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Active Centres in the Polymerisation of Hydrocarbon Monomers by Anionic Coordination

S.S.Medvedev

Several aspects are discussed of the nature and character of the active centres in the polymerisation of diene hydrocarbons (mainly butadiene) initiated by organic compounds of alkali metals or by cobalt and nickel complexes. Such polymerisations occur by a complicated mechanism of anionic coordination, characterised by the presence of active centres in the form of polarised bonds between carbon and metal atoms (the alkali metals and the transition metals in the complexes). The coordinating and anionic functions of the active centres, their combination, and mututal transitions are discussed for the polymerisation of butadiene and other hydrocarbon monomers in the presence of organic compounds of alkali metals.
The Section on polymerisation initiated by complex cobalt catalysts reports research on the role of small amounts of water in the formation and breakdown of the initial active centres. The last Section examines the formation of active centres from complexes of the π-allylnickel halide type and the mechanism of their participation in the polymerisation of butadiene

CONTENTS

I. Introduction 834
II. Nature of active centres in polymerisation in the presence of organic compounds of alkali metals 834
III. Active centres in the polymerisation of butadiene in the presence of complex catalysts based on cobalt and nickel 838

I. INTRODUCTION

Great attention has recently been paid to problems of polymerisation by ionic coordination, because of the wide possibilities it offers for the directed control of the composition and the structure of the polymer chains. However, the study of these processes—especially those which occur in the presence of complex catalysts containing transition metals in various states and combinations—encounters considerable theoretical and experimental difficulties.

An approach which will bring us closer to an understanding of several fundamental aspects of these systems, in particular problems associated with the nature of the active centres of chain propagation, may be to investigate polymerisation in the presence of alkali metals and their organic compounds. These processes represent simpler systems, but cover a wide range of phenomena, while allowing the structure of the active centres to be varied in a known manner, and thereby enabling various types of configuration and relative arrangement of the monomeric units to be realised in the growing polymer chains. In this sense they can serve as simplified models for the discussion of more complicated catalytic polymerisation systems.

Polymerisation in the presence of an alkali metal (sodium) was first used in 1932 in the Soviet Union to obtain synthetic butadiene rubber on the industrial scale by S. V. Lebedev's method.

In 1936 the first kinetic investigation, which used a vacuum technique, was published[1] on the vapour-phase polymerisation of butadiene on thin films of metallic sodium deposited on the walls of the reaction vessel. This work established that polymerisation takes place in a layer of butadiene which deposits on the walls of the vessel (Fig. 1).

The induction period is due to the presence of unchanged metallic sodium (initiation reaction). After the metallic mirror has disappeared, the process occurs at a constant rate. Prolonged interruption of the process (by pumping off the butadiene) with subsequent introduction of butadiene to the appropriate pressure did not affect the rate of polymerisation.

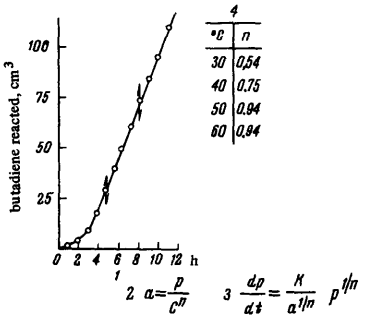


Figure 1. Gas-phase polymerisation of butadiene on metallic sodium mirrors:
1) dependence of conversion of butadiene on time at constant pressure p (the arrows denote interruptions); *2*) a = partition coefficient of butadiene between gas and polymer phases; *3*) rate of polymerisation at constant volume; *4*) dependence of coefficient n on temperature*.

* Curves *2* and *3* have apparently been overlooked (Ed. of Translation).

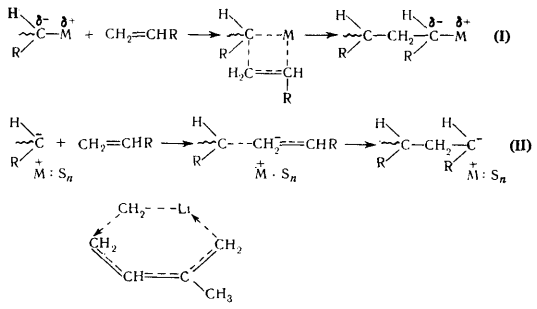
These experiments revealed a novel type of active centre for the growth of polymerisation chains, distinguished by the absence of chain termination and by thermodynamic stability. It was assumed that chain growth took place by incorporation of the monomer in the carbon–sodium bond. These phenomena were subsequently interpreted in terms of "chain catalysis" [2]. In present-day terminology—which is admittedly not perfect—these centres, the first to be discovered, can be termed "live" active centres.

II. NATURE OF ACTIVE CENTRES IN POLYMERISATION IN THE PRESENCE OF ORGANIC COMPOUNDS OF ALKALI METALS

As was mentioned above, the scientific interest and practical value of these processes are due to the presence of a definite relation between the nature of the initiator

(catalyst) and the structure of the active centres for chain growth, which in turn determine the composition, structure, and dimensions of the polymer chains, and to considerable extent the properties of the resulting polymers.

Many research papers have appeared[1-40] on these processes, and the results together with other published data enable the characteristics of the reactions of chain growth to be established. These characteristics can be represented by the scheme



where M is an alkali metal. Two types of active centres for chain growth are shown, differing in the nature of the C–M bond, which determines the rate of the elementary acts of growth and coordination of monomer units in the growing chains.

In the first type the active centres consist of polarised C–M bonds, in which covalent (exchange) forces play an important part. The transition state in reactions of chain growth may be supposed in this case to be a four- or six-membered ring (for vinyl or diene monomers respectively). The metal atom is directly involved in the growth reactions. The two-centre character of the active group determines the system of coordination of a monomer unit in the growing chain. For this reason we shall term this type of process the *coordination mechanism* of the growth of polymer chains.

The second type of active centre is characteristic of chain-growth reactions occurring by an *anionic mechanism*. Increasing polarisation of the C–M bond results in charge separation, depending on the nature of the alkali metal and the properties of the medium: only a certain Coulombic interaction is preserved between the carbanion and the counter ion, an *ion-pair* being formed. In this case the transition state of the growth reactions has a linear structure (one-centre type of active group), and the coordinating effect of the counter ion is small. With further weakening of electrostatic interaction between the ion and the counter ion under the influence of solvation of the latter by strong electron-donor solvents, *free carbanions* are produced. Processes occurring on ion-pairs with complete separation of charges and on free ions may be supposed to involve transition states of analogous structure. The difference is probably that with ion-pairs the growth reactions had to be inhibited by the fact that the solvated counter ion must move along the growing chain.

Actual polymerisation processes initiated by alkali metals and their organic compounds combine in most cases features of both mechanisms, and are processes of *anionic–coordination polymerisation*.

The term "mechanism" may lead to a wrong idea of the essential nature of these processes. It must not be thought that two different types of centres are involved, one of which is responsible for the occurrence of the process by an anionic mechanism, while the other causes polymerisation by a coordination mechanism. The essential point is that the same active centre possesses both anionic and coordinating functions at the same time, but they are combined to different extents depending on the nature of the metal, the properties of the medium, and the temperature. In the limit the predominance of one function or the other may result in either an anionic or a coordination mechanism.

A characteristic feature of processes of anionic–coordination polymerisation is the presence of a reactive C–M bond in the growing chains, the state of this bond—primarily its degree of polarisation—determining the possible relative importance of anionic and coordination mechanisms, the overall rate of the process, and the composition and structure of the polymer chains. Decrease in the degree of polarisation of the C–M bond is accompanied by an increase in the coordinating power of the alkali metals in the active centres. With a given monomer in the absence of electron-donor compounds, this increase in the coordinating factor varies in parallel with the ionisation potentials of the alkali metals:

$$\begin{array}{ccccc} K & < Na & < Li \\ 4.32 & 5.09 & 5.37 \end{array}.$$

Another important characteristic of metals in active centres, affecting the degree of polarisation of the C–M bond, is the presence of vacant orbitals in the metal atoms, as also the ionic radii determining their electron-acceptor properties. The lower the vacant orbitals and the smaller the ionic radii, the stronger is the solvation (or complex formation) of the metal atoms by electron-donor solvents

$$\sim CH_2\overset{R}{\underset{|}{C}}H-\overset{\delta+}{M} + nS \rightarrow \sim CH_2\overset{R}{\underset{|}{C}}H-\overset{\delta_1+}{M}:S_n$$

where $\delta_1 > \delta$ and S is an electron donor. Solvation tends to increase the polarity of the C–M bond and also the proportion of the anionic process. The coordinating power of metals in active centres falls in the same sequence as the atomic radius of the metals decreases:

$$\begin{array}{ccccc} Li & > Na & > K \\ 0.6 & 0.95 & 1.33 \end{array}.$$

The simultaneous development of anionic and coordination mechanisms can be conveniently examined with the anionic–coordination polymerisation of butadiene as example, this leading to the formation of polymer chains containing monomer units differing in structure (1,2, *cis*-1,4, and *trans*-1,4). Table 1 shows that, in hydrocarbon solvents, where solvation of the counter ion† by the monomer is negligible, the coordinating power of the counter ion is most clearly apparent in lithium active centres, the preferential formation of 1,4-polybutadiene. With sodium and potassium centres the extent of participation of the coordinating factor in chain growth diminishes in the sequence K < Na < Li, this being accompanied not only by formation of 1,2-structures but also by decrease in the relative content of *cis*-1,4-structures in the polybutadiene chains. The relative content of *trans*-1,4-structures remains almost constant.

The introduction of an electron-donor compound, which causes solvation of the counter ion, increases the importance of the anionic process (formation of 1,2-structures). These effects are especially marked in the presence of lithium centres, are weaker with sodium centres, and are weak in the presence of potassium centres, in conformity with the solvation sequence Li > Na > K, as is evident

† For simplicity we shall henceforth term C in the C–M bond the anion, and M the counter ion, independently of the mechanism of the process.

from Table 1, which gives experimental results for the addition of triethylamine (TEA, a weak electron donor) and tetrahydrofuran (THF, a strong electron donor). Lowering the temperature, by favouring solvation of the counter ion, increases the role of the anionic factor. In pure tetrahydrofuran, owing to the breakdown of covalent (exchange) interaction between the carbanion and the counter ion, chain growth takes place on *ion-pairs*. Differences associated with the nature of the alkali metals are then smoothed out, and the mechanism of the process becomes predominantly anionic (preponderant formation of 1,2-structures).

Table 1. Effect of conditions of polymerisation on structure of polybutadiene[18].

Metal in bond	Medium	Addition		Temp., °C	Structure of polybutadiene, %		
		cpd.	%		1,2	*cis*-1,4	*trans*-1,4
Li	heptane	—	—	30	6.8	42.8	50.4
Li	toluene	—	—	30	8.7	43.7	47.6
Na	benzene	—	—	25	32.3	22.6	45.0
Na	toluene	—	—	25	31.5	23.1	44.8
K	benzene	—	—	25	35	16.5	48.5
K	benzene–heptane (5:1)	—	—	0	38.1	12.8	49
Li	benzene	TEA	10	25	37.1	22.8	40
Na	benzene	TEA	10	25	43.3	17.3	39.4
K	benzene	TEA	10	25	37.4	16.6	46.0
Li	benzene	THF	1	25	73.6	13.3	13.1
Na	benzene	THF	1	25	44.3	12.8	42.8
Li	heptane	THF	6	—50	91.5	4.1	4.4
Na	cumene	THF	6	—50	88	—	12
K	heptane	THF	6	—50	61.6	5.1	33.3
K	cumene	THF	6	—50	58.8	5.8	35.4
K	cumene	THF	15.5	—50	61.7	5	33.3
Na	THF	—	—	—50	88	—	12
Na	THF	—	—	—90	92.8	—	7.2
K	THF	—	—	—50	84.7	—	15.3
Li	THF	—	—	—50	91	—	9

Similar results on the nature of the active centres and on the combination of anionic and coordination factors depending on the nature of the alkali metals and the properties of the medium have been obtained, in conformity with the ideas developed, in investigations of the composition of copolymers[14,15] and of chain-transfer reactions[14,29].

Examination of rates of growth in the anionic–coordination polymerisation of isoprene, butadiene, and styrene has established that these processes take place by a mechanism of "live" chains. Yet it was found that the rate of the process does not depend on the first power of the initiator concentration, as should have been the case with "live" chains, but is given by the equation

$$v = k_p[M][C]^{1/n} \qquad (1)$$

where [C] is the initiator concentration and $n > 1$ is a constant. The explanation given for these deviations was that in non-polar media the growing chains, with a polar group at the end, form stable association complexes, and these break down into non-associated growing chains in conformity with the equilibrium

$$(M-P)_n \rightleftarrows (M-P)_{n-1}M-P \qquad (2)$$

where P is the polymer chain.

The presence of association complexes in the reaction system has been confirmed by viscosimetric and spectrophotometric methods[25]. The complexes can be supposed to have either a layer or a coiled structure.

Only isolated, non-associated growing chains are active in acts of chain growth. The constant n in Eqn. (1) is a measure of the degree of association, and varies with the nature of the polymer, having values 2 for polystyrene, 3–4 for polyisoprene, and 5–6 for polybutadiene[17].

It was not possible to estimate the equilibrium constants (2) in the case of lithium centres. This constitutes the main obstacle to determining the individual growth rate constants in coordination polymerisations occurring in hydrocarbon media under the influence of alkali-metal compounds.

Several difficulties in determining chain-growth constants arise also from the isomerisation of active centres into centres of diminished activity, discovered spectrophotometrically[41,25]. However, these difficulties are eliminated by conducting the polymerisation at low temperatures (at or below −50°C).

On the introduction of electron-donor additives—tetrahydrofuran, triethylamine, etc.—into hydrocarbon media, the association complexes break down owing to solvation of the counter ions of growing chains in the complexes. Individual growing chains are then formed, with different degrees of solvation of the counter ions in the active centres depending on the electron-donor properties of the medium. The coordinating power of the C–M bond in chain-growth reactions depends substantially on the degree of solvation of the counter ions by the electron-donor compounds. These factors explain the lack of correlation between the rate of polymerisation on potassium active centres and the microstructure of the resulting polybutadienes[37].

Table 2. Effect of additions of tetrahydrofuran on the rate of chain growth in the polymerisation of butadiene and on the structure of the resulting polymers ($[M]_0 = 1$ M; initiator concentration. [KR] = 0.003 M; temperature −50°C).

Solvent	THF, total %	Rate of chain growth $10^3 v$, $M\,s^{-1}$	1,2-Structure, %
Cumene	—	0.0012	56
Cumene	2.7	0.012	56
Cumene	4.7	0.018	58
Cumene	20.0	0.21	64
Cumene	44.0	2.4	66
THF	—	15.6	85

Table 2 shows that the sharp changes in rate of polymerisation caused by the addition of an electron donor to the hydrocarbon medium are accompanied by slight changes in the microstructure of the resulting polymers. In view of the fact that potassium active centres form less stable association complexes and possess diminished electron-acceptor power (compared with lithium and sodium centres), this can be explained by the tendency of added tetrahydrofuran to favour formation from the association complexes of individual, non-associated growing chains, the number of which increases and causes an increase in the rate of polymerisation. However, the degree of solvation of the active centres, which affects their coordinating power, is small, and remains more or less constant as long as association complexes are present in the system. It is significant that, when the degree of solvation of the counter ions is small, covalent (exchange) forces are involved as well as electrostatic forces in the C–M bonds, and to some extent determine the proportion of the coordination mechanism in the chain-growth reactions. It is seen from Table 2 that, even in media containing 44% of tetrahydrofuran, ~ 34% of 1,4-structures are present in the polymer chains. In pure tetrahydrofuran, solvation of the

counter ion increases, covalent interaction in the C–M bonds contracts (screening of the counter ion by the solvate sheath), and the chain-growth reactions take place by an anionic mechanism.

1. Spectrophotometric Investigation of Active Centres for Chain Growth

The first spectrophotometric investigations of the C–M bond in lithium, sodium, and potassium active centres for polyisoprene, polybutadiene, and polystyrene showed that the position of the absorption band maximum λ_{max} is independent of the nature of the metal or the properties of the medium[42]. However, such dependence of the spectra has been detected in the corresponding triphenylmethyl, fluorenyl, indenyl, and 1,1-diphenylbutyl organometallic compounds (λ_{max} shifts to longer wavelengths with increase in polarity of the C–M bond)[25]. Detailed examination of the phenomena led to the conclusion that the spectra found for the first group of compounds ("live" chains of polyisoprene, polybutadiene, and polystyrene) relate not to individual growing chains but to their association complexes, which are characterised by great stability and are present in great quantity. The presence of bulky substituents in the second group of compounds and the consequent steric hindrance prevent the formation of stable association complexes, which readily break down even under relatively slight action by electron donors. Discrete transitions of active centres (the C–M bond) from one form to another depending on the nature of the medium are illustrated by the spectral pattern of 1,1-diphenylbutyl-lithium systems (Table 3).

Table 3. Ultraviolet spectra of 1,1-diphenylbutyl-lithium systems[25].

Solvent	λ_{max}, nm	Temp., °C
Hexane	410	25
Triethylamine	437	25
Hexane + 0.3% THF	440	25
Hexane + 0.3% THF	490	−80
THF	490	25

A sharp change in λ_{max} is observed on passing from hexane (unsolvated counter ions) to triethylamine or to a 0.3% solution of tetrahydrofuran (degree of solvation of counter ions small). A second transition, to completely solvated counter ions, occurs in solutions of pure tetrahydrofuran or when the temperature is lowered to −80°C, which favours solvation.

It has since been shown, by spectrophotometric combined with kinetic methods[30,17], that the degree of association and the stability of the association complexes of lithium active centres in hydrocarbon media depends on the carbanion component in the C–M bond, increasing in the sequence—1,1-diphenylethylene < α-methylstyrene < styrene < isoprene < butadiene.

It has also been established by conductometric methods that, in the polymerisation of α-methylstyrene in electron-donor solvents, the presence of steric hindrance in poly-α-methylstyrene, impeding the formation of association complexes in hydrocarbon media, promotes the dissociation of ion-pairs into free ions[40].

To elucidate the nature of the C–M bond in non-associated growing chains, spectrophotometric investigations have been made under conditions of the maximum concentration predominance of these forms, i.e. at concentrations below 10^{-5} M.[17,42,43]

Development of a special technique for spectrophotometric measurements at high dilutions with live lithium–polystyrene chains as example has shown that change in the concentration of lithium centres in toluene solution from 10^{-3} M to $\ll 10^{-5}$ M is accompanied by a shift in the absorption band maximum λ_{max} of 18 nm to shorter wavelengths. This band corresponds to non-associated and non-solvated active centres of growing chains[30].

The spectrophotometric research results cited support the earlier suggestion that in hydrocarbon media the C–M bond is a polarised bond, not an ion-pair.

2. Active Centres in Pure Electron-donor Media

It has been shown above that the metal atom in the active centres undergoes two types of interaction—with the end of the growing chain and with electron-donor molecules C...M...S_n—the relative strengths of anionic and coordination mechanisms of chain growth depending on the intensity and character of these interactions (exchange and electrostatic forces, solvation). It may be assumed that in pure and strong electron-donor media chain growth will take place solely by the anionic mechanism.

Table 4. Chain-growth rate constants in the anionic polymerisation of butadiene in different solvents, $M^{-1} s^{-1}$.[26]

Counter ion	Tetrahydrofuran						Dimethyl ether	
	+10°C	−30°C	−43°C	−56°C	−82°C	−96°C	−30°C	−56°C
Li	0.85	0.14	—	0.03	—	—	2.2	1.0
Na	5.4	1.8	1.05	0.60	0.40	0.29	23	8
K	70	17	—	3.1	—	0.16	—	16

This conclusion is to some extent confirmed by a detailed investigation of these processes[26], since the variation in the chain-growth rate constants found for the polymerisation of butadiene in tetrahydrofuran over the temperature range from +10° to −56°C corresponds to the sequence Li < Na < K, which is characteristic of an anionic mechanism (Table 4). However, the same investigations have shown that certain restrictions must be placed on this conclusion. It is seen from Table 5 that the microstructure of the polybutadiene formed in tetrahydrofuran medium depends on the temperature and the nature of the metal in the active centre of the growing chains.

The existence of such a relationship, which is shown especially clearly with potassium and caesium active centres and at relatively high temperatures, indicates that the counter ions are to some extent involved in chain growth. The type of dependence on the nature of the metal and the temperature also corresponds to processes of anionic coordination, not purely anionic processes.

In connection with the results obtained, the question arises of the formation of free ions and the part they play in these processes. The decisive role of free ions in the polymerisation of styrene in electron-donor media has been established by Szwarc[44] and by Schulz[45]. However,

the fact that the polymerisation of butadiene under analogous conditions follows the rules of anionic coordination throws considerable doubt on the role of free ions in this system. In fact, direct conductometric examination of these systems not only has strengthened these doubts but has led to the opposite conclusions[33].

Table 5. Microstructure of polybutadiene obtained in tetrahydrofuran[26,32].

Counter ion	Structure,%*	Temperature, °C				
		+40	+10	−30	−56	−96
Li	1	84.0	85.9		91.0	
	2	8.4	7.6	—	9.0	—
	3	7.6	7.2		0	
Na	1		79.3	82.9	88.0	92.7
	2	—	15.5	15.6	12.0	7.3
	3		5.2	1.5	0	0
K	1	56.6	63.5	76.4	83.5	88.3
	2	36.5	30.4	20.7	14.8	11.7
	3	6.7	6.1	2.9	1.7	0
Cs	1		60.6	72.7	82.9	89.0
	2	—	31.4	27.3	17.1	10.9
	3		8.0	0	0	0

* 1 = 1,2-structure; 2 = *trans*-1,4; 3 = *cis*-1,4.

One piece of evidence for the decisive role of free ions in the polymerisation of styrene has been the correspondence between kinetic and conductometric results[44]. However, such correlation has been found to be completely absent in the polymerisation of butadienes[33]: the reactivity of the active centres increases according to the nature of the counter ion in the sequence Li < Na < K (see Table 4), whereas the ability of the centres to dissociate into free ions increases in the opposite sequence K < Na < Li (Table 6).

Table 6. Dissociation constants of live polymers at 25°C ($10^7 K_{diss}$, M).[33]

Counter ion	Carbanion				
	butadiene	styrene	anthracene	butadiene	styrene
	Tetrahydrofuran			Dimethyl ether	
Li	0.85	1.7	—	31	43
Na	0.82	1.0	9.0	5.5	22
K	0.55	0.58	—	2.2	3.2

Thus in electron-donor media the behaviour of active centres in the polymerisation of butadiene is determined not by free ions, although their concentration in these systems is comparable with the concentrations in the case of styrene, but by ion-pairs. This conclusion is further supported by the fact that addition of potassium tetraphenylborate, which lowers the concentration of free carbanions, does not affect the rate of polymerisation of butadiene or the microstructure of the polybutadiene.

Hence it follows that results obtained with one monomer cannot be extended to other monomers without first carefully studying their behaviour, for, as has been shown with butadiene and styrene, different results are obtained depending on the nature of the monomer.

III. ACTIVE CENTRES IN THE POLYMERISATION OF BUTADIENE IN THE PRESENCE OF COMPLEX CATALYSTS BASED ON COBALT AND NICKEL

It has been established above that, in the polymerisation of hydrocarbon monomers, the active centres for growth of polymer chains can be of different types—covalent bonds of various degrees of polarisation, ion-pairs, and free ions—depending on the nature of the alkali metals, the properties of the medium, and the temperature. The structure of complex catalytic systems containing transition metals is, of course, considerably more complicated, and development of their properties is more diverse than with the alkali metals. The ability of transition metals to exist in different states of oxidation, their tendency to various types of complex formation (σ-, π-, and n-complexes), donor–acceptor interaction, and the varied configuration of the complex systems create a certain boundary between the behaviour of the alkali metals and that of the transition metals in processes of ionic–coordination polymerisation.

Nevertheless, these two types of processes exhibit several common features, and therefore the generalisations applicable to ionic–coordination polymerisation occurring in the presence of alkali metals and their organic compounds may serve as an approach to the consideration of the more complicated type of processes, as remarked at the beginning of the paper.

Many published studies of the polymerisation of hydrocarbon monomers (in particular of butadiene) in the presence of complex cobalt and nickel catalysts indicate that the active centres for growth of the polymer chains are $C^{\delta-}-M^{\delta+}$ bonds (where M represents the transition metal) polarised in the direction characteristic of anionic–coordination processes. The degree of polarisation of this bond depends on the structure of the bimetallic complex, the nature of the ligand, the transition metal, and the properties of the medium. The formation of ion-pairs and especially of free ions in these processes, occurring in non-polar hydrocarbon media, is improbable. Certain kinetic features of these systems will be further considered from this point of view.

In many investigations on processes of this type no clear distinction is made between homogeneous and heterogeneous processes, despite the fact that the structure of the active centres and their development in acts of chain growth depend fundamentally on the properties of the reaction media.

The present paper discusses only processes taking place in homogeneous—mainly hydrocarbon—media. Since these processes are extremely sensitive to various impurities, which when present in minute quantities affect polymerisation, and are sometimes difficult to determine by the usual analytical methods, procedures have been developed for purifying the starting materials and also a vacuum dilatometric method, which practically eliminate their presence in the reaction medium and their influence on the processes under investigation.

1. Polymerisation of Buta-1,3-diene in Benzene Solutions in the Presence of the Complex System $CoPy_2Cl_2 + R_2AlCl$

A considerable amount of work has been done[46–51] on the polymerisation of buta-1,3-diene in the presence of complex "cobalt" catalysts, with many interesting observations and several hypotheses on their mechanism. In particular, it has been shown that these processes involve the

formation of polybutadiene chains in which *cis*-1,4-units greatly preponderate (95–98%), this being characteristic of a coordination mechanism.

Nevertheless, many fundamental questions associated with the behaviour of active centres in the systems still remain unanswered, and attempts to settle them have led to contradictory results. Researches with the aim of helping to fill this gap have been conducted in the Lomonosov Moscow Institute of Fine Chemical Technology[34,52-54]. These investigations of the polymerisation of butadiene in the presence of a catalytic system comprising $CoPy_2Cl_2$ and R_2AlCl (where Py represents pyridine, and R isobutyl or ethyl) have established an extremal dependence of the initial rate of polymerisation and increase in molecular weight of the polymers on the concentration of water added in small amounts to the initial reaction mixture. However, the small number of experiments and the order in which water was added in these investigations did not permit accurate determination of the actual concentrations of added water or the corresponding positions of the maxima on the plot of initial rate of polymerisation against initial concentration of water.

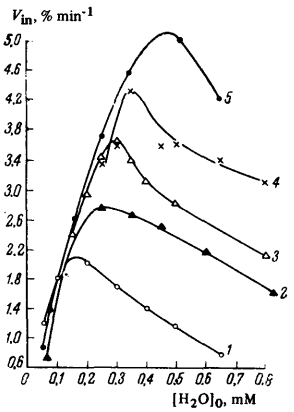


Figure 2. Dependence of initial rate of polymerisation of 1.56 M butadiene on initial concentration of water at 21°C with $[Al]_0/[Co]_0 = 400$ and cobalt concentrations ($[Co]_0$, mM) of:
1) 0.010; *2*) 0.012; *3*) 0.014; *4*) 0.017; *5*) 0.020.

Further examination of these systems by Volkov[55] using an improved dilatometric method has led not only to a more exact determination of the initial concentration of water and the corresponding position of the maxima but also to the possibility of assessing the main features of these processes associated with the properties of the active centres under various conditions. However, the main problem of the structure of the initial complex and its active forms could not be solved unambiguously even in these investigations, owing to the need to conduct the processes at extremely low concentrations and to the instability of the complex system during polymerisation.

In particular, the instability of the initial pure catalytic system is shown by the fact that the polymerisation of butadiene proceeds at a negligible rate, forming a polymer of low molecular weight, and after 2–3% conversion it stops completely. Separate experiments have established that irreversible breakdown of the whole catalytic system has occurred.

On the addition of water the rate increases sharply over the concentration range 0.05–0.8 mM, passes through a maximum, and then falls slowly. The molecular weight of the resulting polymer increases with increase in the initial concentration of water.

These phenomena are illustrated in Fig. 2, which shows the dependence of the initial rate of polymerisation V_0 on the initial concentration of water $[H_2O]_0$ for various initial concentrations of the complex cobalt catalyst $[Co]_0$ at a constant butadiene concentration of 1.56 M and a temperature of 21°C. The ratio between the aluminium and the cobalt components of the combined catalyst was also maintained constant at $[Al]_0/[Co]_0 = 400$. It was shown that, provided that this ratio exceeds 200, further increase in $[Al]_0$ has no effect on the rate of polymerisation[56]. The phenomena illustrated in Fig. 2 therefore depend solely on the initial concentrations of the cobalt component of the catalyst $[Co]_0$ and of the added water $[H_2O]_0$.

It must be remarked that Fig. 2 represents only those reactions which start and are complete in the initial stage of the process and which are very rapid. Among them are formation of the catalytic complex from the initial components, interaction of cobalt complex with water, initiation of the monomer, and reactions leading to a fall in rate after the system has reached the maximum rate of polymerisation V_{max}.

It is evident from Fig. 2 that water tends to favour both formation of an active catalytic system and increase in its activity by increasing the concentration of active centres produced from the initial catalyst as the concentration of added water increases. When the maximum rate of polymerisation is reached, the active centres acquire their greatest stability. Further increase in $[H_2O]_0$ leads to irreversible breakdown of the active centres, which may be supposed to involve their hydrolysis. The conditions under which the maximum rate of polymerisation is reached are listed in Table 7.

Table 7. Conditions for maximum rates of polymerisation.

$[Co]_0$, mM	$V_{0,max}$, % min^{-1}	10^3k, M^{-1} min^{-1}	$[H_2O]_{0,max}$, mM	$\alpha = \frac{[H_2O]_{0,max}}{[Co]_0}$
0.010	2.20	0.55	0.16	16.0
0.012	2.80	0.51	0.25	20.8
0.014	3.65	0.56	0.30	21.4
0.017	4.30	0.56	0.35	20.6
0.020	5.05	0.53	0.45	22.50
				Mean = 21.4

The highest rates of polymerisation and the greatest stability of the active centres are governed by a constant ratio of the initial concentrations of water and the cobalt complex of

$$[H_2O]_0/[Co]_0 = \alpha = 21.4.$$

It follows from Table 7 that the rate of polymerisation in the neighbourhood of the maximum is

$$V_{max} = K_{gr} \cdot K' ([Co]_0 [H_2O]_0)^{1/2} [M]_0,$$

while the concentration of active centres is

$$[\overset{*}{Co}]_{max} = K' ([Co]_0 [H_2O]_0)^{1/2}.$$

Table 7 includes values of the rate constant, which is given by the product $K = K_{gr}K'$.

Polymerisation involving fractional powers of the initiator concentration is not altogether usual with processes in which complex catalysts take part. It is true that a similar relationship is observed when organic compounds of the alkali metals are used as catalysts, and has recently been found (see next subsection) in the polymerisation of butadiene under the influence of π-allyl complexes of nickel. In all these cases the catalyst is associated, being present in particular as dimers, and only their dissociation products possess active properties. It is possible that analogous phenomena take place in the present case.

Thus the highest concentration of initial active centres occurs in the region of the maximum (Fig. 2). The fact that fall in the initial rate of polymerisation following the maximum is due to decrease in the number of initial catalytic centres—not to termination of the growing chains—follows from the linear increase in the molecular weight of the polymers in this region (see below).

It may be supposed that the irreversible breakdown of the initial active centres is due to hydrolytic reactions, when water is present in the system in concentrations exceeding the possible increase in the number of active centres. Hence it follows that decomposition is caused by the excess of water $[H_2O]_0 > [H_2O]_{max}$.

Water has been regarded above as taking part directly in all interactions with the cobalt centre of the catalytic complex. However, the presence of R_2AlCl in large excess can hardly be of no consequence with respect to water. On the other hand, keeping a solution of R_2AlCl, water, and butadiene in benzene under the conditions of the maximum following addition of $CoPy_2Cl_2$ produced no change in the process of polymerisation. This indicates that no bonding of water into any stable compounds occurs as a result of interaction of water with R_2AlCl, but a few unstable active compounds, of enhanced electron-acceptor ability, may be formed, e.g.

$$R_2\overset{\delta-}{Al}\begin{matrix}Cl\\OH\end{matrix}\cdots\overset{\delta+}{H}.$$

As noted earlier, hydrolytic reactions occur at concentrations of water exceeding $[H_2O]_{max}$, and these affect also the R_2AlCl. However, the stable products are inactive towards polymerisation. Several investigators regard aluminium oxide as having an activating function[57]. However, replacement of water by an equivalent amount of aluminium oxide diminished the activity of the catalytic system, and the process ceased at 8–10% conversion.

It follows from the above facts that rapid formation of active centres takes place at the very start of the process, on mixing the initial components, their concentration being determined, it may be supposed, by the further development of polymerisation with time.

This hypothesis is supported by kinetic data obtained under conditions of the maximum $[H_2O]_0 = \alpha[Co]_0$ and with excess of water $[H_2O]_0 > \alpha[Co]_0$. It is seen from Fig. 3 that the rate of polymerisation is actually almost constant up to 30% conversion (curves *3–5*), whereas curves *1* and *2*, obtained in experiments with $[H_2O]_0 < \alpha[Co]_0$, show a fall in rate with time, which indicates that processes leading to breakdown of the active centres occur in these systems.

These phenomena, occurring with small additions of water, can be explained by the decrease with time in the number of initially formed active centres—equivalent in number to $K'([Co]_0[H_2O]_0)^{\frac{1}{2}}$—owing to distribution of the water among the many cobalt centres free from water, which causes instability of the catalytic system as a whole. The development of instability of the system in the range up to the maximum, accompanied by decomposition of the catalyst, can be illustrated by the results plotted in Fig. 4. Curve *1* shows the dependence of the percentage conversion on the time. The spontaneous breakdown of active centres in the catalyst, which is responsible for the decrease in the rate of polymerisation with time, is described by a unimolecular law.

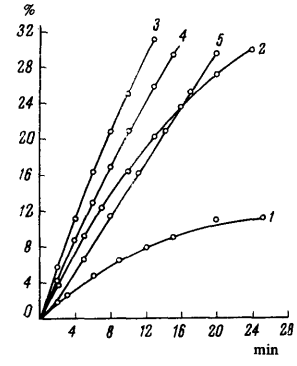


Figure 3. Dependence of percentage conversion of 1.56 M butadiene on time at 21°C with $[Co]_0 = 0.012$ mM, $[Al]_0/[Co]_0 = 400$, and concentrations $[H_2O]_0$ (mM):
1) 0.06; *2*) 0.12; *3*) 0.25; *4*) 0.60; *5*) 0.80.

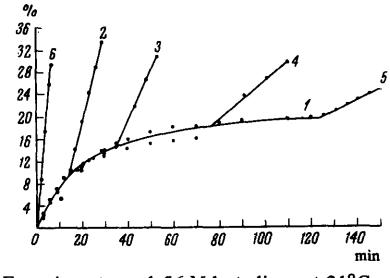


Figure 4. Experiments on 1.56 M butadiene at 21°C with $[Co]_0 = 0.017$ mM, $[H_2O]_0 = 0.05$ mM, and 0.30 mM H_2O added during polymerisation, after (min):
1) no water added; *2*) 15; *3*) 35; *4*) 75; *5*) 125; *6*) 0 (i.e. $[H_2O]_0 = 0.35$ mM, corresponding to $[H_2O]_{max}$).

The straight lines *2–5* in Fig. 4 represent the kinetic effects due to the addition of water in amounts such that its total concentration would equal that corresponding to the conditions of the maximum and described by the straight line *6*. These results show that (1) the rate of processes occurring on the introduction of water at various stages in polymerisation is lower than the maximum rate, although the total added water corresponds to that for the maximum; (2) the rate of these processes falls with increase in the time of introduction of the additional amounts of water; and (3) the rate of freshly occurring processes is constant with time, as is that of the processes occurring in the presence of excess of water, which indicates transition of the initial system from the condition $[H_2O]_0 < \alpha[Co]_0$ to the condition $[H_2O]_0 > \alpha[Co]_0$.

The above generalisations apply to the polymerisation of butadiene, the rate of which is determined by the concentration of the initial active centres, not by chain growth or chain termination. In the region of the maximum, where the system acquires its greatest stability, the rate of polymerisation during the process depends solely on the first power of the varying concentration of the monomer.

The mean molecular weight of the polymers $\overline{M}_\eta$ increases with increase in the concentration of initial water $[H_2O]_0$ and is independent of the extent of polymerisation. Fig. 5 shows that $\overline{M}_\eta$ is a linear function of the initial concentration of water, the major part of the graph relating to the region following the maximum, i.e. to the region in which the rate of polymerisation falls. These results, together with those cited earlier, show that chain termination does not occur in the course of polymerisation, but chain-transfer reactions are clearly evident, and determine the molecular weight of the polymers formed.

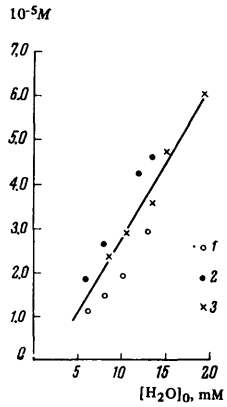


Figure 5. Dependence of molecular weight of polymers on initial concentration of water at 21°C with initially 1.56 M butadiene, $[Al]_0/[Co]_0 = 400$, and concentrations ($[Co]_0$, mM): *1*) 0.010; *2*) 0.012; *3*) 0.017.

Timofeeva [56] has studied the nature of the carrier for the growing chains.

These investigations have established that, with constant initial concentrations $[H_2O]_0$ and $[Co]_0$, the dependence of the reciprocal of the molecular weight on the initial concentration $[R_2AlCl] = [Al]_0$ is described, over a wide range of concentrations, by the relation

$$\frac{1}{\overline{M}_\eta} = a[Al]_0 + C$$

where a and C are constants. These results are consistent with Fig. 5, which shows that the increase in $\overline{M}_\eta$ with increase in $[H_2O]_0$ is smaller the greater the initial concentration $[Al]_0$.

Thus the mean molecular weight of the polymers depend on two factors—(1) interaction with R_2AlCl, which favours chain transfer, and (2) the effect of $[H_2O]_0$, which promotes chain propagation—the ratio $[Al]_0/[H_2O]_0$ reflecting the effect of the two factors, acting in opposite directions, on the molecular weight of the resulting polymers. The reciprocal of the mean degree of polymerisation $\overline{P}_\eta$ can be written

$$\frac{1}{\overline{P}_\eta} = \frac{K_{tr}[Al]_0}{K_{gr}[H_2O]_0}[M]_0$$

where K_{tr} and K_{gr} are constants representing chain transfer and chain propagation respectively. Fig. 6 shows that the direction in which $\overline{M}_\eta$ varies with the initial ratio $[Al]_0/[H_2O]_0$ corresponds to the above equation.

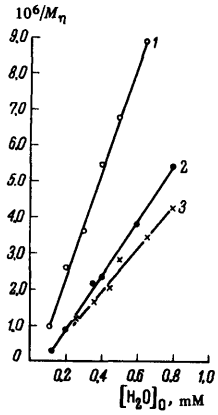
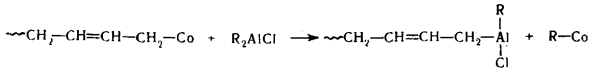


Figure 6. Dependence of $1/M_\eta$ on the ratio $[Al]_0/[H_2O]_0$ under the same conditions as for Fig.5.

The activity parameters of the bond $C^{\delta-}-M^{\delta+}$, on which the microstructure of the polymer chains depends, exhibit considerable stability: under all the conditions employed, polymers containing an overwhelming preponderance (~ 98%) of *cis*-1,4-units are formed, with the exception of polymers of low molecular weight, produced when this catalytic system is used in the absence of water. In the latter case the molecular chains comprise 74.2% of *cis*-1,4-units and 21.4% of 1,2-units.

The carbon–cobalt bond may be either a polarised covalent bond, a bridging bond, a π-allyl bond, etc. Without prejudging the nature of the bond, which requires special consideration, we can confine ourselves to the hypothetical scheme



to illustrate the chain-transfer reactions.

As an electron-acceptor agent, water solvates the cobalt atoms, increases its fractional positive charge, and strengthens the carbon–cobalt bond. The degree of solvation probably increases even after the concentration of water has reached a twentyfold excess over that of cobalt, which is necessary to stabilise the active centre and suppress chain-transfer reactions.

Other electron-acceptor compounds, such as aluminium trichloride, tin tetrachloride, and hydrogen chloride, also tend to strengthen the carbon–cobalt bond, but the concentration curves for the rate of polymerisation do not pass through a maximum, since these compounds are

devoid of the electron-donor properties which water possesses in some measure, as noted previously. The rate of polymerisation reaches a limit as their concentration increases.

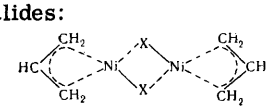
Strong electron-donor compounds (ethers, amines, tetrahydrofuran) tend to break down the active centres [58,59]. This may be supposed to be linked with a tendency to form ion-pairs, which are unstable in the case of the transition metals.

Weak electron donors, such as e.g. dialkyl sulphides, promote polarisation of the carbon–cobalt bond and, as might have been expected by analogy with the alkali metals, change the structure of the polymer units in the direction of forming 1,2-structures [60].

Thus the regularities which have been found determine the nature and the concentration of the initial active centres and the way in which they vary with the initial concentration of water, and correctly describe the changes in the molecular weight of the polymers formed by the polymerisation of butadiene in the presence of the complex system consisting of $CoPy_2Cl_2$, R_2AlCl, and H_2O.

2. Active Centres in the Polymerisation of Butadiene initiated by Nickel Complexes of the π-Allyl Type

The polymerisation of butadiene under the influence of nickel complexes of the π-allyl type now occupies an important place in researches aimed at elucidating the mechanism of polymerisation processes occurring in the presence of complex compounds of transition metals. A comprehensive study of the π-allyl type of complexes has led to several important conclusions on the dependence of their structure on the nature of the metal and the properties of the medium [61–63]. In particular, the structure of the bis-π-allylmetal halides has been established by the application of physical methods [64,65]. The diagrammatic representation of these complexes can be extended also to π-allylnickel halides:



(III)

where X = Cl, Br, I. However, no kinetic investigations were undertaken, which might have given important additional information on the nature of the active centres and their role in the polymerisation of butadiene. Lazutkin and Vashkevich [66] carried out the research necessary to obtain this information, their results being given later.

The pure complexes listed in Table 8 have been obtained by a new method of synthesis [67], and used as polymerisation catalysts. All operations in the preparation, purification, and dispensing of the starting materials and in polymerisation were conducted in a completely sealed apparatus,

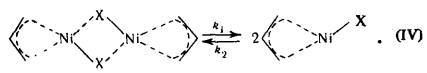
Table 8. Dependence of rate constant on nature of halogen and allyl group in nickel complexes.

Complex	Rate constant (65°C), $M^{-1/2}\,h^{-1}$	Activation energy, kcal mole^{-1}	Pre-exponential factor $10^{-10}A$
π-Allylnickel iodide	1.620	15.3	1.150
π-But-2-enylnickel iodide	1.170	15.2	0.710
π-Methylallylnickel iodide	1.320	15.0	0.590
π-Allylnickel bromide	0.130	15.2	0.078
π-But-2-enylnickel bromide	0.120	15.3	0.085
π-Allylnickel chloride	0.017	15.5	0.015
π-But-2-enylnickel chloride	0.010	—	—
π-Methylallylnickel chloride	0.017	15.5	0.015

which had first been conditioned under a high vacuum. It was found that, independently of the nature of the halogen or the substituents in the allyl group of the initial catalytic complex, the rate of polymerisation in benzene solution was given by

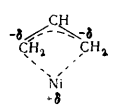
$$-\frac{d[M]}{dt} = k[Cat]^{1/2}[M].$$

This type of dependence of rate of polymerisation on the initial complex, which is unusual for complex systems, indicates that the active centres for chain growth are not dimeric molecules of the original complex but dissociation products:



(IV)

The activity of a monomeric nickel centre is due to its valency unsaturation together with its considerable solvation by benzene. The first stage in formation of an active centre may be addition of a monomer molecule as an adduct to the nickel atom, followed by its rearrangement into a polarised π-allyl bond.

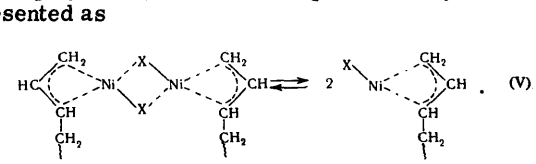


Dissociation of the initial complex is confirmed by the values of the Arrhenius parameters listed in Table 8. The total activation energy is surprisingly stable: for all the catalysts investigated, independently of the nature of the halogen and the allyl group, E_{act} = 15.0–15.5 kcal mole^{-1}. The pre-exponential factors also are practically independent of the nature of the substituent in the allyl group, but they increase substantially with the volume of the halogen atom, in the sequence Cl < Br < I. The increase in volume of the halogen atoms and the consequent steric hindrance constitute the main factor responsible for the increase in rate of polymerisation in the same sequence (Table 8).

All the facts which have been found fit the following kinetic scheme of polymerisation reactions:

1. $A_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2\mathring{A}$
2. $\mathring{A} + M \xrightarrow{k_{in}} \mathring{A}M$
3. $\mathring{A}M_n + M \xrightarrow{k_{gr}} \mathring{A}M_{n-1}$
4. $\mathring{A}M_n + \mathring{A}M_m \underset{k_1}{\overset{k_2}{\rightleftarrows}} M_nA_2M_m$

where A_2 is the initial complex, $\mathring{A}$ the monomeric active centre, M the monomer, and $M_nA_2M_m$ an inactive complex attached to polymer chains. The equilibrium system can be represented as



(V)

The dependence of the rate of polymerisation on the square root of the concentration of the initial complex, which is found to hold over a wide range of concentrations and at various temperatures, leads to two conclusions: (*a*) the equilibrium systems (IV) and (V) are governed by

similar parameters; and (*b*) in the equation for the equilibrium constant

$$K_{eq} = \frac{k_1}{k_2} = \frac{[A^*]^2}{[A_2]} = \frac{(2\alpha)^2[A]}{1-\alpha},$$

the degree of dissociation $\alpha \ll 1$, and then $[A^*] = K_{eq}^{\frac{1}{2}}[A_2]^{\frac{1}{2}}$.

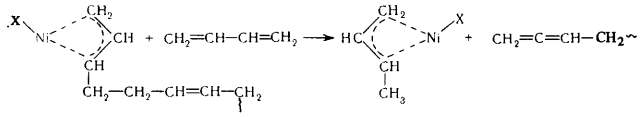
The rates of all the polymerisation processes investigated are given by the general equation

$$-\frac{d[M]}{dt} = K_{gr}K_{eq}^{1/2}[A_2]^{1/2}[M]$$

the changes in rate found with the chloride, bromide, and iodide complexes being determined mainly by variations in K_{eq} under the influence of the volume factor.

trans-1,4-Polybutadiene was always obtained in the presence of iodide and bromide complexes of nickel. The use of chloride complexes of nickel also yields polybutadiene in which *trans*-1,4-units predominate. Sometimes small quantities of *cis*-1,4-structures were also observed, but this cannot be attributed to a specific coordinating effect of the chlorine atoms in the complex. These structural deviations can rather be explained by impurities resulting from decomposition of the complex during prolonged polymerisation, which may last several days.

Chain-terminating reactions, which would have resulted in irreversible deactivation of the active centres, are absent from these processes. The mean molecular weights of the polymers formed are extremely low, varying over the range 10 000–35 000 depending on the condition and the nature of the nickel complexes. Chain-transfer reactions, which determine the molecular weight of the polybutadienes, probably occur as follows:



perhaps with intermediate formation of a hydride bond Ni–H.

Some Aspects of the Modification of Active Centres

The active centres of π-allylnickel halides are extremely sensitive to various substances—oxygen, iodine, Lewis acids, etc.—some of which break down the active centres, whereas others produce new centres possessing a different, sometimes enhanced, activity and, what is especially important, a different stereospecificity.

The system comprising $(NiC_3H_5Cl)_2$ and $TiCl_4$ is one of the large number of such examples[68]. When those substances are mixed in a heptane solution of butadiene, a precipitate of $(NiC_3H_5Cl)_2.TiCl_4$ is formed, and is a new catalyst. It contains all the nickel from the complex (the solution contains only titanium tetrachloride, and possesses no active properties). Polybutadiene of high molecular weight formed on the modified catalyst contains more than 90% of *cis*-1,4-units. This example illustrates an important fact of fairly wide validity: the addition of Lewis acids to solutions of π-allyl systems transfers the process of polymerisation to a heterogeneous phase, thereby changing the parameters of the reactive carbon–hydrogen bond not only owing to formation of a π-allyl complex differing in molecular structure but also in its phase constitution. This is especially significant in the consideration of the phenomena of stereospecificity, which is changed by additions to the reaction medium or the presence of substance of different type.

Another example of processes of this type is provided by results obtained in an investigation of the effect of added allyl halides on polymerisation systems containing π-allylnickel halides[69]. When various quantities of allyl bromide (ABr) are added to a benzene solution of butadiene and π-allylnickel bromide (π-ANiBr), the initial concentration of which in the mixture was the same (Fig. 7), the rate of polymerisation of the butadiene at first increases with increase in the initial concentration $[ABr]_0$, but after an optimum initial ratio is reached, in the present case $[\pi\text{-ANiBr}]_0/[ABr]_0 \simeq 0.5$, remains constant during some initial period (straight line *3*). It is interesting that with high $[ABr]_0$ concentrations the rate of polymerisation tends to a limit, and this occurs sooner the lower the initial ratio $[\pi\text{-ANiBr}]_0/[ABr]_0$ (curves *5* and *4*), which indicates complete decomposition of the initial catalyst (decolorisation of the solution).

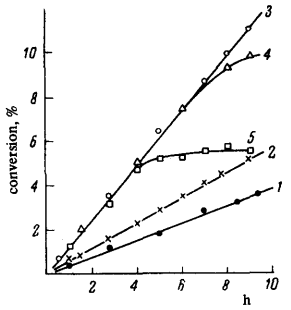
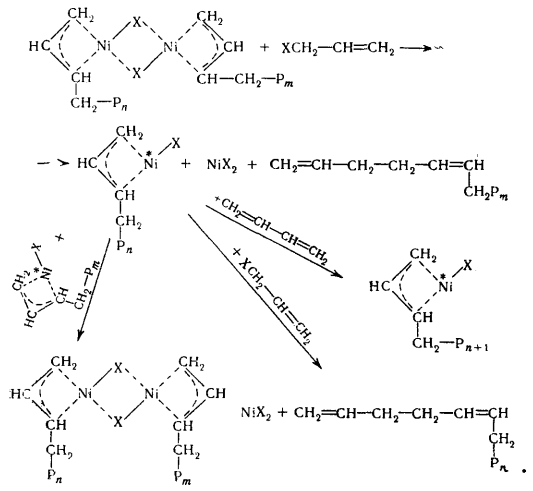


Figure 7. Polymerisation of 1.6 M butadiene in presence of 0.011 M π-allylnickel bromide at 49.3°C and allyl bromide concentrations (M) of: *1*) 0; *2*) 0.00187; *3*) 0.0242; *4*) 0.0512; *5*) 0.1624.

It is especially significant in these phenomena that decomposition of the initial complex π-ANiBr is accompanied by separation of NiX_2 as a highly disperse powder, which with the A_2 or A forms of the initial complex probably forms a new heterogeneous catalyst possessing enhanced total activity. The reactions which are involved in this process can be represented by the scheme



Similar phenomena take place on the addition of various amounts of allyl chloride (ACl) to the system containing π-ANiBr. The difference is that decomposition of the π-ANiBr complex occurs more slowly and with an induction period in the presence of ACl, and a higher $[\pi\text{-ANiBr}]_0/[\text{ACl}]_0$ ratio is required to produce a limiting state than when ABr is added. The total activity of the new complex on nickel chloride is increased several times.

The above results show that the polymerisation of butadiene in systems consisting of π-allylnickel halides and allyl halides involves complicated homogeneous and heterogeneous processes in which active centres of two different types take part, the nature and concentration of which depend on the initial ratio $[\pi\text{-ANiX}]_0/[\text{AX}]_0$ (where the X are halogen atoms which may be the same or different) and on the degree of conversion of the butadiene. The two types of active centres differ in stereospecificity: the homogeneous centres promote formation of *trans*-1,4-polybutadiene, whereas the heterogeneous centres result in preferential formation of *cis*-1,4-units of polybutadiene.

Both types of centre are present together in polymerisation processes, the relation between them being determined by the conditions mentioned above. For this reason the polybutadiene formed in systems containing π-allylnickel bromide have a mixed microstructure depending on the nature of the additions (see Table 9).

Table 9.

Addition	*cis*-1,4, %	*trans*-1,4, %	1,2, %
Allyl bromide	41—74	24—56	2—3
Allyl chloride	76	21	2—3

The facts discussed above provide further confirmation of the need to take into account heterogeneous reactions in the polymerisation of butadiene when considering problems of stereospecificity on the introduction of additives to systems containing the π-allylnickel halide type of complexes.

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Karpov Physicochemical Institute, Moscow

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Relative Strength of CH Acids

A.I.Shatenshtein and I.O.Shapiro

The problem of the differentiating action of solvents on the relative strength of acids is examined from the point of view of the modern theory of acid-base equilibrium, according to which hydrocarbons and their derivatives behave under appropriate conditions as acids. Methods are described for determining the strength of such CH acids. The factors on which the differentiating effect of solvents depends are discussed. The most detailed consideration is given to the question—newly posed in the literature—of the possible causes of the change in the relative kinetic acidity of CH acids produced by solvents, which has been established by measuring the rate of the protophilic isotopic exchange of the hydrogen in them with bases. The bibliography contains 110 references.

CONTENTS

I. Introduction 845
II. Factors determining the differentiating effects of solvents 846
1. Correlation of thermodynamic and kinetic acidities 846
2. Differentiating action of solvents on thermodynamic acidity 846
3. Relative rates of steps and transition-state structures in protophilic isotopic exchange of hydrogen 847
III. Determination of strength of CH acids 848

I. INTRODUCTION

The essential nature of acid–base reactions and acid–base catalysis was explained by Brønsted's theory[1-5], which not only summarised many phenomena occurring in aqueous and non-aqueous solutions and gave a quantitative description of these phenomena but was also able to make predictions. In the course of time, however, facts accumulated which indicated that the theory was limited and imprecise[6,7]. Thus the discovery of the differentiating action of solvents on the relative strengths of acids and bases contradicted the theory. The mechanism of protolytic processes was found to be more complicated than was postulated by the theory, and substances which according to it were aprotic, i.e. incapable of acting as either acids or bases, could take part in such processes. It became obvious that the theory of acids and bases must be reexamined and refined, by changing the actual definitions of concepts. According to the new definitions[3,8] a *base* is an electron-donor reagent, which possesses affinity for a proton; an *acid* is an electron-acceptor reagent, whose hydrogen takes part in an equilibrium reaction with a base. An