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The Reactivity of Aromatic Dialkenyl Compounds in Polymerisation Reactions

R.M.Nasirova, L.S.Murav'eva, E.A.Mushina, and B.A.Krentsel'

An attempt has been made for the first time to survey and describe systematically data on the characteristics of the polymerisation of aromatic dialkenyl compounds. The mechanisms of radical, cationic, and anionic polymerisations of these compounds as well as the structures of the resulting polymers, which are of theoretical and definite practical interest, are examined.
The bibliography includes 36 references.

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I. INTRODUCTION

Aromatic dialkenyl monomers (divinylbenzene and diisopropenylbenzene) are of interest for the synthesis of polymers of various structures by virtue of their ready availability and relative resistance to spontaneous polymerisation.

p-Diisopropenylbenzen (*p*-DIPB) polymerises in the presence of cationic catalysts to saturated and unsaturated polymers containing benzene rings in the main chain. In contrast to the *m*- and *p*-isomers, the radical polymerisation of *o*-divinylbenzene (*o*-DVB) yields a partly cyclised polymer. Anionic processes initiated by organolithium compounds give rise to considerable possibilities for the controlled synthesis of polymers with a definite set of properties, block copolymers, reactive oligomers, and polyfunctional polymerisation catalysts.

The relative reactivity of monomers in polymerisation depends on the polarity of the double bond, the stability of the active species formed when the monomer adds to the growing chain, and the steric hindrance in the transition state. In considering the radical, cationic, and anionic polymerisations of aromatic dialkenyl compounds, we therefore took these factors into account.

II. RADICAL POLYMERISATION

The reactivity of substituted styrenes in radical polymerisation has been widely studied[1]. Styrene is known to have a high electron density in the double bond (−0.80). The benzyl radical is greatly stabilised as a result of conjugation with the benzene ring. Depending on the type of group introduced and its position, in ring-substituted styrenes there is a possibility of both an increase and a decrease of the resonance stabilisation of the radical. The replacement of the hydrogen in the vinyl group of styrene can also influence the polarity of the monomer, the resonance stabilisation of the corresponding radical, and the steric hindrance in the transition state. Thus the presence of the methyl group in the α-position makes the vinyl group more electronegative but less reactive than the vinyl group in styrene, which can be due to steric hindrance.

A substituent in the *para*-position is known to influence the reactivity of styrene; *meta*-substitution has little or no influence on its reactivity. Hart[2] explains this difference by the fact that the *meta*-isomer is incapable of involvement in the resonance stabilisation of the charge, while the *para*-isomer is involved in this type of stabilisation.

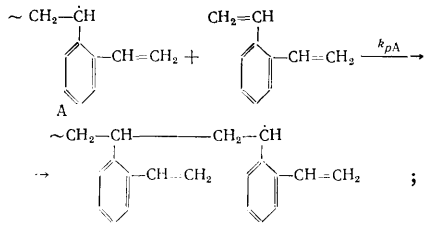
In radical polymerisation the propagation rate constants for the given polymer depends both on the reactivity of the monomer itself and on the reactivity of the radical formed from it. Thus an increase of conjugation energy, which tends to increase the stability of the radical, also increases the reactivity of the initial monomer[3].

It has been shown[4] that *m*- and *p*-divinylbenzenes are fairly actively involved in copolymerisation with styrene, forming three-dimensional copolymers. The copolymerisation of *m*- and *p*-divinylbenzenes with styrene, initiated by benzoyl peroxide, has been studied[5]. Analysis of the copolymer for a degree of conversion of 2−3% led to the following constants for the copolymerisation of styrene (r_1) with *m*-divinylbenzene (r_2) and of styrene (r_1') with *p*-divinylbenzene (r_3): $r_1 = 0.54$; $r_2 = 0.58$; $r_1' = 0.15$; $r_3 = 1.22$, i.e. the vinyl group in *p*-divinylbenzene is more reactive than in *m*-divinylbenzene.

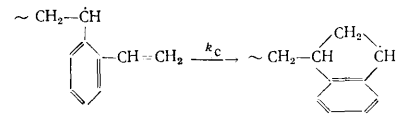
There is a reversal of reactivities in the homopolymerisation of *m*- and *p*-divinylbenzenes using isobutyrodinitrile as the initiator: *m*-divinylbenzene is more reactive than *p*-divinylbenzene, i.e. the alkenyl group in the *para*-position has a stabilising influence on the *p*-divinylbenzene radical[6]. The homopolymerisation of *p*- and *m*-divinylbenzenes has also been studied in the presence of benzoyl peroxide up to the gel point[7]. It was shown that the *meta*-isomer is also more reactive.

In contrast to *m*- and *p*-divinylbenzenes, the polymerisation of *o*-divinylbenzene yields in most cases soluble polymers containing five-membered rings and double

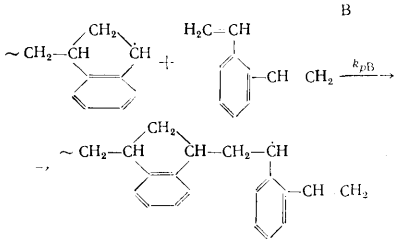
bonds in the side chain. *o*-Divinylbenzene has been polymerised at different temperatures in the presence of α,α'-azobisisobutyronitrile in benzene[8]. The residual unsaturation was determined spectroscopically and by bromination in CCl_4. The study led to three chain propagation mechanisms:



(1)



(2)



(3)

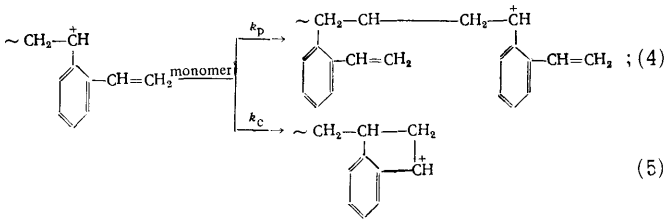
The content of monomeric units with vinyl groups diminishes with increase of the concentration of the monomer in the initial mixture and with increase of polymerisation temperature, since favourable conditions are then created for cyclisation. This finding can be explained by the difference between the activation energies for the propagation of the polymeric chain [reaction (1)] and for the intramolecular cyclisation reaction [reaction (2)]: the growing radical A has a somewhat greater resonance energy than the styrene radical and the cyclic radical B has a smaller resonance energy.

Like other allylic compounds, DIPB has a mobile hydrogen atom at the α-carbon atom. As a result of this, the copolymerisation of various monomers with DIPB leads to copolymers with a low molecular weight[9-11]. The rate constants for chain transfer to DIPB, found from the dependence of the degree of polymerisation of styrene on the concentration of the divinyl monomer in the initial mixture, have been published[12]. They are $8.59 \times 10^{-2} \pm 1.5 \times 10^{-5}$ for *m*-DIPB and $8.43 \times 10^{-2} \pm 3.6 \times 10^{-5}$ for *p*-DIPB (evaluated by the method of least squares), i.e. they are fairly large and almost equal, regardless of the position of the isopropenyl groups in the benzene ring.

III. CATIONIC POLYMERISATION

The cationic polymerisation of aromatic dialkenyl hydrocarbons was studied previously[13,15] in relation to *o*-divinylbenzene and *p*-di-isopropenylbenzene.

It is suggested that the *o*-divinylbenzene chain propagation reaction includes two competing stages: intermolecular propagation [reaction (4)] and intramolecular cyclisation [reaction (5)]:



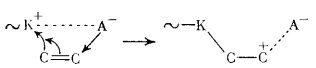
(4)

(5)

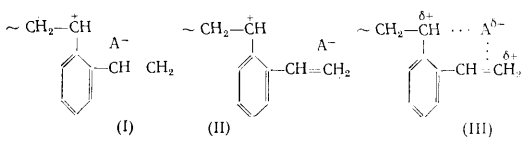
The cyclisation constant is defined as the ratio of two constants:

$$r_c = \frac{k_c}{k_p}$$

In cationic polymerisation, particularly in media with a low dielectric constant where the counterion is linked to the growing centre, the step involving the growth of the polymeric molecule can be represented as a result of the concerted donor–acceptor action by the carbonium ion–counterion pair on the double bond of the monomer:



The structure of the growing ion pair therefore depends on the nature of the anion. Thus the following cases are possible:



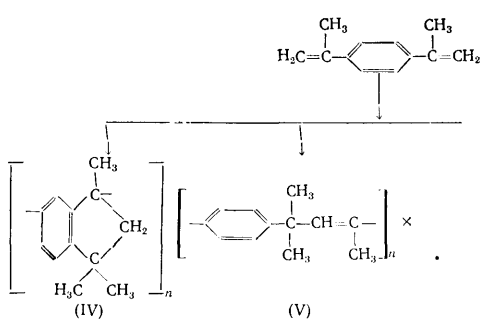
(I) (II) (III)

(Here A^- is the counterion).

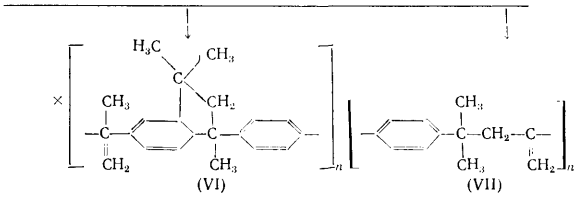
An interesting correlation has been found between r_c and the primary ionisation potential of the metal[13,14]. Thus the sequence of primary ionisation potentials Al > Ti > Sn > Fe > B > Zn agrees with the variation of r_c (excluding Ti and Sn). Strong Lewis acids lead to the ion pair (I) and a low value of r_c.[15] The weak interaction of the cation with the counterion permits the formation of the active cation (II) or the spreading of the positive charge to the vinyl group of (III) which failed to react. In polar highly solvating media the carbonium ion can form a free ion pair. The interaction with the vinyl group is therefore evidently replaced by the interaction with the molecules of the polar solvent, reducing the contribution of intramolecular cyclisation. The constant r_c increases with increasing temperature: 0.22 mole litre^{-1} at −20°C and 1.2 mole litre^{-1} at 20°C [15] (for divinylbenzene).

It has been shown[16,17] that *p*-DIPB polymerises under the influence of a cationic catalyst ($TiCl_4$, $SnCl_4$) to saturated and unsaturated polymers containing benzene rings

in the main chain:



(IV) (V)



(VI) (VII)

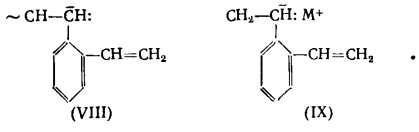
The polymers obtained exhibit a high heat resistance and thermal stability. It has been established on the basis of infrared spectroscopic data [17] that the saturated polymers have structure (IV) (an indan structure), while unsaturated polymers have structures (V)–(VII).

IV. ANIONIC POLYMERISATION

Evidently the possibility of the interaction of the π electrons of the double bond with the active centre in cationic polymerisation promotes cyclisation, whereas this type of interaction is less likely in anionic polymerisation. The polymerisation of *o*-divinylbenzene in the presence of anionic catalytic systems has been investigated [18] under different conditions. It was established that the cyclisation constant in anionic polymerisation is smaller than in the free-radical and cationic polymerisations. It is 2–4 mole litre^{-1} in free-radical polymerisation, 0.1–5 mole litre^{-1} in cationic polymerisation, and in most cases less than 1 mole litre^{-1} in anionic polymerisation.

The influence of solvent polarity, the nature of the alkali metal, and reaction temperature on the cyclisation constant has also been studied [18]. It follows from the experimental data that r_c increases with increasing solvent polarity in the sequence: tetrahydrofuran < ether < dioxan. The constant r_c in tetrahydrofuran varies with increasing temperature from 0.05 mole litre^{-1} at −78°C to 0.56 mole litre^{-1} at 20°C.

The nature of the solvent and the alkali metal (M) is known to influence the reactivity of the ion pair in anionic polymerisation. The uncyclised anion of *o*-divinylbenzene can exist as the free ion (VIII) and the ion pair (IX):



(VIII) (IX)

It was noted that the addition of $NaBPh_4$ to the polymerisation system lowers the reactivity of the ion pair and r_c. A free-anion propagation has therefore been suggested [18] for intramolecular cyclisation. As shown in Fig. 1, r_c diminishes also with increasing ionic radius of the counterion ($Li^+ > Na^+ > K^+$) in tetrahydrofuran; in dioxan the sequence based on the variation of r_c is reversed. It is suggested that the maximum degree of solvation of the Li^+ ion in tetrahydrofuran leads to the most reactive ion pair. In ether r_c diminishes in the sequence $K^+ > Li^+ > Na^+$. [18] The constant r_c in ether (dielectric constant $\epsilon = 4.3$ at 20°C) is intermediate between the value in tetrahydrofuran ($\epsilon = 7.4$ at 25°C) and in dioxan ($\epsilon = 2.2$ at 25°C).

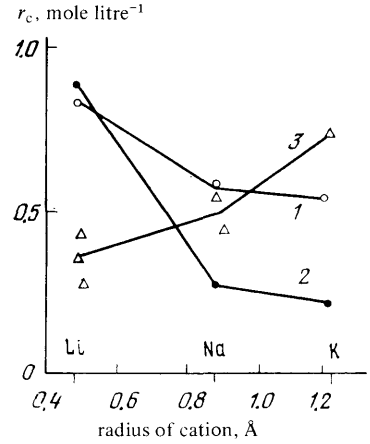


Figure 1. The effect of the counterion on the cyclisation constant of *o*-divinylbenzene in tetrahydrofuran: 1) at 20°C; 2) at 0°C; 3) the effect of the counterion on the cyclisation constant in dioxan at 20°C.

Thus one may conclude that the higher the reactivity of the growing ion pair, the greater the cyclisation constant.

The available data for the influence of the monomer structure on the rate of chain propagation refer mainly to the addition of free ions. The kinetics of many anionic polymerisation processes involving vinyl compounds in tetrahydrofuran with Na^+ as the counterion have now been investigated. The copolymerisation data are most important. Thus the following bimolecular rate constants have been obtained for the addition of a series of dienes to living polystyrylsodium in tetrahydrofuran at 25°C: [19]

Diene	$k_{1,2}$, litre mole^{-1} s^{-1}
Butadiene	32.7
Isoprene	17.0
2,3-Dimethylbutadiene	0.4 - 0.5

Such decrease of the rate can be explained both by the inductive effect of the methyl groups and by steric factors.

In the study of the copolymerisation of α- and β-methylstyrenes with "living" polystyrylsodium it was shown that both isomers are 40–50 times less reactive than styrene.

Steric hindrance is responsible for the very low reactivity of vinylmesitylene. In this case the breakdown of the coplanarity of the vinyl and phenyl groups lowers the reactivity of the monomer[20].

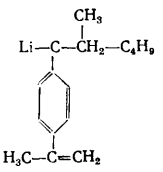
A detailed study of the relation between the structure of the monomer and its reactivity was carried out by Shima et al.[21]; the results are presented in Table 1.

Table 1. The rate constants $k_{1,2}$ for the addition of styrene derivatives to polystyrylsodium in tetrahydrofuran at 25°C.

Monomer	$k_{1,2}$, litre mole^{-1} s^{-1}
Vinylmesitylene	0.9
β-Methylstyrene	18.0
α-Methylstyrene	27.0
p-Methoxystyrene	50.0
p-t-Butylstyrene	110.0
2,4-Dimethylstyrene	160.0
p-Methylstyrene	180.0
o-Methylstyrene	320.0
Styrene	950.0

All the data examined above show that the addition of styrene derivatives to polystyrylsodium has a nucleophilic mechanism.

It might have been expected that the presence of the isopropenyl group in the *para*-position in *p*-DIPB would facilitate the addition of n-butyl-lithium to one of the two isopropenyl groups as a result of the increase in the length of the conjugated chain. However, the compound obtained is not capable of reacting further with n-butyl-lithium under the same conditions owing to the presence of an electron-donating substituent in the *para*-position relative to the isopropenyl group.



The reactivity of hydrocarbon monomers in anionic polymerisation processes has been studied mainly in relation to styrene, its derivatives and dienes. The determination of the characteristics of the anionic polymerisation of aromatic dialkenyl monomers is important for the determination of the relation between the reactivity of the active centres and their structure. The principal features of the anionic-coordination polymerisation of *p*-DIPB have been investigated[22]. The kinetic curves for the polymerisation of *p*-DIPB in benzene at 50°C at different *p*-DIPB and n-butyl-lithium (n-BuLi) concentrations are illustrated in Figs. 2 and 3. The study of the dependence of the rate of polymerisation of *p*-DIPB on the concentrations of the monomer and the initiator showed[22] that the rate of polymerisation is directly proportional to the monomer and initiator concentrations: $w = k[M][n\text{-}BuLi]$. The overall activation energy for this process in the temperature range 30–50°C is 15.3 ± 1.5 kcal mole^{-1}.

The chain propagation reaction under the influence of organolithium compounds is known to involve the interaction of the monomer molecules with an unassociated active centre[23,24].

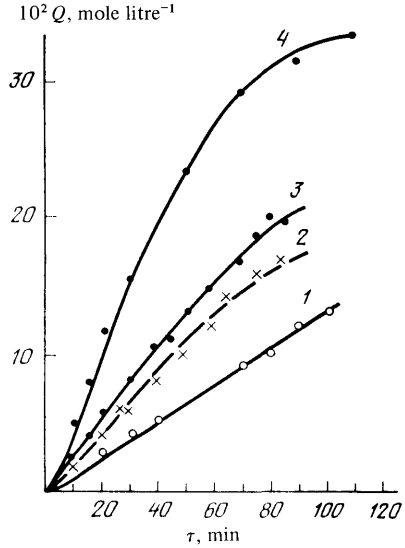


Figure 2. Kinetic curves for the polymerisation of *p*-DIPB under the influence of n-butyl-lithium in benzene at 50°C at different molar n-butyl-lithium concentrations: 1) 1.6×10^{-2}; 2) 3.5×10^{-2}, 3) 5.3×10^{-2}; 4) 8.4×10^{-2}; Q—the conversion of the monomer.

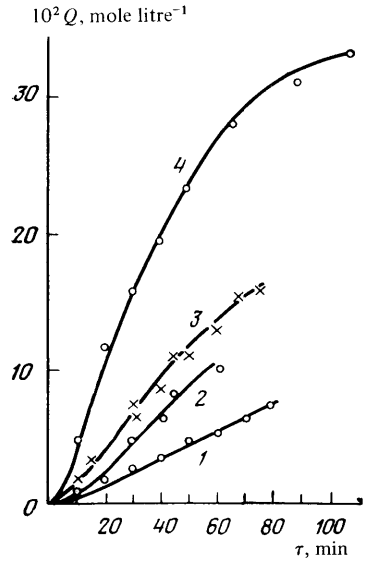


Figure 3. Kinetic curves for the polymerisation of *p*-DIPB under the influence of n-butyl-lithium in benzene at 50°C and different molar monomer concentrations: 1) 0.2; 2) 0.4; 3) 0.6; 4) 0.88.

It has been shown that the number of molecules in the associated species (n) and the stability of the latter increase in the sequence α-methylstyrene < isoprene < butadiene, i.e. the increase of the number and size of substituents in the carbanionic component of the active centre hinders association. Thus estimates by the kinetic method gave $n = 6$ for lithiopolybutadiene, 4 for polyisoprene, and 2 for polystyrene and poly-α-methylstyrene. The steric factors for p-DIPB fully inhibit association, as shown by the identical flow times of solutions of living and deactivated polymers at 50°C.[25]

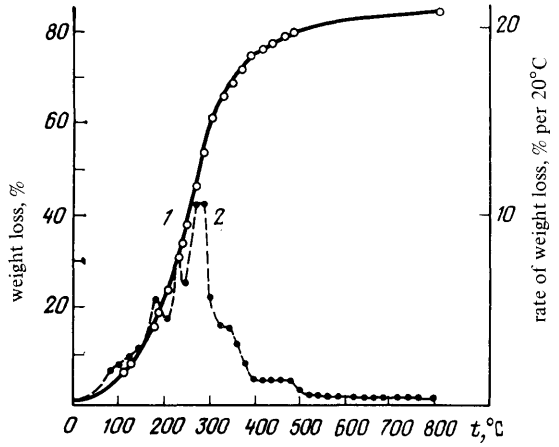


Figure 4. A gravimetric study of poly-p-DIPB in an atmosphere of argon: 1) weight loss (%); 2) rate of weight loss (% per 20°C).

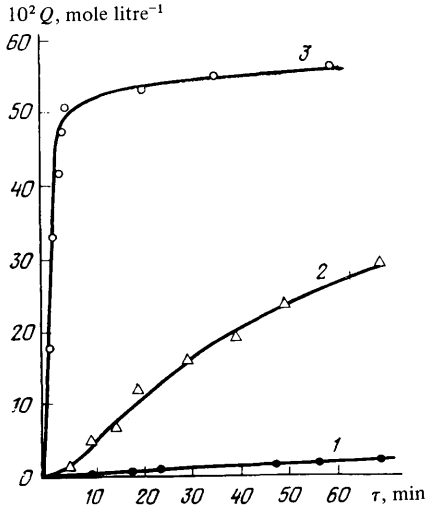


Figure 5. Kinetic curves for the polymerisation of α-methylstyrene (curve *1*), p-DIPB (curve *2*), and m-DIPB (curve *3*) in benzene.

The structure of poly-p-DIPB has been studied by infrared[26,27] and NMR spectroscopy[28]. It has been established on the basis of the changes in the intensity of the overtone C=CH_2 bond vibration band (1785 cm^{-1}), relative to the stretching vibration band (1620 cm^{-1}) characterising the vibration of the p-substituted benzene ring, that only one isopropenyl group is involved in the polymerisation of p-DIPB. The presence of the following structural elements has been established on the basis of the NMR spectra of the polymer: $CH_3-C\lesssim$ (chemical shift $\delta \simeq 0.4$ p.p.m.), $\gtrsim C-CH_2C\lesssim$ ($\delta = 1.4$ p.p.m.), $CH_3C =$ (two partly resolved peaks with $\delta = 2.05$ and 2.13 p.p.m.), CH_2 (several signals in the range $\delta = 5-5.4$ p.p.m.), and p-C_6H_4 (three peaks with $\delta = 6.6$, 6.9, and 7.2 p.p.m.).[28]

According to the results of thermomechanical analysis of poly-p-DIPB and the p-BIPB–butadiene copolymer, the glass point of poly-p-DIPB is 115°C and the yield point is 165°C; the glass point of the p-DIPB–butadiene copolymer is 41°C. A gravimetric study in an atmosphere of argon showed that the maximum extent of the main decomposition reaction of poly-p-DIPB is observed (on the basis of the overall weight loss of 88%) at 260–280°C (Fig. 4).[25]

In order to elucidate the influence of the second isopropenyl group on the polymerisation reaction under the influence of n-butyl-lithium, the authors[22] compared the reactivities of p-DIPB, m-DIPB, and α-methylstyrene. The kinetic curves for polymerisation in benzene (at 50°C) and in tetrahydrofuran (at 28°C), at monomer and initiator concentrations of 0.88 and 0.08 M respectively, established that the reactivities of the monomers decrease in the sequence m-DIPB > p-DIPB > α-methylstyrene[22,29] (Fig. 5).

Table 2. The electrical conductivities of solutions of "living" α-methylstyrene, p-DIPB, and m-DIPB polymers in tetrahydrofuran (cell constant 2.8×10^{-2} cm^{-1})*.

Solution	Resistance, Ω	κ, Ω^{-1} cm^{-1}	$10^{-3}\Lambda$, Ω^{-1} mole^{-1} cm^2
Poly-α-methylstyryl-lithium	$4.6 \cdot 10^5$	$6.0 \cdot 10^{-7}$	$7.1 \cdot 10^{-6}$
Poly-p-DIPB-lithium	$6.0 \cdot 10^4$	$4.7 \cdot 10^{-6}$	$5.6 \cdot 10^{-5}$
Poly-m-DIPB-lithium	$15.0 \cdot 10^3$	$1.9 \cdot 10^{-5}$	$1.2 \cdot 10^{-3}$

*Notation: κ is the specific conductance and Λ the molar conductance.

The high relative reactivities of m- and p-DIPB in the chain propagation steps in polymerisation in the presence of n-butyl-lithium can probably be explained by the decrease of the energy of interaction of the components of the ion pair due to steric factors (the branching of the carbanion). The experimental electrical conductivities of solutions of "living" polymers (Table 2) indicate an increase of the polarity of the lithium–carbon bond on passing from α-methylstyrene to p- and m-DIPB and show that the energy of the interaction of the components of the ion pair of the active centre decreases with increasing role of steric factors[25].

The electronic absorption spectra of "living" p- and m-DIPB polymers[25] (Table 3) showed that, when a more electron-donating solvent is used, the absorption maximum

undergoes a bathochromic shift and λ_{max} for poly-*p*-DIPB-Li, which is close to λ_{max} for 1,1-diphenylalkyllithium (428 μm), is evidently determined by the branching of the carbanion. With decrease of the stability of the associated species owing to steric hindrance, the relative content of the monomeric form increases and therefore at fairly high n-BuLi concentrations (10^{-3} M) there is a bathochromic shift of the absorption maximum on passing from benzene to tetrahydrofuran.

Table 3. The absorption spectra of "living" *p*- and *m*-DIPB polymers (25°C, n-BuLi concentration 10^{-3} M).

Monomer	Solvent	λ_{max}, nm
m-DIPB	benzene	335
m-DIPB	tetrahydrofuran	405
p-DIPB	benzene	424-425
p-DIPB	tetrahydrofuran	448-450

Table 4. The half-wave potentials (relative to the saturated calomel electrode).

Substance	$-E_{1/2}$, V	$I_c = i^*_{lim}/c$, A mole^{-1}
α-Methylstyrene	2.619	$2.3 \cdot 10^3$
p-DIPB	2.448; 2.691	$2.15 \cdot 10^3$, $2.9 \cdot 10^3$
m-DIPB	2.617	$4.6 \cdot 10^3$

*Notation: I_c is the specific current, i_{lim} the limiting current, and c the concentration of the given substance in solution.

Thus the characteristics of the propagation reaction and the nature of the structure of the active centres in the anionic polymerisation of aromatic dialkenyl monomers under the influence of n-butyl-lithium have been elucidated by kinetic, spectrophotometric, and conductimetric methods [27].

V. THE DILITHIUM CATALYST BASED ON *m*-DIISOPROPENYLBENZENE

In the polarographic determination of the electron affinities of α-methylstyrene, *p*-DIPB, and *m*-DIPB, (Table 4) it was found [29] that the addition of electrons to the isopropenyl groups in *m*-DIPB takes place independently; in *p*-DIPB the influence of the isopropenyl groups is manifested by the formation of two separate waves and a considerable displacement of the value of $E_{1/2}$ for the first wave relative to that for α-methylstyrene. Consequently n-butyl-lithium can add to the two isopropenyl groups in *m*-DIPB. This phenomenon, which was previously unknown for the given class of compounds, has been used to obtain dilithium catalysts based on *m*-DIPB. [29] The 890–900 cm^{-1} band was found to be missing from the infrared spectrum of the product of the carboxylation of dilithio-*m*-diisohexenylbenzene, which indicates the simultaneous addition of n-butyl-lithium to the two isopropenyl groups. The 1,3-disubstitution of the ring is responsible for the appearance of bands at 720 and 805 cm^{-1}; the 860 cm^{-1} band refers to the vibrations of the C=O group of the carboxyl. The results of the elemental analysis of this compound are in good agreement with the calculated values [29].

The molecular weight of polystyrene (W), determined from the intrinsic viscosities, was consistent with the relation [30]

$$W = 2M/N,$$

where M is the amount (in grams) of the polymerised monomer and N is the number of moles of catalyst which have been consumed. Consequently the active centres are dianions. The activity of the dilithium catalyst based on *m*-DIPB in the polymerisation of styrene is close to that of s-butyl-lithium (Fig. 6).

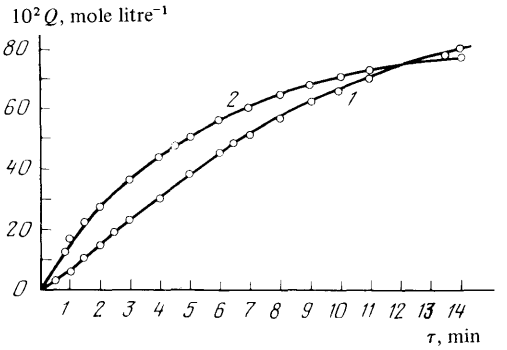


Figure 6. Kinetic curves for the polymerisation of styrene in the presence of dilithio-*m*-diisohexenylbenzene (curve *1*) and *s*-butyl-lithium (curve *2*) at 40°C; lithium concentration 3×10^{-3} M; styrene concentration 1 M; solvent—benzene.

The use of organodilithium compounds leads to extensive possibilities for the synthesis of ternary block copolymers of the type ABA and oligomers with terminal functional groups [31–36]. The previously known dilithium polymerisation initiators are largely insoluble in hydrocarbons or require the use of a homogenising comonomer, are frequently unstable, and require prolonged preparation.

Disodio, dilithio-, and dirubidio-α-methylstyrene tetramers, formed in the reaction between the alkali metal and a solution of α-methylstyrene in electron-donating media, have been described in the literature [34,35].

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Thus the literature data examined in the present paper review and their analysis reveal the considerable possibilities for the employment of aromatic dialkenyl compounds in macromolecular chemistry.

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Topchev Institute of Petrochemical Synthesis, Moscow