process are shown in scheme 2 for an organosodium catalyst.

Scheme 2



Chain termination takes place in the presence of proton-donor compounds or molecules of the type RX (where X = Cl, Br, I, OH, etc.). Chain-transfer reactions are also possible:



It is evident from this scheme that the structure of the active-growth centre differs little from that of the original organometallic compound, only the organic radical linked to the metal being different. Depending on the nature of the radical in the original organometallic compound, the rate of initiation can be less than, equal to, or greater than the rate of growth of the chain. For example, in the polymerisation of styrene in the presence of triphenylmethylsodium, the rate of initiation is less than that of chain propagation[22,23], since the former reaction involves a transition from a more stable to a less stable carbanion.

The influence of the structure of the radical in the organosodium compound on its initiating capacity was studied by Wooding and Higginson[1], who showed that in the majority of cases the latter increased with increase in basicity of the radical.

An interesting feature of polymerisation with organometallic catalysts is the fact that under certain conditions chain growth can continue until the system is completely depleted of monomer. This type of polymerisation without chain termination can be achieved in the absence of chain-terminating impurities, in solvents of low proton-donating capacity, as a result of the relatively low rate of chain transfer for a number of monomers (in comparison with the rate of chain growth). In such systems the molecular weight of the polymers increases with time, and organometallic compounds of very high and comparatively uniform molecular weight, with the alkali metal as an end group, can be obtained[24,25].

The molecular weight is given by the ratio M/c, where M is the amount in grams of monomer which has been polymerised, and c is the number of moles of catalyst.

If on depletion of one monomer another is introduced, so-called block copolymers can be obtained. This peculiarity of organometallic compounds of forming so-called "live" polymers is known in the polymerisation of several monomers with lithium alkyls[26–28] and also in the polymerisation of unsaturated compounds with organosodium compounds[29].

Paul et al.[30] have shown that metallic sodium gives with aromatic hydrocarbons soluble coloured 1 : 1 complexes consisting of a negatively charged aromatic-hydrocarbon ion and the Na^+ ion. The negatively charged hydrocarbon ion of such compounds acts as an electron carrier.

Szwarc and his collaborators[29,31] investigated the polymerisation of various monomers in the presence of complexes of sodium and naphthalene in tetrahydrofuran. It is suggested that in the presence of unsaturated compounds containing conjugated double bonds an electron passes from the naphthalene to the unsaturated compound with formation of the radical–ion $\cdot CH_2-\bar{C}HR$.

At low temperatures they rapidly dimerise, the radicals

* Methods for synthesising these compounds and their properties are described in several monographs[18–20].

recombining and a growing dianion appearing in the system. If polymerisation is carried out with carefully purified reagents (in the absence of moisture or oxygen), the process continues until all the monomer is used up. It has been shown that the molecular weight of the polymers formed is equal to the amount of monomer divided by half the number of moles of catalyst taken (two molecules of catalyst are used in forming a single molecular chain). A similar molecular-weight relationship was observed by Szwarc and his collaborators in the polymerisation of styrene[24], butadiene, and isoprene[31] by means of a sodium–naphthalene complex in tetrahydrofuran. Block copolymers were obtained by successive introduction of different monomers and exhaustive polymerisation of each component.

The kinetics of polymerisation in the presence of alkali metals have been little investigated.

The first studies of the kinetics of anionic polymerisation were made by Abkin and Medvedev[32] on the gas-phase polymerisation of butadiene by metallic sodium. They concluded that this reaction is a catalytic chain process. The rate of polymerisation of butadiene increased as the sodium dissolved, i.e. as it was converted into an organosodium compound. When the metallic sodium was all used up, the process became stationary, and the reaction velocity depended on diffusion of monomer into the polymer, remaining constant after freezing and unfreezing the system and also on successive evacuation and admission of butadiene; this indicates that the anionic process is predominant under these conditions. According to these authors, the activation energy for the polymerisation of butadiene in the presence of metallic sodium is 12 500 kcal/mole.

Owing to the very high rates of polymerisation of monomers by organosodium and organopotassium compounds in the presence of polar additives (ethers, amines) it is difficult to investigate the kinetics of these processes. Mamontova et al.[33] were able to study the kinetics of the polymerisation of butadiene in ethereal solution with α-cumenylpotassium by carrying out the reaction at low concentrations of butadiene (supplied from the gas phase). The activation energy of this process is 7500 kcal/mole.

Kinetic studies of the polymerisation of α-methylstyrene with a sodium–naphthalene complex in tetrahydrofuran were made by Worsfold and Bywater[34]. This process was relatively slow owing to the low reactivity of α-methylstyrene towards anionic polymerisation. The work was carried out at temperatures below 0°, since at higher temperatures depolymerisation of the polymer occurs on a considerable scale. The authors had previously studied the monomer–polymer equilibrium ($P_i + M \rightleftharpoons P_{i+1}$) in this system at various temperatures, and estimated the heat and entropy changes for this reaction[35]: ΔH = 8 kcal/mole and ΔS = = -26.14 cal/mole deg. They showed that depolymerisation is significant only at temperatures above -50°. At -80° no depolymerisation is observed, and the molecular weight of the polymer is given by the relation $M = M/0.5c$. The reaction velocity at temperatures above -50° is given by the equation

$$-\frac{dM}{dt} = kc(M-M_e),$$

where c is the concentration of the sodium–naphthalene complex, M the concentration of monomer at time t, and M_e is the equilibrium concentration of monomer at the given temperature. From the temperature variation the apparent activation energy was estimated as ~ 2–3 kcal/mole.

Polymerisation in the presence of organolithium compounds is very peculiar and will be discussed in a separate section.

III. SPECIAL FEATURES OF POLYMERISATION IN THE PRESENCE OF METALLIC LITHIUM AND ORGANOLITHIUM COMPOUNDS

An interesting feature of polymerisation brought about by organic compounds of the alkali metals is the dependence of the structure of the polymer chain and hence the properties of the resulting polymers on the nature of the catalyst and the medium used.

Yakubchik[36] and Korotkov[37] and their coworkers showed that in the polymerisation of butadiene the proportion of 1,2-structures increases on replacing alkyllithium by alkylsodium and alkylpotassium catalysts.

Using a lithium alkyl, Piotrovskii[38] and Korotkov[37] found that the proportion of 1,2-structures in polybutadiene increases on passing from hydrocarbon solvents to ether and dioxan. Kropachev et al.[39,40] showed that small additions of oxygen, alcohols, phenol, and dialkyl sulphides have a similar effect on the chain structure in the polymerisation of butadiene by organolithium compounds in hydrocarbon solvents.

Tobolsky and Rogers[41] established that the chain structure of polyisoprene, made with the aid of alkali-metal alkyls and aryls, changes according to the nature of the metal and the solvent, but does not depend on the structure of the radical linked to the alkali metal. Table 1 gives some of their data.

TABLE 1. Dependence of the structure of polyisoprene on conditions of polymerisation.

Catalyst	Solvent	1,2, %	3,4, %	cis-1,4, %	trans-1,4, %
n-Butyllithium	n-heptane	0	7	93	0
Lithium	ditto	0	6	94	0
Phenylsodium	»	8	45	0	47
Benzylpotassium	»	10	38	0	52
Lithium	triethylamine	3	45	0	52
n-Butyllithium	tetrahydrofuran	16	54	0	30
Phenylsodium	ditto	13	49	0	38
Sodium	»	15	51	0	34
Benzylpotassium	»	17	40	0	43

Korotkov and his coworkers[37] discovered that the composition of butadiene–styrene copolymers also depends on the nature of the alkali metal and the medium.

An analogous relation between the composition of copolymers and the conditions of polymerisation was observed by Tobolsky et al.[42,43] in the copolymerisation of isoprene with styrene, and by Spirin et al.[28] in the copolymerisation of styrene with α-methylstyrene and of isoprene with butadiene. Relevant data are given in Table 2.

Welch[26] and Spirin et al.[28] have shown that the rate of polymerisation of styrene in the presence of lithium alkyls at concentrations below 0.02 molar in aromatic solvents is

TABLE 2. Dependence of the composition of copolymers on conditions of polymerisation.

M_1	M_2*	Catalyst	Solvent	Initial composition, mole % of M_1	Composition of copolymer, mole % of M_1
Styrene	butadiene	n-butyllithium	heptane	50	5
ditto	ditto	ditto	heptane + ether	50	40
»	»	n-butylsodium	benzene	50	45
»	isoprene	n-butyllithium	benzene	50	14
»	ditto	ditto	tetrahydrofuran	50	72.4
»	α-methylstyrene	ethyllithium	benzene	16.1	79.6
»	ditto	ditto	triethylamine	16.7	96.45
»	»	triphenylmethyl-sodium	benzene + ether	16.7	94.7
Isoprene	butadiene	ethyllithium	benzene	50	24.8
ditto	ditto	ditto	benzene + triethyl-amine	50	14.4
»	»	triphenylmethyl-sodium	benzene + ether	50	13

* M_1 and M_2 represent the monomers undergoing copolymerisation.

proportional to the concentration of monomer and of catalyst. The molecular weight of the polymers increases with increase in the amount of monomer polymerised ("live" polymers) and is given by the ratio M/c, where M is the quantity of monomer in grams, and c is the number of moles of the catalyst. At concentrations > 0.02 molar, the reaction velocity is independent of the concentration of lithium alkyl, which is explained by association between the catalyst molecules[44,45] at these concentrations.

In the polymerisation of isoprene under similar conditions, Korotkov et al.[46] have shown that the reaction velocity is independent of the concentration of lithium alkyl at considerably lower concentrations of the latter, possibly owing to the formation of more stable association complexes in this system. The formation of "live" polymers of isoprene and butadiene has been observed by Korotkov et al.[27] when these monomers are polymerised by butyllithium. Increase in the molecular weight with the amount polymerised occurs in the methyl methacrylate–butyllithium system at low temperatures[47].

Data on the kinetics of the polymerisation of styrene show that, after a short initial period, the rate of polymerisation is equal to the rate of chain growth[26,28].

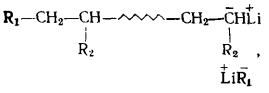
According to Welch[26] and to Spirin et al.[28], the activation energy for chain growth in the polymerisation of styrene by lithium alkyls in a hydrocarbon medium is 17 and 16 kcal/mole, and the frequency factors are 10^{11} and 5×10^{11} litres/mole sec respectively. The rate of polymerisation increases sharply on addition of diethyl ether, tetrahydrofuran, and triethylamine, the greatest effect being exerted by tetrahydrofuran. However, the rate of polymerisation is considerably lower in the presence of lithium alkyls than in the presence of sodium alkyls under the same conditions.

Korotkov[37] and O'Driscoll and Tobolsky[48] concluded from the results that one molecule of ethyllithium is coordinated with two molecules of ether or tetrahydrofuran. On adding ether the reaction velocity increased with increase in its concentration even when a very large excess relative to the catalyst was present[37].

According to Spirin et al.[28], with a triethylamine : catalyst ratio > 20, the rate of polymerisation of styrene is independent of the concentration of the amine. Under these conditions also the molecular weight is given by the ratio M/c, the activation energy and the frequency factor being 13.6 kcal/mole and 6.2×10^{10} litres/mole sec respectively. Comparison of data on the polymerisation of styrene in the presence and absence of triethylamine shows that the increase in the rate caused by its presence is due to a reduction in the activation energy.

α-Methylstyrene has been found to polymerise in the presence of a lithium alkyl[28] as well as with a sodium–naphthalene complex[35]. Owing to the relatively low limiting temperature of polymerisation for this monomer, appreciable yields of polymer can be obtained only by lowering the temperature and increasing the concentration of the monomer[49]. Whereas addition of butadiene diminished the rate of polymerisation of styrene and isoprene in hydrocarbon solvents[37,50], addition of α-methylstyrene to styrene had practically no effect on the reaction velocity[28].

The above facts show that the structure of the polymer chain formed in the separate polymerisation of dienes and in copolymerisation of certain monomers in the presence of a lithium alkyl differs markedly from the structure obtained when organosodium and organopotassium compounds in polar solvents are used. Korotkov and Tobolsky have pointed out that the observed effect is due to the differing polarities of the M–R bond in the organometallic compounds. Mark[51] considers that during polymerisation with organolithium compounds the tip of the growing chain is an ionic quadrupole:



which forms a complex with the monomer and controls the addition of monomer to the growing chain.

Spirin et al.[28] have suggested the following way of regarding the influence of the alkali metal on the structure of the chain. With a typically anionic mechanism (e.g. NaR in an ether) chain growth is determined by reaction of the monomer with a carbanion, and the reactivity of the monomer is determined solely by its electron-acceptor properties. In the series LiR, NaR, KR, the least polar bond is in LiR. These authors suggest that in the presence of LiR reaction of monomer with catalyst is determined both by the electron-donor properties of the R group and by the electron-acceptor properties of the lithium component of the catalyst. The participation of the lithium component in chain growth can occur by the formation of π-complexes with monomers, which polarise the LiR bond. (Because of the relatively feeble electron-acceptor properties of the lithium component of the catalyst[37], only a small proportion of the catalyst is combined as a π-complex with the monomer.) Chain growth then occurs according to the scheme

$$M + LiM_nR \rightarrow M : LiM_nR,$$
$$M{:}LiM_nR \rightarrow LiM_{n+1}R.$$

Spirin et al. also consider it possible that chain growth occurs by a single-stage reaction with simultaneous reaction of a monomer molecule with the lithium and the carbanion component of the catalyst. In this case the transition state is a four-membered ring in the polymerisation of olefins and a six-membered ring in the polymerisation of dienes.

The data of Lyudvig et al.[52] on the kinetics of cationic

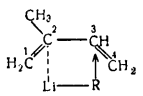
polymerisation show that the ability of monomers to react with electron-acceptors increases with increase in the electron density at the double bond: α-methylstyrene > > isoprene > butadiene > styrene.

Since with an LiR catalyst chain growth is due to reaction of monomer not only with the carbanion but also with the lithium component of the catalyst (an electron-acceptor), the composition of copolymers obtained in the presence of LiR should be different from that produced by a typical carbanion mechanism, in which chain growth is due solely to reaction between monomer and carbanion. This effect is particularly marked when one of the two monomers contains two conjugated double bonds, one of which reacts preferentially with the lithium and the other with the carbanion component of the catalyst.

Spirin et al.[28] point out that to assess the relative reactivities of monomers in a typically anionic polymerisation it is necessary to study copolymerisation brought about by organosodium, organopotassium, or organolithium compounds in the presence of additives with strong electron-donor properties. The above treatment enables the authors to explain the predominance of the *cis*-form in polyisoprene obtained by polymerisation with organolithium compounds in hydrocarbons.

In the polymerisation of isoprene by radical[53] and cationic[53,54] mechanisms a polyisoprene is obtained with a predominantly *trans*-1,4-structure; under conditions typical of an anionic mechanism (NaR + ether)[41] a polyisoprene with a predominantly *trans*-1,4 and *trans*-3,4 form of addition is obtained. It may be assumed that with 1,4-addition, the *trans*-structure corresponds to a lower activation energy than the *cis*-form in all three mechanisms*. This hypothesis is supported by data on the radical polymerisation of isoprene[53], according to which the proportion of the *cis*-structure increases with rise in temperature.

In the presence of LiR the 1,2-double bond of isoprene, which possesses a greater electron density, will react preferentially with the lithium component of the catalyst, and the carbanion component R will react with a fourth carbon atom of the isoprene molecule, so that the spatial arrangement will be most favourable to *cis* addition:



An analogous mechanism for producing polyisoprene with a predominantly *cis*-1,4 mode of addition was suggested by Gaylord and Mark[54] for the polymerisation of isoprene with lithium and organolithium compounds in a hydrocarbon medium. They suggest that in order to obtain *cis*-1,4-polyisoprene the process must be carried out under hetereogeneous conditions.

It is also possible that polymerisation with combined catalysts of the Ziegler–Natta type does not take place by a typically anionic mechanism, but the monomer molecule reacts simultaneously with the two components of the complex catalyst, leading to a selective orientation of the monomers and a stereospecific polymerisation.

* The fact that *trans*-1,4-addition by three different mechanisms evidently has a lower activation energy is probably associated with a greater heat of reaction for this structure, and hence, in conformity with Polanyi's rule[55], a lower activation energy.

IV. POLYMERISATION IN THE PRESENCE OF ALFIN CATALYSTS

While investigating the polymerisation of monomers with alkali-metal alkyls and aryls, Morton et al.[56] found that a combined catalyst consisting of a sodium alkyl, alkoxide, and salt is very active in the polymerisation of butadiene and other unsaturated molecules. Particularly interesting results were obtained with allylsodium associated with sodium isopropoxide and chloride, the so-called "Alfin"* catalyst, which is insoluble in hydrocarbons and is used in the form of dispersions in hydrocarbon media. It was shown that in such systems polymerisation occurs only on the surface of the catalyst, the homogeneous solution being inactive.

Replacement of allylsodium by an Alfin catalyst greatly increased the rate of polymerisation of butadiene (~ 50–60 times) and also the molecular weight of the resulting polymer (from 100 000 to 7 000 000). The number of terminal double bonds was diminished (from 60 to 20%), and a polybutadiene with a predominantly *trans*-1,4 mode of addition was obtained. A similar, but less marked, increase in reaction velocity and molecular weight was observed on passing from sodium alkyls to an Alfin catalyst in the polymerisation of styrene[57]; a smaller effect was observed in the polymerisation of isoprene.

In a later paper Morton and Ward[58] showed that when butadiene is polymerised with pentylsodium additions of triethylamine and caustic soda also cause a sharp increase in the *trans*-1,4 mode of addition (from 23 to 64%).

Williams et al.[59,60] found that the polystyrene resulting from polymerisation of styrene with an Alfin catalyst has a regular structure, and passes into a highly crystalline polymer on heating in various solvents. When the process was carried out with an Alfin catalyst in polar solvents — diethyl ether, dioxan, pyridine — the rate of polymerisation was increased, and an amorphous polystyrene of irregular structure was obtained. The catalyst was inactivated by prolonged contact with ether. These workers suppose that the change in the structure of polystyrene and the increase in activity of the catalyst in the presence of polar solvents are due to the formation of complexes between solvent molecules and sodium ions at the surface of the catalyst, which accelerate polymerisation and prevent the selective orientation of the monomer.

At the present time very few quantitative data are available on the mechanism of polymerisation in the presence of Alfin catalysts.

Morton[61] suggests that polymerisation in the presence of Alfin catalysts occurs by adsorption of the reactants on an ionic aggregate with coordination and activation of the monomer molecule at the surface, followed by its reaction with an anion located on the surface. Study of the influence of the physical parameters of the components which affect the surface properties of the catalyst showed[62] that the nature of the alkali metal and the anion of the inorganic salt have a substantial effect on the activity of the catalyst. Among inorganic alkali-metal salts those are active in which the sum of the ionic radii d is greater than 2.75 Å.

* The name "Alfin" arose in the early stages of the investigation when it was supposed that only two components — a sodium alkoxide and an olefin — were required to produce this catalyst. Further work showed that a third component — an inorganic salt — is necessary.

Thus NaCl (d = 2.81 Å) can be replaced by KCl (3.14 Å), but its replacement by LiCl (2.57 Å) markedly diminishes the activity of the catalyst. When lithium chloride is replaced by lithium iodide (3.02 Å), the catalyst exhibits considerable activity.

Much is still obscure in the mode of action of Alfin catalysts. However, the nature of the catalyst and the observed behaviour support an anionic mechanism of polymerisation in these systems.

Korotkov[37] investigated the copolymerisation of several pairs of monomers by Alfin catalysts and showed that the composition of the resulting copolymers was close to that characteristic of anionic polymerisation. The observed activity series of the monomers in individual Alfin polymerisations — butadiene > styrene > isoprene — is the same as that for the reactivity of these monomers in copolymerisation with Alfin[37] and anionic catalysts (see Part VII). The specific features of Alfin polymerisation, as compared with polymerisation by alkali-metal alkyls and aryls in hydrocarbon solvents, can be explained by the following factors: (1) the presence of polar additives (sodium isopropoxide, sodium chloride), which polarise the Na–R bond and thus sharply accelerate polymerisation, and (2) the insolubility of the associated ionic aggregate of the catalyst in the hydrocarbon solvent, which governs the selective orientation of monomer at the catalyst surface.

As pointed out above (Part II), very high polymerisation rates were also observed in the presence of sodium alkyls with polar additives.

The high molecular weights of Alfin polymers is evidently connected with the characteristic ability of anionic polymers to form "live" polymers (see Part II); in conjunction with the high reaction rates produced by polar additives and the small number of active centres (only surface complexes are effective), this may be the reason why products of very high molecular weight are formed after a short period of polymerisation.

V. SIMULTANEOUS ANIONIC AND RADICAL POLYMERISATION IN THE PRESENCE OF ALKALI METALS

Several investigations have shown that formation of a radical-ion by reaction of an alkali metal with an unsaturated molecule does not always lead solely to anionic polymerisation. In a number of cases the competing radical polymerisation predominates, and sometimes the two processes occur simultaneously.

Overberger et al.[63] found the rate of polymerisation of methacrylonitrile in liquid ammonia to be considerably greater with lithium than with lithium amide, and the laws governing the process were also different. Thus, for example, with lithium amide the molecular weight was independent of the catalyst concentration, whereas with lithium itself the molecular weight fell with increasing concentration of catalyst. These workers assume that lithium reacts with the monomer to form a radical-ion:

$$Li + CH_2{=}CHR \rightarrow \cdot CH_2{-}\bar{C}HR\overset{+}{L}i.$$

Comparison of the rates of polymerisation in the two systems, containing lithium and its amide, lead to the conclusion that radical polymerisation predominates in the reaction of lithium with methacrylonitrile in liquid ammonia. The dependence of the molecular weight on the catalyst concentration also suggests a radical mechanism in this system. O'Driscoll et al.[64,65], from the composition and properties of styrene–methyl methacrylate copolymers formed in the presence of metallic lithium, also concluded that two competing processes, radical and anionic, are occurring. At lower temperatures the anionic polymerisation predominates; this is explained by a sharper change in the velocity of radical polymerisation with temperature.

In the polymerisation of isoprene in a hydrocarbon medium with a dispersion of lithium anionic polymerisation, by the organolithium compounds formed, evidently occurs preferentially and the proportion of radical polymerisation is small, since under these conditions the polyisoprene obtained has a predominantly *cis*-1,4-structure (96%)[66] (see Part III).

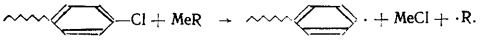
Hirota et al.[67] used a paramagnetic-resonance method to detect the presence of radicals during the polymerisation of styrene in the presence of metallic sodium. They consider that a radical-ion,

$$\cdot CH_2{-}\underset{\displaystyle R}{\bar{C}H}{-}\overset{+}{N}a$$

is formed, and that both radical and anionic polymerisation occur.

On passing to polar solvents, or in the presence of monomers containing polar groups, only anionic polymerisation is observed with metallic sodium. Thus, for example, copolymers of styrene and methyl methacrylate obtained with metallic sodium and with triphenylmethylsodium have the same composition[68].

Spirin et al.[23], studying the copolymerisation of styrene with *p*-chlorostyrene in the presence of various organometallic compounds, also observed the presence of two competing reactions, anionic and radical polymerisation. Radicals were formed in this system by the interaction of the organometallic compound with the *p*-chlorostyrene by a Wurtz type of reaction:



Either radical or anionic polymerisation predominated depending on the experimental conditions. The former predominated in the presence of ethyllithium in a hydrocarbon medium, and the latter with organolithium and organosodium compounds in the presence of triethylamine.

The kinetics of polymerisation of styrene with ethyllithium show that after a short initial period all the ethyllithium molecules have been transformed into organometallic compounds of lithium with polystyrene, which form the active centres of growth. In the absence of chain-terminating impurities, these compounds become "live" polymers. When *p*-chlorostyrene is present, it reacts with the lithium compound to produce chain termination and formation of free radicals. Owing to the relatively low reactivity of the chlorine atom in the benzene ring, this reaction is slow. The number of radicals formed in the system from the start of the reaction until the catalyst has been completely decomposed is double the original number of active centres, i.e. of carbanions formed from the ethyllithium.

Data relating to the rates of chain growth in the polymerisation of styrene by a radical mechanism and with an ethyllithium catalyst at 30° are given in Table 3. They show that the rate of chain propagation is greater for the radical polymerisation of styrene than for its polymerisation with ethyllithium even in an amine medium.

TABLE 3. Velocity constants for chain growth in the polymerisation of styrene by a radical mechanism and with an ethyllithium catalyst.

Catalyst	Solvent	Rate, moles litres^{-1} sec^{-1}	Reference
Benzoyl peroxide	—	53	69
Ethyllithium	toluene	0.131	28
ditto	toluene + triethylamine	8.5	28

Data on copolymerisation show that the rates of chain growth in the radical polymerisation of styrene and of *p*-chlorostyrene are similar[70]; when polymerisation is carried out with the aid of ethyllithium in an amine medium the relative reactivity of *p*-chlorostyrene is six times as great as that of styrene itself[23]. Combination of these results with the data in Table 3 shows that rates of chain growth for *p*-chlorostyrene are similar for radical polymerisation and in the presence of ethyllithium together with an amine. Nevertheless, anionic polymerisation predominated in the copolymerisation of *p*-chlorostyrene with styrene in the presence of ethyllithium and an amine, obviously because of the considerably longer life of an anionic active centre compared with a radical one. In polymerisation with ethyllithium in a hydrocarbon medium, radical polymerisation predominated in spite of the shorter life of a radical active centre, since under these conditions the rate of chain growth by an anionic mechanism is 400 times lower than by a radical mechanism.

VI. PREPARATION OF POLYMERS OF REGULAR STRUCTURE BY ANIONIC POLYMERISATION

During recent years there has been a considerable expansion of work on the synthesis of polymers of regular structure, the so-called isotactic and syndiotactic polymers. Crystalline polymers, corresponding to polymer chains of isotactic and syndiotactic structures, usually differ markedly in physical and mechanical properties from the corresponding atactic amorphous polymers.

With polymers of the diene series, the presence of a double bond in each structural unit makes possible, in addition to these types of polymers of regular structure, the existence of *cis*- and *trans*-isomers with the 1,4-structure, produced by different arrangements of the first and fourth carbon atoms of the monomer unit relative to the double bond.

In the development of work on the preparation of stereoregular polymers with combined Ziegler–Natta catalysts the insolubility of the catalyst in the hydrocarbon solvents generally employed has led to the quite widely held view that stereospecific polymerisation can occur only in the presence of an orienting surface in heterogeneous systems. Several investigators have shown, however, that isotactic and syndiotactic polymers can also be obtained under homogeneous conditions and not only by ionic but also by radical polymerisation[71].

In 1944 Huggins[72] noted that in the homogeneous polymerisation of vinyl monomers different types of addition of the monomers may be expected in chain-growth reactions, distinguished by the distribution of the substituents H and R relative to the plane of the C–C bonds in the main chain; by varying the conditions of polymerisation it is possible to achieve the predominance of one of the possible arrangements.

Fox et al.[71] and also Colleman[73] made a statistical analysis of the conditions leading to the formation of polymers of one structure or the other. Their basic idea was that any polymer could be regarded as a copolymer consisting of isotactic and syndiotactic groups and that the two types of addition might have different energies and entropies of activation. From the statistical analysis they obtained an expression for the probability of an isotactic or a syndiotactic chain structure as a function of the differences in energies and entropies of activation. Knowing the magnitudes of these differences, it was possible to estimate in what temperature range one or other structure would predominate.

Thus both this general discussion and direct experimental results indicate that stereoregular polymers can be obtained not only under heterogeneous but also under homogeneous conditions.

With anionic polymerisation, polymers of regular structure have been obtained both in heterogeneous systems and in a homogeneous medium. As already mentioned, lithium alkyls in a hydrocarbon solvent give a polyisoprene mainly with a *cis*-1,4 mode of addition. Isotactic and syndiotactic poly(methyl methacrylate) and isotactic polystyrene have also been obtained by anionic polymerisation. Fox et al.[74] have shown that isotactic poly(methyl methacrylate) is formed by homogeneous polymerisation of methyl methacrylate with organic compounds of lithium in toluene at low temperatures, owing to the orienting influence of the lithium component of the catalyst on chain propagation. Isotactic poly(isopropyl and cyclohexyl acrylates) have been obtained under similar conditions[75]. In the presence of the polar solvent 1,2-dimethoxyethane syndiotactic poly(methyl methacrylate) is formed. The structure of this polymer was established by Stroupe and Hughes[76].

Miller et al. obtained a highly crystalline poly(t-butyl acrylate) by polymerisation with a dispersion of lithium[77], and a crystalline poly(methyl methacrylate) by carrying out polymerisation in the presence of a Grignard reagent[78]. By varying the conditions of polymerisation they also obtained isotactic and syndiotactic poly(methyl methacrylate). Crystalline polystyrene was obtained with organopotassium[79] and organosodium[80] compounds in hexane, and also with an Alfin catalyst[59,60], i.e. in systems containing the catalyst in suspension.

Polymers of regular structure have thus been obtained by anionic polymerisation under homogeneous conditions only in the presence of organolithium compounds, as a result of the orienting influence of the lithium component, which takes part, together with the carbanion component of the catalyst, in the chain growth process*.

VII. ANIONIC COPOLYMERISATION

Copolymerisation is widely used for the synthesis of polymers with valuable properties. Apart from the

* These polymers are formed only from those monomers which contain at least two functional groups, one of which reacts with the lithium and the other with the carbanion component of the catalyst, resulting in the selective orientation of the monomer unit.

TABLE 4. Composition of styrene—methyl methacrylate copolymers obtained by different mechanisms of polymerisation. (Initial molar ratio 1 : 1).

Catalyst	Composition of copolymer, mole % of styrene	Mechanism of polymerisation
BF_3 etherate	99	cationic
Benzoyl peroxide	51	radical
Triphenylmethylsodium	~1	anionic

TABLE 5. Copolymerisation constants for different pairs of monomers in the presence of alkali metals and their compounds as catalysts.

Monomers		Catalyst	Solvent	r_1	r_2**	Reference
M_1	M_2*					
Isoprene	butadiene	butyllithium	hexane	0.47	3.38	50
»	diisopropenyl	»	»	17	0.06	85
»	piperylene	»	»	17	0.06	85
»	»	»	hexane + ether	5	—	85
Methyl methacrylate	styrene	sodium	liquid ammonia	6.4	0.12	86
ditto	methacrylonitrile	sodamide	ditto	0.61	5.2	87
»	acrylonitrile	»	»	0.25	7.9	88
»	methyl acrylate	»	»	0.1	4.5	88
»	vinyl acetate	»	»	3.2	0.4	88
Acrylonitrile	butyl vinyl sulphone	»	»	1.1	0.2	89
p-Chlorostyrene	styrene	ethyllithium	benzene + triethylamine	6.5	0.1	23

* M_1 and M_2 represent the monomers undergoing copolymerisation.

** r_1 and r_2 are copolymerisation constants.

practical value of this method, it is a useful source of information about the relative reactivities of monomers and hence the nature of the active centres, which is particularly important in the application of new catalysts.

The composition of several copolymers differs markedly according as the process occurs by a cationic, an anionic, or a radical mechanism. Among these must be mentioned the styrene–methyl methacrylate system, which is frequently employed by investigators to determine the mechanism of polymerisation. The compositions of copolymers of this system for radical, cationic, and anionic polymerisation are given in Table 4 [68,81].

In an investigation of some new catalysts — cadmium alkyls [82], boron alkyls [83], and $CaZn(C_2H_5)_4$ [84] — the composition of the products showed that a radical mechanism was operative with the first two catalysts, and that anionic polymerisation took place with the third.

Copolymerisation constants for several pairs of monomers in the presence of alkaline catalysts are given in Table 5.

The copolymerisation constants obtained for the isoprene–butadiene, isoprene–diisopropenyl, and isoprene–piperylene systems with a butyllithium catalyst in a hydrocarbon medium do not indicate the relative reactivities of these monomers when undergoing polymerisation by a carbanion mechanism (see Part III). If ether [85] or triethylamine [28] is added, i.e. with carbanion polymerisation, the content of butadiene and piperylene in the copolymer is greater than in that obtained with organolithium compounds in a hydrocarbon medium [28,50,85].

All the remaining systems in Table 5 were studied in polar solvents, and the corresponding copolymerisation constants are a measure of the relative reactivities of the monomers in carbanion polymerisation.

From the data in Table 5 and Part III the monomers can be arranged in the following order of relative reactivity: acrylonitrile > butyl vinyl sulphone > methyl acrylate > > methacrylonitrile > methyl methacrylate, *p*-chlorostyrene > vinyl acetate > butadiene > styrene > isoprene > α-methylstyrene.

As already mentioned, an interesting feature of anionic polymerisation is that in several cases the rate of polymerisation is equal to the rate of chain growth. For these systems the rate constants for chain growth can be obtained directly from kinetic data. Combination of these data with the copolymerisation constants for these monomers with another monomer, the same in all cases, enables us to estimate in the usual way [90] the relative reactivities of carbanions of different structure towards the given monomer.

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With regard to anionic polymerisation, little quantitative information is yet available on how the reactivity of catalysts, monomers, and the corresponding carbanions depends on their structures, or on how the conditions of polymerisation affect the structure and properties of the polymers formed.

The quantitative study of these systems is difficult since conditions of great purity are necessary — traces of oxygen, moisture, sulphur compounds, or other impurities which react with the catalyst and the carbanion, must be absent.

Furthermore, the rate of polymerisation in anionic systems is often so great (e.g. the polymerisation of styrene with a sodium–naphthalene complex in tetrahydrofuran) that accurate kinetic measurements are impossible by the dilatometric method, which is widely used to measure rates of polymerisation. Other methods are required to determine the velocity constants for chain propagation in such systems.

The development of this work should lead to wider and more quantitative information about the mechanism of these very unusual and practically valuable processes.

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CATALYTIC HYDROGENATION OF PHENOLS

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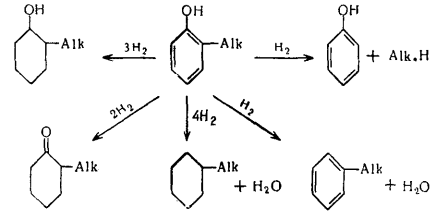
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INTRODUCTION

The primary tar obtained on processing a solid fuel contains a considerable quantity of phenols. Phenol itself and, to some extent, the cresols, are widely employed in industry for the preparation of plastics, synthetic fibres, dyes, chemical insecticides, anti-oxidants, tanning agents, varnish resins, etc. However, xylenols and other higher phenols have so far been insufficiently utilised. Any widespread use of these phenols is prevented by the absence of satisfactory methods for isolating them from the primary tar and for separating them. For this reason, besides the investigation of ways of effectively utilising individual phenols, efforts have been directed towards finding a method of converting the separate fractions of the primary tar into chemical products of value to the economy without isolating the individual components. A hydrogenation treatment is of great importance for exploiting phenols in this way, as it allows either phenol and cresols or hydrocarbons to be obtained from the higher phenols. Hydrogenation has now achieved wide application not only in laboratory practice but also in industry. The hydrogenation of coal, the reductive cracking of petroleum products, and also the refining and stabilisation of crude fuel have been extensively developed.

The hydrogenation of phenols can produce several types of changes: (1) hydrogenation of the benzene ring with retention of the hydroxyl group; (2) hydrogenation to hydroaromatic ketones; (3) conversion of phenols into aromatic and alicyclic hydrocarbons; and (4) reductive dealkylation of higher phenols with the formation of lower phenols:



In a review of published results it is convenient to separate these types of reactions. A description of earlier work on the changes undergone by phenols on hydrogenation has been given by Sabatier[1], Ellis[2], as well as in papers by Tishchenko and Belopol'skii[3], Petrick[4], Moldavskii and Lifshits[5,6] and Rapoport[7], and in the monograph by Lozovoi and D'yakova[8].

The literature on the hydrogenation of phenols is quite extensive. The majority of papers, however, are concerned with the hydrogenation of phenol itself, cresols, and to some extent xylenols. The behaviour of the higher phenols under conditions of hydrogenation has been quite inadequately studied. Investigation of the catalytic changes undergone by the higher fractions of the primary tar, both under conditions of hydrogenation and during processes of alkylation and dealkylation, is necessary for the successful solution of the problem of the effective utilisation of primary tars. It is therefore useful to investigate catalytic changes which occur on hydrogenation, both of the individual phenols in the higher fractions of the primary tars, and of narrow fractions in which one or other component has been concentrated. These fractions can be isolated by fractionation and chromatography. Up to the present, unfortunately, too little attention has been paid to these methods.

I. HYDROGENATION OF PHENOLS TO HYDROAROMATIC ALCOHOLS

The hydrogenation of phenol was first accomplished by Sabatier and Senderens in 1903 by passing phenol vapour together with excess hydrogen over reduced nickel at 215°–230°.[1] The main product was cyclohexanol mixed with cyclohexanone and small quantities of cyclohexene, cyclohexane, and benzene. At highter temperatures (250°–