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Spectroscopic and Quantum-chemical Studies on the Active Centres in Anionic Polymerisation

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The mechanisms and consequences of complex formation in systems incorporating organometallic compounds are discussed on the basis of spectroscopic and quantum-chemical characteristics of alkyl, alkenyl, and aryl derivatives of lithium and certain other metals in the absence and presence of electron donors. Particular attention is devoted to "living" anionic chains. The bibliography includes 129 references.

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I. INTRODUCTION

Many of the anionic polymerisation processes initiated by organometallic compounds take place with participation of "living" polymers, i.e. growing chains which retain their capacity for the propagation reaction even after the complete exhaustion of the monomer or after the attainment of a state of equilibrium in the polymer–monomer system. In order to determine the relation between the experimental effects observed in such processes and the characteristics of the growing chains active in the system, it is necessary to investigate independent physicochemical characteristics of the corresponding "living" polymers. The first information of this kind was restricted to conductimetric data for and the electronic spectra of solutions containing agents of this kind. The constants for the dissociation into free ions were determined on the basis of such data for a number of compounds and the type of the initial ion pairs, which can be either contact or solvent-separated pairs of specially introduced electron donors (ED), was established[1]. In subsequent years these characteristics were supplemented by infrared and NMR spectroscopic data, which made it possible to improve significantly the available knowledge of the structure of the anionic active centres, particularly for metal alkenyls and their complexes with electron donors. The formulation of correct conclusions concerning the structure of the active centres requires information about the low-molecular-weight organometallic compounds which initiate anionic polymerisation. A survey of the available information about the infrared and NMR spectra of the above agents is the main subject of the present review. Due attention has been devoted to the results of theoretical calculations of the electronic structures and geometries of the agents simulating anionic active centres. Both experimental and calculated characteristics of compounds of the above type are known mainly for lithium derivatives.

II. LOW-MOLECULAR-WEIGHT ORGANOMETALLIC COMPOUNDS

1. Lithium Alkyls

The compounds RLi are known to be strongly associated in hydrocarbon solutions, the size of the aggregate being determined by the structure of R.[2-4] According to modern ideas, the association is due to the formation of many-centre linkages involving the vacant p orbitals of the lithium atoms and the sp^3 orbitals of the carbon atoms. Depending on the degree of branching of R and the nature of the medium, hexa-, tetra-, di- and mono-meric forms of RLi may exist[4]. In non-polar media the hexamers and the tetramers predominate for straight-chain and branched groups respectively. There is a mobile equilibrium between the different forms, which has been described in terms of dissociation via dimeric forms[5] and, according to Brown[3], the fastest exchange with a low activation energy occurs when the system contains hexamers:

$$(RLi)_6 \rightleftarrows (RLi)_4 + (RLi)_2, \quad (1)$$

$$(RLi)_2 + (RLi)_6 \rightleftarrows 2\,(RLi)_4. \quad (2)$$

The C–Li bond in lithium alkyls is a polar covalent linkage[1,4]. The carbon in the α-position relative to lithium is sp^3-hybridised in lithium alkyls and sp^2-hybridised in lithium aryls, which follows from a comparison of the α-^{13}C chemical shifts in the spectra of the lithium compounds with data for the corresponding hydrocarbon. The characteristics of certain compounds RLi obtained by NMR are presented in Table 1†.

Table 1. The differences between the chemical shifts ($\Delta = \delta_{RH} - \delta_{RLi}$, p.p.m.) in the ^{13}C NMR spectra of the compounds RLi and the corresponding hydrocarbons in benzene[6].

R	α–C	β–C	γ–C	δ–C	R	α–C	β–C	γ–C	δ–C
$(CH_3)_2CH$	−5.9	+8.1	—	—	$CH_3CHCH_2CH_3$	(−8)	+6.3; +6.0*	+2.6	—
$CH_3CH_2CH_2CH_2$	−1.4	+6 9	+6.4	+0.7	$(CH_3)_3C$	−10.7	+9.0	—	—

* For the CH_3 group.

† The chemical shifts in all the Tables are quoted in terms of the δ scale.

It follows from the NMR data[6,7], that n-butyl-lithium (BuLi) differs from s- and t-BuLi and isopropyl-lithium (iso-PrLi) by the absence of spin–spin splitting due to the $^{13}C-^{7}Li$ bond, which can be in principle accounted for by a rapid intermolecular exchange[8] via the mechanism described by Eqns. (1) and (2). On the other hand, in solutions of iso-PrLi the hexameric form is also present[8], but the natures of the NMR spectra of the compounds iso-PrLi and BuLi are different. The infrared method makes it possible to determine the fraction of the associated species $(iso\text{-}PrLi)_n$ differing in the value of n, because the stretching vibrations of the Li–C bond in the tetramer and the hexamer are characterised by absorption bands at 475 and 510 cm^{-1} respectively[9] (Fig. 1)‡.

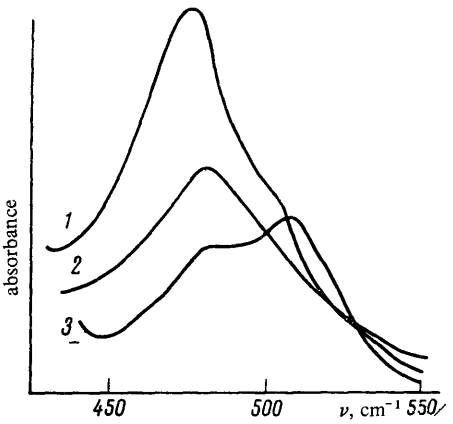


Figure 1. Infrared spectra of isopropyl-lithium in isooctane[9]; concentration (M): 1) 0.24; 2) and 3) 1.2; temperature (°C): 1) −100; 2) 12; 3) 1.2.

The correct assignment of the ν(C–Li) absorption bands was carried out for the first time by West and Glaze[11] on the basis of the method involving the isotopic substitution of ^{7}Li and by ^{6}Li and of H by deuterium. The infrared characteristics of a number of compounds RLi are now known (Table 2). In his study of the reaction between the $CH_3^{\cdot}$ radical and metallic lithium in a solid argon matrix, Andrews[12] isolated the absorption bands due to CH_3Li in the infrared spectra. Comparison of his values with data for solid methyl-lithium[11] led him to the conclusion that the hypsochromic shift of the ν(C–Li) band in the spectrum of monomeric CH_3Li, greater than by 100 cm^{-1}, is due to the decrease of the C–Li bond length to 2.10 Å (compared with 2.28 Å in solid CH_3Li); this effect decreases the force constant. The nature of the C–Li bond vibrations in the associated species is complicated by the interaction of the vibrations of the fragments of the associated molecules.

‡According to theoretical considerations[10], the difference between the chemical shifts of the tetramer and the hexamer should be 0.1 p.p.m. Nevertheless the ^{7}Li NMR method does not permit the detection of the above forms of the iso-PrLi.

Table 2. Stretching vibration frequencies of the C–Li bond (cm^{-1}) in the compounds RLi in a hydrocarbon medium.

R	$\nu(C-^{7}Li)$	$\nu(C-^{6}Li)$	Refs..	R	$\nu(C-^{7}Li)$	$\nu(C-^{6}Li)$	Refs.
CH_3	417; 530 *	446; 558 *	11, 12	s-Bu	455; 515	528	9, 17
C_2H_5	532	550	13, 14	t-Bu	420; 480	429; 496	18
C_3H_5	535	565	11	$n\text{-}C_5H_{11}$	548	569	13
iso-Pr	475; 510 **	530	9	$n\text{-}C_{12}H_{25}$	550	—	13
n-Bu	545; 550	—	15, 16	C_6H_5	421	429	11

*Monomer.
**Hexamer.

Table 3. The charge characteristics (q) and association energies (E_a) of methyl-lithium.

Method of calculation	CNDO/1 (Ref.19)	Non-empirical method (Ref.20)	Method of calculation	CNDO/1 (Ref.19	Non-empirical method (Ref.20)
	CH_3Li			$(CH_3Li)_4$	
q_C	−0.39	−0.58	q_C	−0.26	−0.97
q_{Li}	+0.53	+0.57	q_{Li}	+0.04	+0.61
			E_a, kcal mole^{-1}	112.5	110.5

Quantum-chemical calculations on the CH_3Li and $(CH_3Li)_4$ molecules, carried out by the semi-empirical CNDO/1 method[19] and the non-empirical method[20], indicate a considerable energy gain on formation of aggregates. On the other hand, conclusions concerning the change in the polarity of the C–Li bond, which follow from the data of Cowley and White[19] and Guest et al.[20] do not agree (Table 3).

2. Complexes of Lithium Alkyls with Electron Donors

It follows from NMR and osmometric data[3,4] that lithium alkyls are tetrameric in polar solvents [diethyl ether, tetrahydrofuran (THF), and trimethylamine]. It has been suggested[8,21] that the hexamer is converted into the tetramer already for the molar ratio ED : $(RLi)_6 \simeq 1-2$. Intermolecular exchange can proceed as follows:

$$(RLi)_4 . n\text{ED} \rightleftharpoons 2(RLi)_2 . n/2\,\text{ED}.$$

The existence of the monomeric form RLi, which follows from kinetic polymerisation data[5], could not be demonstrated with the aid of the above methods.

The NMR spectra of $(CH_3Li)_4$–polar solvent systems[3,4] indicate the occurrence of spin–spin splitting due to the $Li-^{13}C$ bond, which is evidence for an appreciable contribution of the covalent component to the C–Li bond. On the other hand, a significant spin–spin $^{6}Li-^{7}Li$ splitting is not observed, whence it follows that there is no bond between lithium atoms, i.e. that the aggregation effect is caused by the formation of Li–C–Li bridge bonds. It has

been established for the BuLi–THF system in a hydrocarbon medium[8] that there is no change in the ^{7}Li chemical shift in the range of THF : BuLi ratios from 1 to 14. This can be accounted for either by the formation of the complex $(BuLi)_4.4$ THF when the component ratio is only unity or by the impossibility of detecting separately the chemical shifts of various intermediate aggregates owing to the rapid intermolecular exchange even at −100° C. The NMR method has also been used to characterise qualitatively the formation of BuLi complexes with dioxan, dimethoxymethane, and tetrahydropyran[22].

Table 4. The stretching vibration frequencies of n-BuLi complexes of electron donors (cm^{-1}).

$(BuLi)_6$	T.ED	T.2ED	T.3ED	T.4ED	BuLi in THF
550	535—537	530	512—525	504	500

Table 5. The spectroscopic characteristics of electron donors and their complexes with n-butyl-lithium (cm^{-1}).

Electron donor	Absorption frequency: C–O–C stretching vibrations, symmetrical, free	symmetrical, bound	asymmetrical, free	asymmetrical, bound	Refs.
DME	924	920	1096	1087	24
DEE	846	—	1120	1097	27, 28
DEE	837	—	1153	—	27, 28
DEE	—	—	1075	1068	27, 28
Ethyl methyl ether (EME)	855	—	1122	1097 (T.ED)	27, 28
EME	—	—	—	1099 (T.4ED)	27, 28
EME	843	—	1070	1070	27, 28
DBE	898	893	1120	1075	16
THF	912	898	1074	1050	24
Dimethoxyethane	850	—	1115	1100—1105	27
d,l-DMB*	848	900	1080	1050	26
d,l-DMB*	—	—	1105	1095	26
d,l-DMB*	—	—	1116	—	26
meso-DMB*	848	865	1085	1076	26
meso-DMB*	894	900	1122	1110	26
meso-DMB*	972	—	—	1085**	26
Dimethoxymethane (DMM)***	927	927 (A); 915 (B)	1045	1030 (A); 1027 (B);	29
DMM***	—		—		29
	CH_2 stretching vibrations				
	free		bound		
DMM	1108		1105 (A); 1096 (B)		29
DMM	1138		1138 (A); 1131 (B)		29
	C–N bond stretching vibrations				
Trimethylamine (TMA)	828		822		30
Triethylamine (TEA)	1073		1064		30

*Vinogradova et al.[26] used more carefully separated DMB stereoisomers than in the work of Kalnin'sh et al.,[16] which is the reason for the difference between the two sets of data.

**The above band is manifested for the ratio Li : ED = 8 with the simultaneous disappearance of the 1076 and 1110 cm^{-1} bands. The tentative composition of the corresponding complex is DMB.2T.

***Here (A) is the monodentate complex T.4DMM and (B) is the bidentate complex T.2DMM.

The enthalpy of formation of the BuLi complex with diethyl ether (DEE) was estimated by gas–liquid chromatography (GLC)[23]; the value −5 ± 0.5 kcal $mole^{-1}$ was obtained for the complex $(BuLi)_6$.DEE.

Table 6. Thermodynamic characteristics of the BuLi–electron donor systems obtained by the infrared spectroscopic method.

ED	t, °C	K_C, litre $mole^{-1}$*	$-\Delta H$, kcal $mole^{-1}$	Refs.	ED	t, °C	K_C, litre $mole^{-1}$*	$-\Delta H$, kcal $mole^{-1}$	Refs.
THF	30	8 (K_1)	5±2	24	TMA	−20	40±20 (K_2)	4±0.5**	30
EME	0	1(litre $mole^{-1})^2$**	7±2	28	TEA	−20	3.5±1 (K_2)	4±1	30
DMM	0	5 (K_1)	4±1.5	29					

*See Eqns. (3) and (4).

**The quantity quoted corresponds to the case where 2ED T.2ED → T.4ED.

Zgonnik and coworkers[16,24-26], who used the infrared spectroscopic method, showed in relation to dimethyl (DME), diethyl, and dibutyl (DBE) ethers, THF, and 2,3-dimethoxybutane (DMB) that the formation of a complex with BuLi entails bathochromic shifts of the ν(C–Li) and ν(C–O–C) bands. Systems with participation of DME and THF were studied in greatest detail[24]. It was established that the complexes are formed stepwise via n-butyl-lithium tetramers (T), differing in the degree of solvation:

$$2\,(BuLi)_6 + 3ED \overset{K_1}{\rightleftarrows} 3\,T \cdot ED,\ T \cdot ED + ED \overset{K_2}{\rightleftarrows} T \cdot 2ED, \quad (3)$$

$$T \cdot 2ED + ED \overset{K_3}{\rightleftarrows} T \cdot 3ED,\ T \cdot 3ED + ED \overset{K_4}{\rightleftarrows} T \cdot 4ED. \quad (4)$$

The values of ν(C–Li) corresponding to the products of these reactions are listed in Table 4. The first two ED molecules are linked to T very strongly, which follows from the almost complete absence of changes in the infrared spectra as the temperature is altered for complexes formed for the initial ratios THF : BuLi = 0.25 and 0.5.

The spectroscopic characteristics of a number of electron donors, both free and bound in complexes with BuLi, are listed in Table 5. The complex formation constants K_C and the enthalpies of complex formation were calculated from the absorption band intensities associated with the free and bound electron donors in some of the systems (Table 6).

The results presented in Tables 5 and 6 may be supplemented by the following comments. The preferential transformation of the *trans,trans*- and *trans*-conformations of the free electron donors into the *trans,gauche*-, and *gauche*-conformations on formation of the complexes of the electron donor with BuLi was demonstrated for DEE and MEE[27,28]. The maximum coordination saturation of lithium is rather difficult to achieve in the case of DEE and MEE; the complex corresponding to the composition T.4ED is formed to only an insignificant extent in the case of DEE even at −95° C.[28] The type of the complex of BuLi with DMM (Table 5) is determined by the temperature for a constant reactant ratio or by the DMM : BuLi ratio for a constant temperature. In particular, an increase of the BuLi concentration and a decrease of temperature promote the formation of the complex (B). The energy of the (B) ⇌ (A) transition is 12 ± 1 kcal $mole^{-1}$.[29]

The values of K_c could be estimated in only a limited number of cases, but the results permit the conclusion, the same as the familiar conclusions in the literature[31,32], that there is no simple relation between the physicochemical properties of the electron donors and their capacity for complex formation. Thus a number of data[16,24-29] make it possible to arrange the electron donors investigated in terms of the following activity series relative to BuLi as regards the relative amounts of the free and bound electron donors: DMB ≃ THF > DMM > DME > DEE > DBE. Since it does not agree with the variation of the ionisation potential I_p§, the steric structure of the electron donor and the number of heteroatoms may be regarded as the principal factors which determine the stability of the complexes. Data characterising the BuLi–NR_3 and BuLi–tetramethylethylenediamine (TMED) systems lead to an analogous conclusion. Thus I_p for trimethylamine (TMA) is higher than for triethylamine (TEA) (7.82 and 7.67 eV respectively[30]), but the former donor forms in the temperature range from −70° to −100°C appreciable amounts of the T.4ED complex, while the latter has been found to form only the T.ED and T.2ED complexes[30].

The complexes formed by BuLi with TMED, investigated for the first time by Langer[33,34], are known to be highly stable. In the reports quoted above, the determination of the infrared and NMR spectra of the complexes is mentioned, but no experimental results are given. The data of Zgonnik and coworkers[25], characterising the infrared spectra of the same system, indicate stepwise complex formation. Depending on the initial reactant ratio, complexes of the type T.*n*TMED, where *n* varies from 1 to 4, are formed; they are hardly dissociated and their composition is insensitive to changes in temperature between −30°C and 25°C.

The complexes of BuLi with another bidentate donor, namely DMB, whose *meso*-form has been studied[26], are much less stable. The limiting stoichiometry of the complexes in this instance also corresponds to the formula T.4ED, but, for an initial 1 : 1 reactant ratio (at 20°C in a hydrocarbon medium) there is an equilibrium between the free and bound molecules. The infrared spectra of this system, obtained in the presence of an excess of BuLi at −30°C, indicate the coexistence under the above conditions of the mono- and bi-dentate complexes. The characteristics of the $(BuLi)_4.nED$ complexes, obtained by the ^1H NMR method[35] at 20°C in iso-octane, are listed below (Δ is the chemical shift of the α-CH_2 group in BuLi):

ED	*n*	Δ, p.p.m.	K_c, litre mole^{-1}
DME	4	0.21	8 ± 2
DEE	3	0.14	6 ± 2
TEA	3	0.19	5 ± 2
DES	2–3	0.10	1

Comparison of the relative activities of several electron donors with different heteroatoms, including diethyl sulphide (DES), led to the following activity series: DME > DEE > DEA > DES.[35]

The formation of mixed complexes of electron donors with BuLi has been demonstrated for TMA and THF.[30] For the initial ratios BuLi : THF : TMA = 1 : 1 : 1 (in iso-octane as the solvent) and at −100°C, the complex includes approximately four times more THF than DMA; with increase of temperature, the DMA content rises somewhat.

§THF has a smaller ionisation potential than DME, but, within the limits of the DME–DBE series, I_p decreases from 10.00 to 9.59 eV.[28]

Infrared spectroscopic data for systems with TMA, MEE, and THF also indicate the conversion of the complexes T.2ED in the range between −70° and −100°C into the complexes T.4ED (an absorption appears at 504 cm^{-1}; see Table 4). The absorption in the high-frequency region observed under these conditions (Fig. 2) led to the hypothesis[9,30] that the observed effects are due to the disproportionation of the complexes T.2ED, one of the products of which is the complex of the BuLi hexamer with ED. It is quite possible that the formation of the solvated hexamer compensates the energy gain accompanying the dissociation of the complex of the butyl-lithium tetramer.

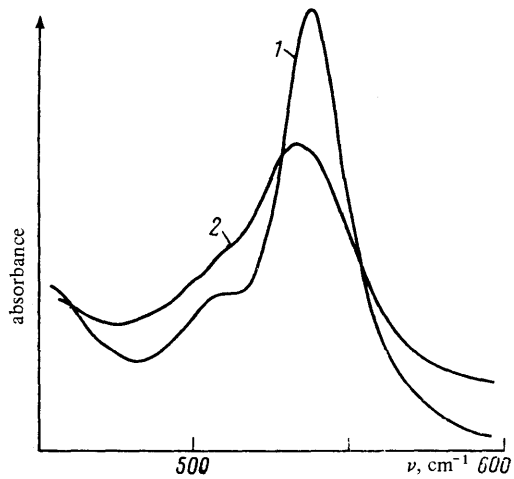
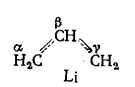


Figure 2. Infrared spectra of the 2.36 : 1 n-butyl-lithium–TMA-complex in iso-octane[30] at −17°C (curve *1*) and −100°C (curve *2*).

3. Allyl Compounds of Alkali Metals and Magnesium

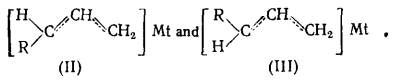
The allyl derivatives of alkali metals are soluble only in electron-donating solvents or in a hydrocarbon medium containing an electron donor[36]. According to spectroscopic data (mainly NMR), under these conditions the C–Li bond in allyl-lithium (AllLi) is ionic at room temperature[36-39] and the allyl group has the delocalised structure



(I)

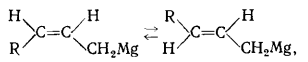
with free rotation about the Cα – Cβ and Cβ – Cγ bonds[36,37]. The infrared spectrum of AllLi exhibits a ν(C–C) = 1535 cm^{-1} absorption, which is characteristic of a delocalised structure with sp^2 hybridisation of the α-carbon atom[40]. Analogous data for the AllLi structure have been obtained[6] by ^{13}C NMR. According to Dolinskaya's data[36] for DME and West's data[39] for DEE and THF, the ^1H NMR spectra of AllLi at approximately −90°C demonstrate the presence of two types of terminal protons, which is a consequence of the complete inhibition of rotation about the above bonds. In asymmetric allyl derivatives, where the degree of delocalisation is reduced, the rotation about the

$C\beta-C\gamma$ bond is already inhibited close to room temperature[36,39]. In a study of the vibrational spectra of the allyl compounds of lithium, sodium, and potassium, Lanpher[40] demonstrated the presence of two absorption bands corresponding to the following structures (where Mt is the metal):



(II) (III)

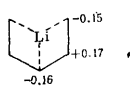
[In particular, the 1525 and 1560 cm^{-1} bands correspond to the pentenylsodium structures (II) and (III) respectively]. On the other hand, only one band is characteristic of the symmetrical derivatives (for example at 1520 cm^{-1} for 2-methylallylsodium). The allyl derivatives of magnesium exist at room temperature in an ethereal medium in the form of the equilibrium system



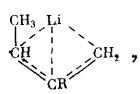
and with increase of the bulk of the substituent the fraction of the *cis*-isomer diminishes[41,42].

Among the quantum-chemical calculations for allyl compounds, the greatest interest attaches to AllLi data obtained by the non-empirical method[43]. According to these results, the symmetrical π-allyl structure with charges of $-0.197e$ at the α- and γ-carbon atoms, $-0.063e$ at the β-carbon atom, and $+0.159e$ at the lithium atom, is energetically most favourable. Calculations for the model complex $AllLi.2H_2O$ confirm the conclusion that the delocalised structure of allyl-lithium has the highest stability. Comparison of the AllLi dimerisation energy with the energies of formation of AllLi complexes with electron donors permit the conclusion that the formation of associated forms is favourable only in non-polar media.

The CNDO/2 semi-empirical method has been used in calculations on the $CH_2=CH-CH=CH-CH_2Li$ molecules with limited optimisation within the limits of several possible conformations[44]. The symmetrical structure illustrated below in a simplified form proved to be preferable:

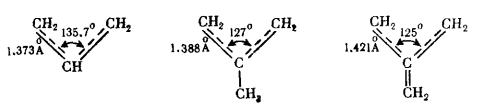


The same method has been used[45] in calculations on models of the terminal units of growing butadiene and isoprene chains associated with lithium counterions. The limiting *cis*- and *trans*-structures in their π- and σ-forms were compared. The most stable of these are structures of the type



R = H or CH_3.

The idea that the geometry of the carbanionic components of analogous compounds depends on the intrinsic structure of the alkenyls arises from the results of calculations on free allylic anions (the MINDO/3 method)[46]:



We may note that the last of the above structures may be adopted as the model of the fragment of the terminal unit in "living" buta-1,2-diene chains.

Sourisseau et al.,[38] who investigated the solid allyl compounds of lithium, sodium, and potassium by infrared spectroscopy, concluded that the allyl group has an ionic structure, which differs from its structure in π-allyl complexes of transition metals[47,48] and in covalent compounds of the type of allylmercury[49,50]. The assignments of the principal absorption bands of allyl derivatives of solid non-transition metals are listed below[38]:

Frequency, cm^{-1}	600	740	1000—1240	1400; 1460	1530	2900—3100
Assignment	δ (CCC)	r_0 (CH_2)	δ (CH); ν_s (CCC)	δ (CH_2)	ν_{as}(CCC)	ν (CH); ν (CH_2)

A set of bands in the broad range 100–600 cm^{-1} is characteristic of the C–metal bond; their multiplicity is attributed to the polymeric structure of the compounds. The force constants of the C–metal bond in the allyl compounds were found to be 0.31, 0.44, 0.55, and 0.80 mdyn $Å^{-1}$ for sodium, lithium, potassium, and magnesium derivatives respectively[38,46]. It follows from the above quantities that the bond is less stable than the C–metal bond in the analogous alkyl derivatives; thus the force constants of the C–Li bond in CH_3Li is 0.78 mdyn $Å^{-1}$.[12]

The infrared spectra of ethereal solutions of allyl compounds of lithium and magnesium contain, instead of the 600 cm^{-1} band (characteristic of the compounds in the solid state), two bands at 580 and 630 cm^{-1}, which have been attributed[38] to the effect of association. The infrared spectrum of a crotylmagnesium derivative, obtained from butadiene and magnesium in THF[51], contains bands at 1590 and 1615 cm^{-1} in the region of the ν(C=C vibrations), which the authors assigned to complexes with THF differing only in the degree of solvation (noting, however, that distillation of THF does not entail changes in the infrared spectrum of the system)[51].

The estimates of the dependence of the relative C–metal bond strengths on the nature of the substituent, carried out for alkyl and alkenyl derivatives of lithium[52], merit attention. The estimates were based on the enthalpy of alcoholysis (ΔH) of the etherates of various compounds RLi. The results, in the calculation of which account was taken of the degree of association of the initial compounds and of solvation effects, indicate a reduced strength of the bond in 2-propenyl lithium compared with other compounds investigated:

R	ethyl	allyl	*trans*-propenyl	2-propenyl
ΔH, kcal $mole^{-1}$	-7.1 ± 1.3	4.3 ± 1.3	5.4 ± 0.5	20.1 ± 2.8

III. "LIVING" POLYMERS

1. Non-polar Chains with a Lithium Counterion

In order to investigate systems simulating the active centres in the anionic polymerisation of non-polar monomers, use is frequently made of the NMR method, which makes it possible to obtain information about the structure of the terminal unit, the distribution of charges in the latter, and the type of the C–lithium bond. Low-molecular-weight adducts, formed when diene monomers (M) and s- or t-butyl-lithium interact in the proportions M : BuLi ≃ 1, have been studied as models of this kind. In order to eliminate the influence of preceding units, which complicate the NMR spectra, "living" oligomers, containing deuterated monomeric units in the main chain and a non-deuterated terminal unit, were used in a number of studies[53–56].

It follows from the chemical shifts of the α- and γ-protons of the $\sim \overset{\delta}{CH_2}-\overset{\gamma}{CH}=\overset{\beta}{CH}-\overset{\alpha}{CH_2}Li$ unit that in non-polar media most of the charge is at the α-carbon atom with a proportion of the negative charge at the γ-carbon atom. In a polar medium an upfield shift of the γ-H signal and a downfield shift of the α-H signal are observed, which indicates an increase of electron density at the γ-carbon atom. In a study of the NMR spectra of alkenyl compounds of lithium Bywater et al.[6] showed that in the THF the allyl group of allyl-lithium has the structure of a symmetrical anion with sp^2 hybridisation. It follows from the data for crotyl-lithium that the introduction of a substituent causes the breakdown of the symmetry of the anion with retention of the type of hybridisation. The chemical shifts of the α- and γ-carbon atoms in the ^{13}C spectrum of crotyl-lithium differ from the corresponding values for allyl-lithium by −14.7 and +18.7 p.p.m. An analogous effect was observed for models of "living" chains with terminal butadiene and isoprene units, which consisted of the adducts of t-BuLi with the corresponding monomers. These adducts were investigated in a non-polar medium which led to an appreciable alteration of the nature of hybridisation, namely from sp^2 to sp^3. In particular, the butadienyl derivative contains only approximately 1/3 of the charge at the γ-carbon atom relative to the charge at the γ-carbon atom of allyl-lithium.

Table 7. The ^1H NMR chemical shifts (Δ) in the model compounds RM_nLi obtained by reaction with t-BuLi.

M	n	t, °C	Solvent	Δ, p.p.m. α-CH_2		Δ, p.p.m. γ-CH	Refs.
Butadiene	1.2	20	methylcyclohexane–THF (1:1	*cis*	1.09	3.40	56
				trans	1.18	3.68	
Butadiene	1	30	toluene-d_8	*cis*	0.811	4.50	57
				trans	0.775	4.64	
Butadiene	1	20	benzene-d_6		0.6	4.6	56
Butadiene	1	30	THF-d_8	*cis*	1.19	3.35	57
				trans	1.29	3.63	
Butadiene	1	0	THF-d_8		1.2	3.5	56
Butadiene	1	20	THF-d_8	*cis*	1.1	3.0	53.*
				trans	1.2	—	
Butadiene	3—4	20	benzene-d_6		1.25	4.55	36
Butadiene	3—4	20	DME		1.20	3.0—3.75	36
Isoprene**	1	25	benzene-d_6		619	236	58
	1	0	THF		631	403	
	1	60	THF		621	363	
Isoprene	5	20	benzene-d_6		0.45	4.8	54
2-Ethylbutadiene	1	20	benzene-d_6	*cis*	—	4.72 ***	59
				trans	—	4.55 ***	
Phenylbutadiene	1	20	benzene-d_6	*cis*	0.5—2	4.70	59
				trans	—	4.95	
2,3-Dimethylbutadiene	1	20	benzene-d_6	*cis*	0.8	—	36
cis-Penta-1,3-diene	1	20	benzene		2.9	5.5	36
			benzene + DEE		4.0	3.9	
trans-Penta-1,3-diene	2.7	20	benzene-d_6		—	3.1 ****	55
					—	4.6	
2-Methylpenta-1,3-diene	1	20	benzene-d_6	*cis*	0.8	4.6	59
				trans	—	4.3	
Hexa-2,4-diene	2.2	20	benzene-d_6		—	3.1	55 *****

*Initiator—deuterated ethyl-lithium.
**The chemical shifts are quoted relative to benzene.
***Triplets.
****Initiator—isopropyl-lithium.
*****Initiator—s-BuLi.

The principal results of Bywater et al.[6] are listed below [$\Delta = \delta_{RH} - \delta_{RLi}$ (p.p.m.) is the difference between the chemical shifts]:

R	Solvent	Δ, p.p.m. α-C	β-C	γ-C
$CH_2=CH-CH_2$	THF	31.7	13.6	−64.8
$CH_3CH=CH-CH_2$	THF	17.0	19.5	−46.1
$(CH_3)_3CCH_2CH=CH-CH_2$	C_6H_6	5.3	16.2	−25.2
$(CH_3)_3CCH_2CH=C(CH_3)-CH_2$	C_6H_6	3.9	17.2	−21.6

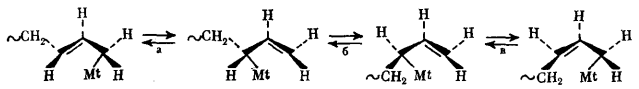
A compilation of ^1H NMR data characterising the chemical shifts of the protons attached to the α- and γ-carbon atoms in low-molecular-weight organolithium compounds with terminal units consisting of diene monomers is presented in Tables 7 and 8. Despite the abundance of such data, there is no unanimous view in the literature concerning the type and state of the terminal unit. Nevertheless the conclusion that it has the 1,4-structure (or the 4,1-structure for isoprene) with limited rotation about the $C\beta - C\gamma$ bond, responsible for the coexistence of the *cis*- and *trans*-isomers, is fairly general. In a polar medium (in contrast to a non-polar medium) the *cis*- and *trans*-structures are in equilibrium and, as shown for butadiene[60] and isoprene[58,61] isomers, the *cis*-structure predominates at approximately −70°C.

Table 8. ^1H NMR chemical shifts (Δ) in the model compounds $RM_nM'_mLi$ obtained by reaction with C_2D_5Li (measurements in benzene-d_6 at 20°C).

M	n	M'	m	Δ, p.p.m. α-CH_2	Δ, p.p.m. γ-CH	Refs.
Butadiene-d_6	20	butadiene-H_6	2.4	0.8	4.75	53
Butadiene-d_6	20	isoprene-H_8	8.8	0.87	4.75	54
Butadiene-d_6	20	2,3-dimethylbutadiene-H_{10}	2	0.7	—	54

Morton and Fetters[62] assume the existence in a non-polar medium of two types of active centres of dienyl (living) chains—a localised centre (with a C–lithium σ bond), responsible for the formation of the 1,4-units, and a delocalised centre giving rise to 1,2-units. There is no direct evidence for the presence of the π-allyl structure of agents of this kind in non-polar media. Nevertheless, according to Morton and Fetters, the content of vinyl units in the chains of the corresponding diene polymers may be regarded as an indirect indication of the presence of active centres of the σ-allyl types in numbers undetectable by NMR. According to this view, the *cis–trans* isomerisation proceeds via the structure $\sim \overset{1}{CH_2}-\overset{3}{CH}(Li)\overset{2}{CH}=\overset{1}{CH_2}$ in which there is free rotation about the $C_{(2)} - C_{(3)}$ bond. Morton and Fetters base their hypothesis on the nature of the ^1H NMR spectra of oligopentadienyl-lithium (OPL) in benzene[55], attribute the chemical shift of 3.1 p.p.m to the γ-proton (Table 7), and conclude (by analogy with data for oligobutadienyl-lithium in THF) that the terminal OPL unit has a π-allyl type of structure; the chemical shift of the α-proton is not quoted. Dolinskaya[36], who found chemical shifts of 2.9 and 5.5 p.p.m. for the α- and γ-protons of *cis*-OPL in benzene respectively, concluded that a different isomerisation mechanism operates, namely that the reaction proceeds via the delocalised structure (I) with free

rotation about the Cβ – Cγ bond (see above); this structure is consistent with data which she obtained[36] for the change in the chemical shifts of OPL on passing from a non-polar to a polar medium (Table 7). Glaze and coworkers[63,64] postulate the possibility of the oscillation of the metal atom between two potential minima for each geometrical isomer (equilibria *a* and *c*); isomerisation (equilibrium *b*) is significant only for magnesium derivatives at an elevated temperature:



We may note that all the results quoted for non-polar media refer to associated lithium alkenyls. The monomeric forms $RM_nLi.ED$ are apparently formed in polar media. As regards their nature, they should differ appreciably from the monomeric forms RM_nLi, which, according to generally accepted views, are the most active species in the polymerisation of unsaturated monomers in a hydrocarbon medium.

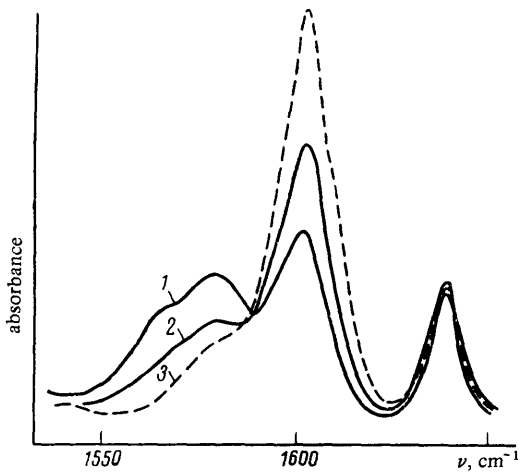


Figure 3. Infrared spectra of an artificial 1 : 1 OBL–s-BuLi mixture (curves *1* and *2*) and OBL (curve *3*) in iso-octane[17] at different temperatures (°C): 1) −31; 2) −1.5; 3) −31.

Glaze and Jones[65] were the first to use the infrared spectroscopic method in the study of compounds simulating the active centres in anionic polymerisation. The authors observed absorption bands at 1597 and 1577 cm^{-1} in the infrared spectrum of the product of the interaction of t-BuLi with butadiene and assigned them to the vibrations of the C=C bonds of the terminal units in the *cis*- and *trans*-structures respectively. These studies were developed further by Basova and coworkers[66–68] and Zgonnik and coworkers[69–71]. In particular, a detailed study of oligobutadienyl-lithium (OBL), obtained by reaction with s-BuLi, revealed a dependence of the 1602 and 1580 cm^{-1} absorption bands on the initial monomer : initiator ratio and temperature. It follows from the analysis of the infrared spectra of artificial mixtures of the initiator and OBL that the latter band refers to mixed associated species $(OBL)_3.BuLi$ (Fig. 3).

Infrared spectroscopy was then used for a more detailed investigation of OBL and was extended to the study of other "living" chains with the lithium counterion[67–76]. Zgonnik et al.[69–71] made the most complete assignment of the absorption bands in the infrared spectrum of OBL, based on the isotopic substitution of ^7Li by a ^6Li and selective deuteration of butadiene. The characteristics of the terminal unit of OBL and its deutero-analogues in the range 400–1200 cm^{-1}, presented in Table 9, demonstrate a significant contribution of the deformation vibrations of the α-CH_2 group to the 600, 775, 850, and 940 cm^{-1} bands. The isotopic shift factor for the majority of bands in the infrared spectra of the deutero-derivatives does not exceed 1.2, indicating an appreciable mixing of the vibrations of the α-CH_2 and =CH groups, which makes the out-of-plane =CH vibrations in the terminal units less characteristic. It appears that the 895 and 695 cm^{-1} bands in the spectra of OBL and OBL-d_6 respectively refer to the *trans*-structure of the terminal unit.

Table 9. The assignment of the principal absorption bands (cm^{-1}) in the infrared spectra of oligobutadienyl-lithium (OBL) and its deuterated derivatives (OBL-d_n).[71]

C–Li	α=CH_2	α-CH_2+ =CH	=CH	C–Li	α-CH_2	α=CH_2+ =CH	=CH
	OBL				OBL -d_4(1,1′, 4,4′)		
430 m. 482 m.	600 s.	775 s.	895 s.	427 m. 475 m.	525 s.	670 s.	817 m.
	OBL -d_2(2,3)				OBL -d_6		
425 m. 475 m.	582 s. 850 m.	758 s.	770 sh.	425 m. 475 m.	515 s. 766 w.	633 s.	695 s.

Note. s = strong (intense) absorption band, m. = moderately intense band, w. = weak band, sh. = shoulder.

The stretching vibration band of the double bond in the terminal unit is sensitive to the type of deuteration:

Compound	OBL-H_6	OBL-d_2 (2,3)	OBL-d_4 (1,1′, 4,4′)	OBL-d_6
$\nu_{C=C}$, cm^{-1}	1602	1568	1594	1564

It is a single band (only a slight shoulder was noted at 1580 cm^{-1})¶, which indicates the preferential existence of a structure of one type. The direction of the shift on deuteration is consistent with the NMR data and the 1,4-structure of the terminal unit.

Oligoisoprenyl-lithium (OIL)[72,73] and oligo-2,3-dimethylbutadienyl-lithium (ODMBL)[75] were investigated similarly. The frequencies (cm^{-1}) of the absorption bands of the terminal OIL and ODMBL units (in iso-octane) are listed below:

Compound	C–Li		α-CH_2	C=C	References
OIL	455,475	575	600	1600	72
OIL-d_4 (1,1′, 4,4′)	455,475	500	540	1600	73
ODMBL	445,495	560	595	1600	74,75

¶This shoulder may, in principle, refer to another structure of the terminal unit responsible for the formation of 1,2-units in the polymer; its contribution does not exceed 10%.

We may note that the low-frequency shoulder characteristic of OBL is absent from the spectra of OIL and ODMBL, indicating a more homogeneous structure of the terminal units of OIL and ODMBL, which evidently have the *trans*-4,1-structure.

Table 10. The NMR characteristics of the terminal units of the "living" chains of styrene and α-methylstyrene with a lithium counterion.

Compound	Solvents (deuterated)	Chemical shifts of signals due to protons at C atoms, p.p.m.			Charges on ring C atoms			Refs.
		o-	*m*-	*p*-	*o*-	*m*-	*p*-	
OStL	benzene	5.98	6.53	5.52	−0.11	−0.06	−0.16	77
OStL	THF	5.87	6.32	5.12	−0.12	−0.08	−0.19	
OMStL	benzene	5.67	6.23	4.66	−0.16	−0.09	−0.24	77
OMStL	THF	5.57	6.10	4.46	−0.17	−0.10	−0.26	
OMStL*	benzene	109.4	129.0	97	−0.13	−0.01	−0.19	6

*The chemical shifts of the signals due to the ^{13}C nuclei.

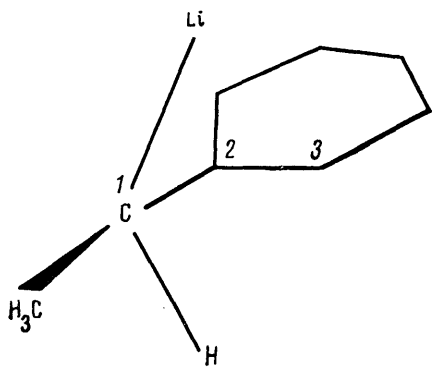


Figure 4. The optimised geometry of the model active centre $CH_3CH(Li)C_6H_5$.[80] Li–C distance (Å): 1) 2.1; 2) 2.2; 3) 2.2.

Different spectroscopic characteristics have been obtained for oligostyryl- and oligo-α-methylstyryl-lithium (OStL) and (OMStL). The ^1H NMR spectra led to the conclusion that at least half of the charge of the anionic component is concentrated on the benzene ring[6,77-79], the fraction of this charge increasing on passing from benzene solution to THF solution (Table 10). A paper[76] dealing with the infrared spectra of OStL lists the following characteristics of the terminal unit:

ν, cm^{-1}	505	1585	2800
assignment	δ (Li—CH)	in-plane C_6H_5 vibrations	ν(C–H) vibrations of CHLi

The appreciable difference between the intensity of the 1585 cm^{-1} absorption band of the terminal unit of OStL and the data for the internal units (by a factor of approximately 10) indicates the interaction of the terminal benzene ring with the counterion. This conclusion is consistent with the results of a quantum-chemical calculation on the $CH_3CH(Li)C_6H_5$ model compound by the CNDO/2 method[80], according to which the lithium atom in the optimised structure is significantly closer to the C_6H_5 group (Fig. 4); see also below.

Wicke and Elgert[81] arrived at a similar conclusion in a study of the ^{13}C NMR spectra of the compound $(CH_3)_3CCH_2C(CH_3)Li$, simulating the terminal unit of the

$$\begin{array}{l} \\ | \\ C_6H_5 \end{array}$$

growing chain of α-methylstyrene. The orientation of the lithium atom relative to the benzene ring which they propose[81] agrees in principle with the geometry illustrated in Fig. 4.

2. Complexes of the Compounds RM_nLi with Electron Donors

The results of studies on the interaction of "living" hydrocarbon chains with small amounts of electron donors in non-polar media are considered in this section. Under such conditions, monodentate donors do not cause the decomposition of associated groups of "living" chains on formation of compounds of different stoichiometries. Thus, according to isothermal distillation and conductimetric data[82], the reaction of oligobutadienyl-lithium tetramer (T) with THF in iso-octane results in the formation of the complexes T.4THF and T.8THF at room temperature. Measurements of the electrical conductivity of the second complex showed that its ionic dissociation constant is 10^{-13} mole litre^{-1}. Data for the dielectric constants of the OBL tetramer and its complexes yielded the following dipole moments:

Compound	T	T.4THF	T.8THF
μ, D	4.0	7.7	10.4

Such high constants indicate the asymmetry of the OBL tetramer, which becomes more pronounced in its complexes.

A large amount of information has been obtained in studies of the mechanism of the formation of complexes between "living" oligomers and electron donors by infrared spectroscopy[67-76,83]. For ED/Li ratios ensuring the formation of 1 : 1 complexes with DME,[69] DMM,[83] and THF,[69-71] the infrared spectra in the region of the stretching vibrations of the C=C band of the terminal units are virtually identical: the 1600 cm^{-1} absorption band is displaced in steps to 1570 cm^{-1} as the electron donor concentration is increased. Qualitatively analogous effects have been described in other studies[67,68] devoted to the formation of complexes by polybutadienyl-lithium with THF and TEA. Such a shift corresponds to transitions of the type

$$T \overset{ED(K_1)}{\rightleftarrows} T.ED \overset{ED(K_2)}{\rightleftarrows} T.2ED \overset{ED(K_3)}{\rightleftarrows} T.3ED \overset{ED(K_4)}{\rightleftarrows} T.4ED \quad , \qquad (5)$$

and $K_1 > K_2 > K_3 > K_4$. The bathochromic shift of the ν(C=C) band is apparently caused by the partial delocalisation of the double bond on formation of a complex by the counterion of the "living" chain with the electron donor. The 1570 cm^{-1} band may be fairly confidently assigned to the complex T.4ED. The overlapping of the bands characterising each individual complex has not so far permitted the determination of the individual constants K_1–K_4; only certain average values of the complex formation constants (K_C) have been estimated.

The spectroscopic and thermodynamic characteristics obtained for several systems of the type under consideration are listed in Table 11. We shall consider some of

them in somewhat greater detail and will supplement them with data not included in Table 11. An increase of the ED :OBL ratio to 10 does not alter the nature of the infrared spectrum of DME and DMM, but does entail the appearance in the case of THF of a new band in the region of ν(C=C) (1555 cm^{-1}) and a sharp decrease of the intensity of the 450 cm^{-1} band associated with the C–Li bond[71]; these changes have been attributed to the decrease of the degree of association of OBL under the influence of the excess of THF. The decrease of temperature in the last of the systems indicated to −100°C results in the appearance of a new intense band (447 cm^{-1})[71] in the region of the stretching vibrations of the C–Li bond and of two extremely intense bands (550 and 607 cm^{-1}) in the region of the deformation vibrations of the C–H bond, instead of the previous relatively low-intensity band at 600 cm^{-1}. Such changes can be accounted for either by a rearrangement in the α-CH_2Li group due to association–dissociation steps[71] or, on the basis of data obtained by other methods (NMR[60], ultraviolet spectroscopy[85], and chemically[61]), in terms of the *cis–trans* transitions in the terminal unit.

Table 11. Complex formation in M_nLi–ED–non-polar solvent systems at 20°C.

M	ED	ED:Li	$\nu_{C=C}$, cm^{-1}	K_C, litre $mole^{-1}$	$-\Delta H$, kcal $mole^{-1}$	Refs.
Butadiene	DME	1	1570—1580 (1602) *	8 **	7 **	69
Butadiene	THF	1	1565—1580 (1602) *	20 **	9 **	70, 71
Butadiene	THF	10	1555—1580	—	—	70, 71
Butadiene	DMM	1	1570 (1602) *	3	3	83
Butadiene	TMED	1	1525, 1550	—	—	88
Isoprene	THF	1	1570 (1602) *	8.5	4	72
Isoprene	THF	30 ***	1575	—	—	72
Isoprene	Dimethoxyethane	1	1570	—	—	73
Isoprene	Dimethoxyethane	4	1590	3.5	5 ****	84
Isoprene	Dimethoxyethane	10	1530—1585	—	—	84
Isoprene	TMED	1	1570 *****	—	—	87
2,3-Dimethyl-butadiene	TMED	1	1528 (1582)	1.0	2.0	74
	TMED	4	1528 (1582)			
2,3-Dimethyl-butadiene	THF	1	1580 (1602) *	—	—	75

* The characteristics of the part of the "living" chain not bound in a complex.

** Values calculated from data in Refs. 69 and 70.

*** THF used as reaction medium.

**** Value corresponding to the complex OIL.2ED.

***** Data refined after the publication of the paper of Davidyan et al.[84]

The formation of complexes between THF and OIL[72,73] is somewhat less vigorous than the reaction involving OBL. The stepwise bathochromic shift of ν(C=C) reaches a limit (1570 cm^{-1}) for an equimolar reactant ratio in the complex and remains unchanged up to the ratio ED :OIL = 10 in the reaction mixture. Only when THF is used as a solvent is a shift of the 1570 cm^{-1} band to 1575 cm^{-1} observed; the previous bands, due to the C–H bond, disappear and are replaced by a single intense absorption at 690 cm^{-1}. Monomeric complexes of the type OIL.*n*ED are apparently formed in THF; other workers[86], who investigated the analogous system by ultraviolet spectroscopy, arrived at the same conclusion.

Glyme, a bidentate electron donor, has a different effect on the terminal unit of OIL[84]. For the ratio glyme :OIL = 4 at a low temperature, unassociated complexes OIL.2ED are already formed (the absence of association was demonstrated viscometrically). However, the frequency of the absorption band of the C=C bond in the terminal unit corresponding to these complexes is higher (1590 cm^{-1}) than in the case of complexes involving THF.

We shall now compare results referring to the formation of complexes by different oligodienyl-lithium derivatives with TMED. The simplest situation is observed for OIL[73,87]. For an initial reactant ratio of unity, the ν(C=C) band is displaced to 1570 cm^{-1}, which corresponds to a 1 :1 complex, an increase of the TMED concentration and a decrease of temperature not resulting in a shift of this band. Consequently, even for the equimolar ratio of OIL and TMED, a stable complex of a definite type (apparently monomeric) is formed. A similar conclusion is reached on the basis of the ultraviolet spectra of the same system; they are characterised by a single maximum at 330 nm, which is independent of temperature and the excess of TMED. The following absorption bands are characteristic of complexes of other oligodienyl-lithium complexes with TMED in the region of ν(C=C) vibrations: 1528 and 1550 cm^{-1} for OBL[88] and 1528 and 1582 cm^{-1} for ODMBL[74,75]. The first complex is very stable and its infrared spectra (as well as ultraviolet spectra; λ_{max} = 320 nm) are insensitive to the presence of an excess of TMED and a change of temperature. When the ratio TMED :Li = 1, complexes with the 1 :1 composition are formed and are present in solution in a monomeric form[88]. ODMBL exhibits a much lower capacity for complex formation. Analysis of the infrared spectra obtained for different TMED :ODMBL ratios (from 0.27 to 4.6) shows[74,75] that complete coordination saturation of the tetramer is not attained under the given conditions: only the formation of the complexes $(ODMBL)_4$.TMED and $(ODMBL)_2$.2TMED was observed.

According to the data described above, the stability of the complexes of the compounds considered and the electron donors decreases in the sequence OBL > OIL > ODMBL, probably primarily due to the steric structure of the electron acceptors.

The spectroscopic effects observed in the OStL–ED systems differ from those described for diene derivatives. A hypsochromic shift of the 1585 cm^{-1} band to 1590 cm^{-1} is characteristic of the benzene ring[76]. This result is probably due to the breakdown of the specific interaction between lithium on the aromatic ring (see above concerning the characteristics of the terminal unit of OStL). We may note that an analogous hypsochromic shift of the ν(C=C) band was observed[89] after the introduction of diethyl ether to a hydrocarbon solution of γ-butenyl-lithium, which forms an intramolecular π-complex in the absence of an electron donor.

Genkin and Moiseeva[90] investigated the stabilities of the complexes of OBL, OIL, and OPL with TMED, DEE, and di-isopropyl ether (DIPE) by GLC. K_1 was calculated [see Eqn. (5)], since, according to the conditions employed in the method the electron donor chromatographed is present at infinite dilution in relation to the oligomers. The characteristics obtained agree with the activity series of the electron acceptors (OBL > OIL > OPL) and donors (DME > DEE > DIPE). From the large number of quantities quoted by the above workers[90], we shall select only

data for complexes of lithium alkenyls with DME:

Acceptor	OBL	OIL	OPL
K_1, litre mole^{-1} (20°C)	305	211	204
$-\Delta H$, kcal mole^{-1}	8.6	7.7	7.3

The study of the products of the deactivation of "living" oligomers of the diene series confirmed the 1,4(4,1)-structure of the terminal unit and showed that the fixation of the chain structure takes place in the propagation stage only in the penultimate unit[91-93]. Apart from the nature of the monomer and the solvent, the structure of the terminal unit is influenced also by the nature of the deactivating agent[93-95]; it has been suggested[93] that the chain termination reaction proceeds under these conditions via a complex formation stage.

3. Derivatives of Sodium, Potassium, and Magnesium

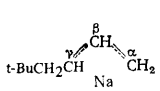
"Living" chains with a sodium counterion, with a limited solubility in hydrocarbons, have been investigated mainly in polar media. The electronic spectra indicate a much lower stability of such systems compared with the corresponding lithium derivatives[96], which is manifested in a number of irreversible reactions (the transfer of a hydride ion to the counterion[97], intramolecular proton transfer[98], the formation of alkoxides[99,100], and metallation of the solvent[101]). The *cis–trans* isomerisation of the terminal unit has also been noted[64,85]. Sodium derivatives of dienes in THF are less stable at room temperature than the corresponding derivatives of styrene[101,102], but in the region of low temperatures (−30° C), the opposite effect is observed[101,103]. These characteristics determine the temperature and time limits of the experimental study of the agents under consideration†.

Gourdenne and Sigwalt[103] showed that sodium-butadiene chains are more stable than the isoprene chains, but both undergo changes on being kept in THF (some of them reversible), which are manifested in the electronic spectra. Thus the 293 ⇌ 384 → 435 and 308 ⇌ 358 → 435 nm shifts of λ_{max} were observed for butadienyl and isoprenyl derivatives of sodium respectively‡. The terminal products of these reactions are inactive in relation to dienes.

The ^{1}H NMR chemical shifts (p.p.m.) in neopentylallyllithium (NPAL) and neopentylallylsodium (NPAS) are listed below (solvent—THF)[60,64]:

Compound	*cis*-Proton		*trans*-Proton		References
	α-C	γ-C	α-C	γ-C	
NPAS	1.52	2.85	—	3.55	64
NPAL	1.19	3.35	1.29	3.63	60

It follows from the data presented that NPAS is more ionic. The temperature at which the rotation about the Cβ – Cγ bond in the structure



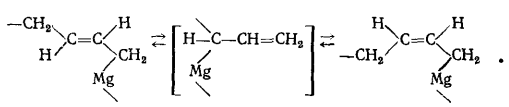
is inhibited (in terms of the NMR time scale) proved to be −20° C for NPAS and −55° C for NPAL, which indicates a higher Cα – Cβ bond order, i.e. a greater amount of ionic character of the C–Na bond compared with C–Li. The difference between the ultraviolet characteristics of NPAS and NPAL (λ_{max} = 293 and 278 nm respectively[60,63], conflicting with the hypothesis that the absorption maximum of the All–Mt contact ion pairs increases with the atomic number of the metal[104] and that absorption at longer wavelength is characteristic of more polar bonds, was explained by Glaze by the higher fraction of the *cis*-form in NPAS compared with NPAL; absorption in the region of shorter wavelengths is characteristic of the *cis*-form[100,101]. This conclusion was confirmed by the analysis of the corresponding hydrolysis products (Table 12). Garton and Bywater[85] explained the changes in the ultraviolet spectra of the polybutadienyl chains with lithium and sodium counterions after the introduction of the monomer at a low temperature (in THF) by the isomerisation of the terminal unit. The 285 and 336 nm absorption bands were assigned to the more stable *cis*-forms, while the 320 and 350 nm bands, arising after the introduction of the monomer, were assigned to the *trans*-forms of the lithium and sodium derivatives respectively.

Table 12. Structures of the hydrolysis products of the neopentylallyl derivatives of lithium, sodium, and magnesium (NPAM).

Compound	Solvent	Content of units, %			Refs.
		trans-1,4	*cis*-1,4	1,2	
NPAS	THF	27	54	20	64
NPAL	n-pentane	75	23	2	57
NPAL	DEE	68	21	11	60
NPAL	THF	49.4	36.9	13.7	
NPAM	n-pentane	42.7	19.2	38.1	63
	DEE	17.7	11.7	70.5	

The study of "living" chains with a potassium counterion is complicated by the still more intense irreversible changes which occur even at −70° C.[85] Basova and coworkers[67,68] studied polybutadienylsodium (PBS) and polybutadienylpotassium (PBP) in a hydrocarbon medium by infrared spectroscopy. In the region of the stretching vibrations of the terminal C–C bond, the following absorption bands were found (cm^{-1}): 1555 (main band) and 1535 and 1570 (shoulders) for PBS and 1570 (main band) and 1535 and 1555 (shoulders) for PBP. These characteristics indicate a greater degree of delocalisation of the above bond in PBS and PBP than in the lithium derivatives (see above). The authors attribute the 1555 cm^{-1} band in the spectrum of PBS to the presence of a certain amount of lithium alkoxide formed in the course of the synthesis[68] and interacting with the sodium counterion and assume that lithium alkoxide may not affect PBP owing to the low electron-accepting capacity of potassium[67,68].

The state of the terminal alkenyl unit with a magnesium counterion is described by a scheme[63] based on ^{1}H NMR data for a solution of neopentylallylmagnesium (NPAM) in THF at room temperature:



At a reduced temperature (~ −40° C) the attainment of equilibrium is retarded and the signals due to the *cis*- and

† The references to earlier studies by Medvedev and coworkers, who considered these questions, are listed by Medvedev and Gantmakher[101].

‡ Data for −40° C; the "living" polymers were obtained under the influence of sodionaphthalene.

trans-isomers, present in comparable amounts, are distinguishable. The contents of units having different structures in the hydrolysis products of an ethereal solution of NPAM were 17.7, 11.7, and 70.5% for the *trans*-1,4-, *cis*-1,4-, and 1,2-units respectively. Consequently the conclusion that the content of the *cis*-units is reduced with decrease of the amount of ionic character of the C–Mt bond has been confirmed in this instance too. On the other hand, the content of the 1,2-units in NPAL, NPAS, and NPAM is not directly related to the electronic structure of the corresponding alkenyl units (Table 12).

4. Derivatives of Polar Monomers

The formation of "living" chains of the type M_nMt, where M is a polar monomer, is usually difficult owing to their lower stability compared with the hydrocarbon chains and the side reactions, which occur differentially in the initial stage of the synthesis [107]. Side reactions can be virtually eliminated by a procedure involving the interaction of the "living" hydrocarbon chains (for example, butadiene or styrene chains) and small amounts of polar monomers. When certain conditions are observed, this ensures the introduction into the non-polar chain of several terminal units of the polar monomer. This procedure has proved particularly useful for acrylonitrile (AN) and methacrylonitrile (MAN), whose polymers are soluble only in solvents which tend to interact irreversibly with organometallic compounds (dimethylformamide, dimethyl sulphoxide, etc.). The determination of the spectroscopic and electrochemical characteristics of the chains corresponding to these monomers is possible only for macromolecules containing a fairly long non-polar block. Some of the data of Tsvetanov and coworkers [108,109] for the electronic spectra and dissociation constants (K_d) of macromolecules of the above type, consisting of a butadiene block (40–50 units) and 2–3 terminal AN units, are presented below (25°C):

Solvent	Iso-octane		THF		
Mt	Li	Na	Li	Na	K
λ_{max}, nm	330.5	337.5	342	345	351
$10^9 K_d$, mole litre^{-1}	—	—	2.4	4.0	30.0

The infrared spectra of analogous substances with a styrene main block, recorded in benzene (20°C) and THF (–40°C) [110], indicate a significant difference between the absorption band due to the nitrile group of the –CH(CN)Mt fragment and the band characteristic of the usual nitriles, including polyacrylonitrile (PAN). Thus "living" chains with Li^+, Na^+, and K^+ counterions absorb in the range 2030–2040 cm^{-1}, while PAN absorbs at 2235 cm^{-1}. The first of the above bands refers to chains containing one AN unit. An increase in the number of such units leads to a hypsochromic shift of this band (particularly 2032 → 2040 and 2042 → 2049 cm^{-1} for chains with potassium and lithium counterions respectively) and to the appearance of new bands, including a band which virtually coincides with that observed in the spectrum for the unperturbed nitrile group (2235–2040 cm^{-1}).

The conclusion concerning the strong interaction of the counterion and the polar group of the macromolecule, which follows from these results, agrees with the finding in one of the studies quoted above [109] that there is no association between the chains and the lithium counterion in a hydrocarbon medium (this conclusion is based on viscometric data), which distinguishes them from organolithium compounds with non-polar constituents. Strong intramolecular interactions apparently rule out in this instance intermolecular interactions, responsible for the formation of associated forms $(RLi)_n$, typical for lithium alkyls and lithium alkenyls. The same factor can also account for the much lower values of K_d (approximately by two orders of magnitude) compared with the analogous values for hydrocarbon chains M_nMt. [5]

Results similar to those described above have been obtained for MAN. [111] The use of oligostyryl-lithium as the initial organometallic compound made it possible to obtain soluble blocks of "living" oligomers containing up to six MAN units in the chain. The dependence of the spectroscopic characteristics of these substances on the number of MAN units is illustrated in Fig. 5.

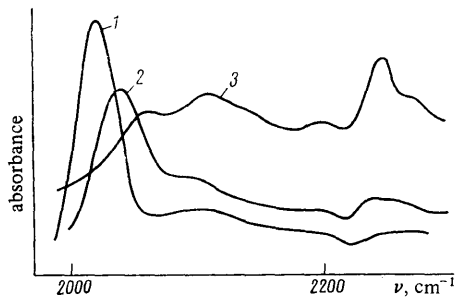
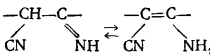
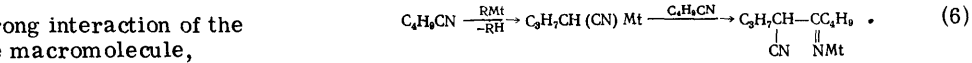


Figure 5. Infrared spectra of oligostyryl chains with terminal MAN units and a lithium counterion in benzene at 20°C. [110] Initial MAN :OStL molar ratio: 1) 1; 2) 2.2; 3) 5.5.

In order to achieve a correct assignment of the absorption bands and bands located in the intermediate region (between –2100 and 2200 cm^{-1}), the infrared spectra of model compounds based on valeronitrile (VN) and trimethylacetonitrile (TN) were obtained [110,111]. Oligostyryllithium was used as the organometallic component in these systems. When the ratio BH : RMt = 1 (with THF as the solvent), the infrared spectrum shows bands at 2030 (the most intense) and 2100 cm^{-1}. An increase of the BH : RMt ratio to three causes the disappearance of the first band and a significant increase of the intensity of the second. Treatment with ethanol of the reaction mixture obtained for the ratio BH : RMt = 3 causes the appearance of the spectroscopic characteristics of the equilibrium system [112]:



This is a direct indication of the presence in the initial reaction mixture of imidonitriles, the formation of which has been described schematically as follows [110]:

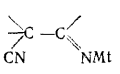
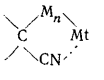


(6)

Among the data obtained for systems with participation of TN, those for the interaction of TN with an active reagent containing a terminal MAN unit are of interest. Steric hindrance rules out in this instance the occurrence of a type (6) reaction and limits the interaction to complex

formation, as shown by the appearance of a new band in the high-frequency region (2260 cm^{-1}), the intensity of which increases with increase of the concentration of any component. We may note that a small shoulder has been noted in this region in the infrared spectrum of chains with an increased number of MAN units (Fig. 5), which may be attributed to the formation of intramolecular complexes of the counterion with a nitrile group in the polymer chain.

The results described make it possible to adopt the following assignment of the infrared bands for the "living" AN and MAN chains:

ν, cm^{-1}	2030—2050*	2100—2170	2250—2260
Group			
	(IV)	(V)	(VI)

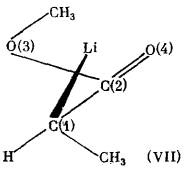
*Similar frequencies (2050–2071 cm^{-1}) were obtained by Yuchnovski[113] for lithioacetonitrile in polar solvents and in the solid state; the bands in this region were assigned to the ionic structure $(CH_2{=}C{\equiv}N)^-Li^+$.

In real AN anionic polymerisation processes the formation of macromolecules is ensured by substances (IV). The formation of intra- or inter-molecular complexes of type (VI), which are capable of being converted into imidonitriles (V), is favoured when the reaction is carried out in non-polar media. The sequence of steps (IV) → (VI) → (V) is responsible for the low effectiveness of initiation in AN–RMt–hydrocarbon solvent systems; the formation of imides (V) is virtually equivalent to kinetic chain termination. The occurrence of the last reaction can be readily detected from the presence of carbonyl groups in deactivated AN polymers and oligomers[114,115].

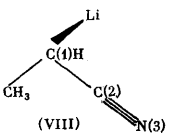
The infrared spectra of compounds simulating the anionic active centres of methyl methylacrylate (MMA) are more difficult to interpret. Lochmann and Lim[116], who synthesised the compound $(CH_3)_2C(COOCH_3)Li$, attributed the absorption of its THF solution in the region of 1676 cm^{-1} to the carbonyl group; in the spectrum of the initial methyl isobutyrate the absorption at 1730 cm^{-1} corresponds to this group. According to Panayotov and coworkers[117,118], the absorption in the range 1605–1635 cm^{-1} (in THF) is characteristic of terminal MMA–Mt units, where Mt = Li, Na, or K. Zgonnik et al.[119] obtained the infrared spectra of the products of the interaction of various compounds RLi with MMA in non-polar media. The following absorption regions, referring to terminal units, were observed: 1620–1645, 1670–1680, and 1710–1755 cm^{-1}. The last of these may be due to the formation of intra- and inter-molecular complexes analogous to those noted above for "living" AN chains [see structure (VI)].

According to Figueruelo[120], the values of K_d for "living" MMA chains with Li^+ and K^+ counterions are 0.44×10^{-9} and 0.21×10^{-9} respectively (THF, −78° C). Quantities of a similar order of magnitude have been obtained[121] for "living" chains of 2-vinylpyridine (VP): 0.83×10^{-9} (Na); 2.45×10^{-9} (K); 1.05×10^{-9} (Cs) (in THF at 23° C). The different types of dependence of K_d on the nature of the counterion for "living" chains based on AN, MMA, and VP are striking. It appears that this is caused by the difference between the relative energy contributions; due to the decomposition of the intramolecular complexes and the solvation of the counterion.

The conclusion that there are intense intramolecular interactions in organometallic compounds with polar substituents agrees well with the results of quantum-chemical calculations by the CNDO/2 method for structures simulating the anionic AN and methyl acrylate active centres, namely $CH_3CH(Li)CN$ and $CH_3CH(Li)COOCH_3$.[80] Their optimum geometry indicates a significant mutual approach of the counterion and the polar group of the active centre:



(VII)



(VIII)

	structure (VII)			structure (VIII)			
X	C (1)	C (2)	O (3)	O (4)	C (1)	C (2)	N (3)
Li—X, Å	2.2	2.4	2.9	3.0	2.1	2.2	2.8

IV. CONCLUSION

In conclusion we shall attempt to estimate the importance of information of the above kind for the determination of the mechanism of the formation of macromolecules in anionic systems. A detailed examination of this problem, different aspects of which have been discussed in many original and review publications (see, for example, Refs. 5, 62, 101, 122–125), is outside the framework of the main topic of the present review. We shall therefore confine ourselves to several comments on polymerisation under the influence of lithium compounds.

In all the "living" dienyl chains investigated the existence of only the 1,4 (or 4,1)-structure of the terminal unit has been noted with the predominant content of the *trans*-form in non-polar media and of the *cis*-form in ethereal media. When an attempt is made to reconcile this finding with the opposite type of structure of the polymers formed in the corresponding systems (the maximum content of the *cis*-1,4-units in polybutadiene and polyisoprene is reached in polymerisation in a non-polar medium), it is necessary to take into account at least two factors. The first and possibly the most important factor is that the fixation of the structure of the elementary unit of the growing chain occurs only after the addition of the succeeding monomer molecule to the terminal unit. This result indicates a conformational rearrangement of the terminal unit (characterised by a partly delocalised electronic structure) in the propagation stage. The second factor is the different states of organolithium compounds: stable associated species $(RM_nLi)_x$ in non-polar media and monomeric forms of the complexes $RM_nLi.mED$ in media of the ethereal type. At the same time, under the polymerisation conditions usually employed, the main contribution to the propagation reaction comes from the unassociated forms of the growing chains regardless of the nature of the medium. The experimental difference between the structures of the terminal units in media of different polarities cannot therefore be regarded as a basis for inferring the structural characteristics of the active centres operating in the same media. It is quite likely that the terminal units of the monomeric forms of the "living" polydiene chains with a lithium counterion have the *cis*-structure in non-polar media; this view can be found in the literature[56,126]. Another important problem concerns the 1,2-units (or 3,4-units) in polydienes, i.e. structural units whose appearance in macromolecules is most difficult to attribute to the direct experimental characteristics of the

"living" chains. In relation to non-polar media, the solution of this problem may be based on the concentration (with respect to the growing chains) variation of the polymer structure; the content of vinyl(or isoprenyl) groups in polydienes increases with increase of the initiator concentration[56,91,127,128]. One of the possible explanations of this effect is the involvement of the associated forms of the growing chains in the progagation reaction and the increase of the relative contribution of these steps with increase of the initiator concentration[56,128]. According to Glaze et al.,[57] the reaction between the monomer and the associated species $(RM_nLi)_x$ can occur to a large extent as a result of attack on the γ-carbon atom of the terminal unit, since the α-carbon atom in the associated species is highly shielded. A natural consequence of the attack on the γ-carbon atom is the formation of 1,2- or 3,4-units. The decrease of the content of 1,4-units in polydienes on passing from non-polar to polar media and in the presence of catalytic amounts of polydentate electron donors can be explained similarly. We have in mind the partial shielding of the α-carbon atom in the solvation shell of a polar solvent surrounding the counterion, in the first instance, and the analogous effect in the formation of complexes of the active centres with electron donors containing bulky substituents or having large intrinsic dimensions, in the second. Together with steric considerations, account must be taken of the charge redistribution in the carbanionic fragment of the terminal unit on complex formation, namely the increase of the negative charge of the γ-carbon atom, which follows from NMR data[6,36,60,62].

We may note finally that the formation of intermediate complexes of the counterion with the monomer may be important for the microstructure of the polymers. In particular, the conformation of the monomer molecule in such complexes may be regarded as one of the factors determining the site of the attack on the terminal unit in the propagation stage. Unfortunately, this problem, as well as certain others among those discussed above, have not so far been studied experimentally. The quantum-chemical research technique applied to systems approaching real systems to the maximum possible extent may prove fruitful. Naturally the extent of studies in this field is still insufficient for more definite comments on this topic. Nevertheless the likely usefulness of this approach, which follows partly from the data presented in the present review, is evident from our point of view. The problem is discussed in greater detail by Eizner and Erusalimskii[129].

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