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U. D. C. 542.952.6 : 541.65

COPOLYMERISATION OF HYDROCARBONS IN THE PRESENCE OF IONIC CATALYSTS

L. S. Bresler

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1. INTRODUCTION

Comparison of the relative activities of monomers in copolymerisation has been successfully used to study the mechanism of chain growth in radical polymerisation. The copolymerisation constants yield quantitative estimates of the relative reactivities of monomers and of the corresponding active centres.

During recent years a great deal of attention has been paid to catalysts which bring about polymerisation by an ionic mechanism, in connection with the use of catalysts of ionic type for the synthesis of several polymers having valuable properties, especially stereoregular polymers. Data on copolymerisation provide a deeper insight into the mechanism of chain formation in cationic, anionic, and coordination–ionic polymerisation.

2. THEORETICAL CONCEPTS

A theoretical treatment of the problems involved in radical copolymerisation has been given, and we must therefore examine the possibility of applying to ionic polymerisation the relations obtained. Scheme (1), suggested by Alfrey and Goldfinger[1], considers four possible modes of chain growth in the copolymerisation of two monomers: i.e. the reactivity of the growing polymeric ion is assumed to depend on the nature of the terminal active unit in the chain, and the rate constant for chain growth to be determined by the reactivity both of the monomer and of the active centre. Here M* denotes a cation in the case of cationic polymerisation, and an anion in anionic polymerisation, while in the case of coordination-complex polymerisation it represents a catalytic complex bound to the active end of the growing chain.

$$\begin{aligned} &\sim M_1^* + M_1 \xrightarrow{k_{11}} \sim M_1^*, \\ &\sim M_1^* + M_2 \xrightarrow{k_{12}} \sim M_2^*, \\ &\sim M_2^* + M_2 \xrightarrow{k_{22}} \sim M_2^*, \\ &\sim M_2^* + M_1 \xrightarrow{k_{21}} \sim M_1^*. \end{aligned} \qquad (1)$$

When the concentration of growing chains is constant, we can apply the relationship that has been termed the fundamental equation of copolymerisation[1,2]

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]}\right), \qquad (2)$$

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are copolymerisation constants for the first and second monomers, representing the relative activities of the monomers towards addition to the active centres $\sim M_1^*$ (r_1) and M_2^* (r_2). Eqn. (2) is applicable to ionic copolymerisation only if the concentration of active centres remains constant during such processes. The necessity for this condition had already been noted by Landler[3,4], who was the first to generalise data on ionic polymerisation.

The presence of a constant concentration of active centres in several cases of cationic[5,6] and anionic[7-9] polymerisation has now been established by direct measurement, from the ultraviolet absorption spectrum, of the concentration of growing polymeric cations and anions during polymerisation. In the presence of complex organometallic catalysts, too, the concentration of active centres is usually constant as a result of the catalytic character of the process[10]. Consequently the general equation of copolymerisation is applicable to most cases of ionic copolymerisation. The relative reactivity of monomers in the growth reaction can be measured by the copolymerisation constants calculated from experimental data by the usual procedures developed for radical copolymerisation — by the intersection method based on the integral or differential equation of Mayo and Lewis[2,11] by Alfrey's method of trial and error[1], or by the method of Fineman and Ross[12].

Constancy of the concentration of active centres has different causes in radical and in ionic polymerisation. In the former case it arises from the fact that, during a given period of time, equal quantities of radicals are formed by initiation and disappear by termination reactions which lead to the destruction of active centres. In ionic processes, active centres cannot be destroyed by interaction with one another, because the polymer chains bear charges of the same sign[13]. Therefore the constancy of the concentration of active centres is not due to a balance between processes of creation and destruction but to the fact that many ionic processes are unaccompanied by the destruction of active centres — by processes of chain termination[6,10,13,14] — and active centres, once formed, can cause chain growth until no monomer remains. If in such cases initiation is sufficiently rapid, and formation of all the active centres is complete within a time which is considerably shorter than the duration of the whole process of polymerisation, a constant concentration of active centres will be established during the process[5-10].

In cationic polymerisation, initiation is usually rapid, and all the active centres begin to take part in chain growth almost at the same time[6,15]. With anionic polymerisation cases are known in which initiation occurs throughout the process of polymerisation, and then the condition that the concentration of active centres should be constant is not satisfied. This is observed when polymerisation occurs under the influence of organolithium compounds in hydrocarbon solvents at a catalyst concentration exceeding 0.02 M.[9,16] The low rate of initiation in these cases is explained by the high degree of association of the organolithium compound[9]. When copolymerisation is carried out under such conditions, account must be taken, in deriving the equation for the composition of the copolymer, of the initiation stage[17] (i.e. of the rate of interaction with the catalyst of each of the two monomers)

$$A^- + M_1 \xrightarrow{k_1} AM_1^-, \qquad A^- + M_2 \xrightarrow{k_2} AM_2^-, \qquad (3)$$

and only after this are the usual four possible growth reactions (1) considered.

Even in this case, however, the Alfrey–Goldfinger equation (2) is incapable of giving the composition of the copolymer correctly only when the anions formed from the different monomers differ greatly in activity. If the initiator can react with both monomers, while the anion AM_2^- is practically unable to add on the monomer M_1, the composition of the copolymer in the initial stages of polymerisation will be represented by the equation

$$\frac{d[M_1]}{d[M_2]} = (k_{11}/k_{12})(k_1/k_2)\left(\frac{[M_1]}{[M_2]}\right)^2, \qquad (4)$$

instead of by the fundamental equation of copolymerisation.

In the copolymerisation of styrene with methyl methacrylate, for example, the polystyrene anion initiates the polymerisation of both these monomers[18], whereas the poly(methyl methacrylate) anion does not bring about the polymerisation of styrene[19]. In this case — Eqn. (4) — the ratios of the mole fractions of styrene and methyl methacrylate in the copolymer and the monomer mixture are actually linked by a relation of the second degree[17].

The above can be summarised in the statement that equations obtained from an examination of radical processes of copolymerisation are general for all mechanisms of polymerisation, being inapplicable only in isolated special cases.

We at once adopted Alfrey and Goldfinger's scheme (1) to represent processes of ionic copolymerisation, i.e. we took into account the different reactivities both of the monomers and of the active centres formed from them. Differing activities of two polymeric anions is clearly exhibited in the above case of the copolymerisation of styrene and methyl methacrylate[18,19], in which the less active anion — the poly(methyl methacrylate) anion — does not initiate polymerisation of the less active monomer (styrene). Comparison based on quantum-mechanical calculations[20] of the reactivities of various monomers and of the ions obtainable from them has shown that, in cationic and anionic polymerisation, the more active monomer always yields the less active ion, just as in radical polymerisation the more active monomer gives the less active radical[21,22]. The correctness of this conclusion is confirmed by measurements of the absolute rate constants of all four stages of the growth reaction in copolymerisation. In the case of cationic polymerisation such data have been obtained[23] for the copolymerisation of isobutyl vinyl ether with chloroethyl vinyl ether under the influence of iodine in dichloroethane solution (Table 1). The less active monomer — 2-chloroethyl vinyl ether ($k_{12} < k_{11}$) — forms the more active cation ($k_{22} > k_{12}$).

TABLE 1. Absolute rate constants (in litre × × mole^{-1} min^{-1}) for the growth reactions in the copolymerisation of isobutyl vinyl ether (M_1) and 2-chloroethyl vinyl ether (M_2) in the presence of iodine in dichloroethane solution at 30°.

k_{11}	k_{12}	k_{22}	k_{21}
390	195	520	260

In the case of anionic polymerisation under the influence of "live" polymers, monomers which are less active than styrene ($k_{12} < k_{11}$) give an anion to which styrene adds on more rapidly than to the anion of polystyrene ($k_{21} > k_{11}$) (Table 2)[24]. Thus with anionic polymerisation, too, the less active monomer forms the more active anion. The only exception is provided by the anion of the dimer of 1,1-diphenylethylene, but this is due to the greater steric hindrance to the addition of styrene caused by the two phenyl groups of the anion.

Until recently most investigators, when discussing experimental data on ionic copolymerisation, ignored differences in reactivity between polymeric ions differing in their

TABLE 2. Absolute rate constants (in litre mole^{-1} s^{-1}) for the growth reactions in the copolymerisation of styrene (M_1) with other monomers in the presence of "living" polymers with Na as counter-ion in tetrahydrofuran solution. (Concentration of active centres 0.003 M at 25°.)

M_2	e_1	e_2	k_{11}	k_{12}	k_{22}	k_{21}
α-Methylstyrene	—0.80	—1.27	550	26	2.5	800
β-Methylstyrene	—0.80		550	18		
2,4-Dimethylstyrene	—0.80		550	160		
p-Methylstyrene	—0.80	—0.88	550	180	220	1000
o-Methylstyrene	—0.80	—0.78	550	330		
1,1-Diphenylethylene	—0.80		550	350		1
2-Vinylpyridine	—0.80	—0.50	550	30000	3500	very low rate

active terminal units ($\sim M_1^*$ and $\sim M_2^*$). It was usually accepted that the rate of addition of a monomer is independent of the nature of the end group in the polymeric ion[25-33]. Only two chain-growth reactions were then taken into account in copolymerisation[34]. Such a simplified view of ionic copolymerisation arose from an incorrect interpretation of the frequently observed cases of ideal copolymerisation in ionic processes[4,33]. In ideal copolymerisation $r_1 r_2 = 1$, i.e. $k_{11}/k_{12} = k_{21}/k_{22}$. Although it is sufficient, for this equation to be valid, that the rates of addition of monomer M_1 to the two polymeric ions should differ from the rates of addition of M_2 to these ions by the same factor ($k_{11} = Xk_{21}$ and $k_{12} = Xk_{22}$), Flory concluded that each monomer adds on to any ion at the same rate, i.e. $k_{11} = k_{21}$ and $k_{12} = k_{22}$, and thus the equation for the composition of the copolymer assumes the form of Wall's equation[34]

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1]}{k_{22}[M_2]}. \qquad (5)$$

It follows from these concepts that the copolymerisation constant for monomer M_1 with monomer M_2, $r_1 = 1/r_2 = k_{11}/k_{22}$, should be equal to the ratio of the rate constants for chain growth in the homopolymerisation of these monomers. However, this conclusion is contradicted by the experimental results. In the copolymerisation of butadiene with isoprene[29] and of butadiene[26,27,32] or isoprene[25,30,31] with styrene under the influence of organolithium compounds, the more active monomer (according to copolymerisation data) possesses the lower rate of homopolymerisation. In order to explain the "reversal of activity" the concept is introduced[25-32,35-48] of a selective solvation of an active centre by one of the monomers, which thus proves more active in copolymerisation. Calculation[26] based on kinetic data for the copolymerisation of butadiene with styrene in the presence of butyllithium has shown that, in order to explain the experimental differences between the copolymerisation constant and the ratio of the rates of homopolymerisation, the ability of butadiene to solvate an active centre must exceed that of styrene by a factor of 80. It is difficult to explain such a large difference in solvating power by the structural differences between butadiene and styrene.

If differences in the activity of polymeric ions towards the same monomer are taken into account, the contradictions discussed above do not arise. The more active monomer yields the less active ion[20]; if the ions exhibit greater differences in activity than do the monomers, the rate of homopolymerisation of the more active monomer will be smaller than that of the less active monomer ("reversal" of activity). Direct measurement of all four rate constants for chain growth in the copolymerisation of butadiene with styrene in the presence of butyllithium[35] has shown that the rates of addition of the butadiene molecule to the anions of polystyrene and of polybutadiene differ by a factor of 75, while the rates of addition of the two different monomers (styrene and butadiene) to the same anion (polystyrene or polybutadiene) differ by factors of 15 and 3 respectively. Thus it is evident that in this case the "reversal of activity" of the monomers in homopolymerisation compared with copolymerisation[26,27] is actually due to the greater differences in activity between the polymeric anions than between the monomers, not to selective solvation of an active centre by one of the monomers. If the simultaneous occurrence of four different reactions of chain growth is taken into account, it is possible[36] by means of the usual kinetic equations to calculate a rate curve for the copolymerisation of butadiene with styrene which agrees with the experimental results. Consequently the results of a kinetic study of copolymerisation also show that, in ionic as in radical copolymerisation, ions with different end-groups, as well as the monomers, show differences in activity.

Copolymerisation constants can be used to compare the relative activities of a series of monomers only when they relate to copolymerisation of all these monomers with the same standard monomer. It is therefore desirable for ionic copolymerisation to generalise all known values of relative reactivity in the form of a scheme resembling the $Q-e$ scheme of Alfrey and Price[21]. With ionic, in contrast to radical, copolymerisation however, the copolymerisation constants are usually found to depend on the nature of the catalyst and of the polymerisation medium[25,26,28,31,32,37-44] (Table 3, pairs 3, 4, 7, 8, and 11; Table 5, pairs 1, 4–6, 10, and 12). As a consequence, it has not yet proved possible to set up a scheme which will take into account all the factors influencing the relative activity of monomers in ionic copolymerisation.

Hammett's rule[45,46] is widely used for the quantitative correlation of the reactivity of monomers in ionic copolymerisation with their structure. This rule links the rate constants for reactions of benzene derivatives with the electronic characteristics of their substituents in the formula

$$\log(K/K_0) = \rho\sigma, \qquad (6)$$

where K and K_0 are rate constants (or equilibrium constants) for substituted and unsubstituted benzene derivatives in reactions of a given type, ρ is a constant characteristic of a given reaction (the reaction constant), and σ is a constant characterising a given constituent in all types of reactions. The actual value of the substituent constant σ depends on the type of reaction taken as standard, and is a quantitative expression of the electron-acceptor or electron-donor character of this substituent. The standard is chosen in such a way that the σ constant of electron-acceptor substituents is positive[45,46]. The influence of the polar effects of substituents on the rate constants is associated with a change in the activation energy during the reaction; if steric effects predominate, deviations from the Hammett rule are observed[45,46]. In comparing the activities of monomers undergoing polymerisation, the polar effect can be allowed for, not by means of the Hammett σ constant, which is known only for substituents in the benzene ring, but from the magnitude of the polar factor in the $Q-e$ scheme, since the quantity e also characterises the electron-donating or electron-accepting power of a substituent,

TABLE 3. Copolymerisation in the presence of catalysts of cationic type.

No. of pair	M_1	M_2	Catalyst	Medium	r_1	r_2	Ref.
1	2	3	4	5	6	7	8
1	styrene $e=-0.80$	*p*-chlorostyrene $e=-0.33$	$SnCl_4$	CCl_4	2.5±0.4	0.30±0.03	56
			$SnCl_4$	CCl_4	2.7±0.3	0.35±0.05	65
			$SnCl_4$	CCl_4–nitrobenzene (1 : 1)	2.2±0.2	0.45±0.02	56
			$SnCl_4$	nitrobenzene	2.2±0.05	0.35±0.05	56
			$AlBr_3$	CCl_4–nitrobenzene (1 : 1)	2.2±0.2	0.34±0.05	58
			$FeCl_3$	ditto	2.0±0.1	0.43±0.03	58
			$TiCl_4$	»	2.2±0.2	0.45±0.02	58
			TCl_4+CCl_3COOH	»	2.0±0.4	0.50±0.05	58
			I_2	dichloroethylene	2.5	0.45	68
2		*m*-chlorostyrene	$SnCl_4$	nitrobenzene	3.3±0.4	0.3 ±0.05	57
3		*p*-methylstyrene	I_2	dichloroethylene	0.2	4.2	68
		$e=-0.88$	$TiCl_4$	toluene, 0°	0.54±0.4	3.6 ±0.1	37
			$TiCl_4$	toluene, −78°	0.55±0.06	1.18±0.06	37
			$TiCl_4$	CCl_4	0.32±0.10	1.08±0.14	37
			$TiCl_4$	nitrobenzene	0.68±0.04	1.10±0.05	37
			$SnCl_4$	CCl_4–nitrobenzene (1 : 1)	0.48±0.07	1.18±0.14	37
4		*p*-methoxystyrene $e=-1.11$	$SnCl_4$	nitrobenzene	(0.01)	100	57
			$SnCl_4$	CCl_4–nitrobenzene (1 : 1)	−0.04±0.04	19±3	37
			$SnCl_4$	ditto	−0.02±0.07	29±5	37
			$AlCl_3$	»	0.34±0.05	11±1	37
			$TiCl_4$	»	0.12±0.07	14±3	37
			$TiCl_4$	CCl_4	0.05±0.04	46±3	37
			$TiCl_4$	CCl_4	0.00±0.03	31±6	37
			$TiCl_4$	CCl_4–nitrobenzene (1 : 1)	−0.12±0.12	35±5	37
			$TiCl_4$	nitrobenzene	0.48±0.08	5.6 ±0.8	37
			$TiCl_4$	nitrobenzene	0.22	7.6	37
			$TiCl_4$	toluene	0.01	72	37
			$TiCl_4$	toluene	−0.33±0.3	12±2	37
5		*m*-methoxystyrene	$SnCl_4$	nitrobenzene	0.90±0.15	1.1±0.15	57
6		*m*-nitrostyrene $e=+0.81$	$SnCl_4$	»	20±4.0	0.03±0.03	57
7		3,4-dichlorostyrene	$SnCl_4$	CCl_4	3.1±0.1	0.48±0.08	38
			$AlBr_3$	»	6.8±0.8	0.0 ±0.2	38
			$AlCl_3$ (solid)	»	2.8±0.2	0.45±10	38
			$TiCl_4$	»	7.2±0.5	0.38±0.20	38
			$BF_3\cdot(C_2H_5)_2O$	»	5.9±0.2	0.27±0.07	38
			$ZnCl_2+(C_2H_5)_2O$	»	4.2±0.2	0.10±0.05	38
			H_2SO_4	nitrobenzene	3.0±0.5	0.20±0.15	38
			$AlCl_3$ (solid)	»	3.5±0.5	0.0 ±0.2	38
8		*α*-methylstyrene $e=-1.27$	$SnCl_4$	C_2H_5Cl	0.05	2.90	67
9		isoprene $e=-1.22$	$SnCl_4$	C_2H_5Cl	0.8	0.1	65
10		butadiene $e=-1.05$	$AlCl_3$	monomer	$r_1 >$	r_2	60
11		chloroprene $e=-0.02$	$BF_3\cdot(C_2H_5)_2O$	cyclohexane	15.6	0.24	61
			$BF_3\cdot(C_2H_5)_2O$	n-hexane	12.8±0.3	0.06±0.01	40
			$BF_3\cdot(C_2H_5)_2O$	nitroethane	33.0±0.5	0.15±0.05	40
			$AlBr_3$	benzene	6.9±0.5	0.04±0.01	40
			$AlBr_3$	nitrobenzene	16.0±0.05	0.065±0.01	40
12		2-methylpropene $e=-0.96$	$AlCl_3$	CH_3Cl	1.99±0.24	9.02±0.77	66
			$SnCl_4$	C_2H_5Cl	0.17	1.6	67
13	*p*-chlorostyrene $e=-0.33$	*p*-methylstyrene $e=-0.88$	$SnCl_4$	nitrobenzene	0.22±0.05	4.5 ±0.7	57
			I_2	dichloroethylene	0.19	6.5	68
14		*m*-methoxystyrene	$SnCl_4$	nitrobenzene	0.38±0.05	2.6 ±0.4	57
15		*p*-bromostyrene $e=-0.35$	$SnCl_4$	»	1.0 ±0.1	1.0 ±0.1	57
16		*p*-ethylstyrene	$SnCl_4$	CCl_4–nitrobenzene (1 : 1)	0.29±0.04	4.1 ±0.5	59
17		*α*-methylstyrene $e=-1.27$	$SnCl_4$	ditto	0.35±0.05	15.0±1.5	59
			$SnCl_4$	CCl_4	0.3 ±0.05	15.5±1.5	57
18		*trans*-*β*-methylstyrene	$SnCl_4$	CCl_4–nitrobenzene (1 : 1)	0.74±0.06	0.32±0.04	59
19		*cis*-*β*-methylstyrene	$SnCl_4$	ditto	1.0 ±0.1	0.32±0.2	59
20		*β*-ethylstyrene	$SnCl_4$	»	0.88±0.33	0	59
21	*p*-chlorostyrene $e=-0.33$	2-methylpropene $e=-0.96$	$SnCl_4$	benzene	2.8 ±0.3	12.2±1.0	39,40
			$SnCl_4$	nitrobenzene	1.25±0.1	8.6±0.2	39,40
			$AlBr_3$	benzene	0.99±0.10	1.14±0.10	39,40
			$AlBr_3$	n-hexane	1.02	1.01	39,40
			$AlBr_3$	dichloroethylene	0.89	2.80	39,40
			$AlBr_3$	nitrobenzene	0.53±0.04	14.9±0.2	39,40
			$AlBr_3$	benzene–nitrobenzene (1 : 1)	0.75	18.0	39,40
			$AlBr_3$	nitromethane	0.73±0.05	22.2±0.5	39,40
22	*α*-methylstyrene $e=-1.27$	*p*-methoxystyrene $e=-1.11$	$SnCl_4$	nitrobenzene	0.30±0.1	15±5	57
23		*p*-dimethylaminostyrene $e=-1.37$	$SnCl_4$	»	0.035±0.015	31±19	57
24		*m*-methoxystyrene	$SnCl_4$	»	5±1	0.3±0.1	57
25		isoprene $e=-1.22$	$SnCl_4$	C_2H_5Cl	7.1	1.6	62
26	*p*-methylstyrene $e=-0.88$	*p*-methoxystyrene $e=-1.11$	$TiCl_4$	nitrobenzene	0.58±0.06	1.54±0.10	37
			$TiCl_4$	CCl_4	−0.03±0.07	3.7 ±0.4	37
			$SnCl_4$	CCl_4–nitrobenzene (1 : 1)	0.14±0.14	1.9 ±0.3	37
			I_2	dichloroethylene	0.30	4.3	68
27	isoprene $e=-1.22$	propene	$AlCl_3$	C_2H_5Cl	0.50	0.23	64
28		2-methylpropene $e=-0.96$	$AlCl_3C_2H_5$	benzene	r_1	$<r_2$	66
29		butadiene $e=-1.05$	$AlCl_3C_2H_5$	»	3.4±0.4	0.12±0.015	69
30	butadiene $e=-1.05$	2,3-dimethylbutadiene $e=-1.81$	$AlCl_3C_2H_5$	»	0.053±0.005	4.24±0.41	70

and is linearly related with σ, as has been shown for substituted styrenes[47,48].

Work on ionic copolymerisation is discussed in greater detail below. Results on copolymerisation in the presence of alkali metals and of the sodium–naphthalene complex are not included, since these processes involve the intermediate formation of ion-radicals[13,49,50], and may be complicated by simultaneous polymerisation by ionic and radical mechanisms[51-54].

3. COPOLYMERISATION BY MEANS OF CATALYSTS OF CATIONIC TYPE

In polymerisation by a cationic mechanism the growing chain is a carbonium ion[5,15,55]. Various Lewis acids are catalysts for cationic polymerisation. Results obtained for processes of copolymerisation occurring by a cationic mechanism are given in Table 3.[37-41,56-70]. Comparison of the copolymerisation constants shows that, when reacting with the same polymeric cation, the more active monomer is usually that in which the electron density on the double bond is the greater, in agreement with the view that growth of the polymer chain takes place with the latter in the form of a cation. The above rule is observed in the copolymerisation of styrene (Table 3, pairs 1–8), *p*-chlorostyrene (pairs 13–20), and α-methylstyrene (pairs 22-24) with nuclear-substituted styrenes, of styrene with chloroprene (pair 11) and with methylpropene (pair 12), of *p*-chlorostyrene with methylpropene (pair 21), of α-methylstyrene with isoprene (pair 25), of *p*-methylstyrene with *p*-methoxystyrene (pair 26), and of butadiene with isoprene and with 2,3-dimethylbutadiene (pairs 29 and 30). An exception is observed only in the copolymerisation of styrene with isoprene and with butadiene (pairs 9 and 10), when styrene is the more active monomer, although it has the lower value of e in the Q–e scheme (and hence a lower electron density on the double bond). Gantmakher and Medvedev[62] explain this exception by the participation of double bonds of the polymer in interaction with the active centres, as a result of which data on the composition of the copolymer do not reflect the true relation between the activities of the monomers in chain growth.

By means of the Hammett rule it is possible to obtain a quantitative estimate of the variation in copolymerisation constants with the electron-donor or electron-acceptor character of the substituent. The copolymerisation of *para*-substituted styrenes satisfies the relationship

$$\ln r_1 = \ln (k_{11}/k_{12}) = \ln k_{11} - \ln k_{12} = \rho_1(\sigma_1 - \sigma_2), \qquad (7)$$

where σ_1 and σ_2 are the constants of the substituents in the monomers M_1 and M_2. Table 4, taken from a paper by Tobolsky and Boudreau[37], gives values of ρ_1 for the copolymerisation of substituted styrenes in the presence of various catalysts (from data for the pairs 2–6 and 13–15 in Table 3). The negative value of the reaction constant ρ_1 also agrees with the concept of cationic chain growth in the presence of Lewis acids as catalysts. Furthermore, the linear dependence of $\ln r_1$ on σ shows that differences in the relative activity of *para*-substituted styrenes are determined not by steric but by polar factors — by differences in electron density on the double bonds of the monomers.

TABLE 4. Reaction constants ρ_1 in the cationic copolymerisation of substituted styrenes.

Catalyst	Medium	ρ_1	Monomer M_1
$TiCl_4$	nitrobenzene	−1.5±0.4	styrene
$TiCl_4$	»	−2.2±0.4	*p*-methoxystyrene
$TiCl_4$	»	−1.1±0.5	*p*-methylstyrene
$SnCl_4$	CCl_4–nitrobenzene (1 : 1)	−4.0±0.5	styrene
$SnCl_4$	ditto	−3.3±1.0	*p*-methylstyrene
$TiCl_4$	CCl_4	−4.2±0.8	styrene

Steric hindrance determines the relative activity of the monomers only when β-substituted styrenes are involved in copolymerisation (pairs 18–20). When reacting with a β-alkylstyrene end-group, the *p*-chlorostyrene molecule is more active than the β-alkylstyrene molecule ($r_2 < 1$), although the electron density on the double bond in *p*-chlorostyrene is smaller owing to the presence of an electron-acceptor substituent in the ring[59]. In copolymerisation with α-methylstyrene the relative activity of the monomers is determined by the relative electron densities on their double bonds (pairs 8, 17, and 22–25). This difference in steric hindrance, produced by substituents in the α- and β-positions of the vinyl group in styrene, is consistent with the view that attack by the polymeric carbonium cation is directed mainly on the β carbon atom of styrene (since the phenyl-substituted cation should be thermodynamically the more stable[71]).

The influence of the gegenion and that of the solvent on the kinetics of cationic homopolymerisation are usually attributed[55] to changes in the concentration of active cations resulting from different degrees of dissociation in solvents differing in dielectric constant or in ion-pairs with different gegenions. However, variation in ionic concentration would probably affect equally all four rates of growth in copolymerisation, and then the copolymerisation constants would not depend on the nature of the solvent or on that of the gegenion. Nevertheless, the relative activities of the monomers depend in several cases (pairs 3, 4, 8, 11, and 21) both on the nature of the gegenion and on that of the medium in which polymerisation is carried out. In the presence of different catalysts in the same solvent, the copolymerisation constants depend to different extents on the polarity of the monomer (this corresponds to different values of the reaction constant ρ_1 in the copolymerisation of substituted styrenes, Table 4). Variation in the copolymerisation constants when the process is carried out in different solvents or in the presence of different catalysts shows that, at least in some solvents, chain growth involves not free ions but ion-pairs.

Thus study of copolymerisation in the presence of Lewis acids has shown that — (1) the relationship between the relative activities of the monomers and the electron densities on their double bonds corresponds to a cationic mechanism of chain growth; (2) steric hindrance produced by β-substituents in styrene is consistent with the view that the styrene molecule adds on to the growing chain by the β carbon atom; and (3) since the use of different catalysts and solvents affects not only the kinetics of homopolymerisation but also the copolymerisation constants, the growing chain is usually not a free cation, chain growth probably occurring in ion-pairs.

4. COPOLYMERISATION BY MEANS OF CATALYSTS OF ANIONIC TYPE

The polymerisation of hydrocarbon monomers by an anionic mechanism is initiated by various organometallic

compounds and their complexes. According to modern views, first put forward by Ziegler[72], growth of the polymer chain occurs by introduction of monomer at a polarised metal–carbon bond, when separation of the charges on the polarised bond may lead to the formation of an ion-pair in which the active end of the growing chain is the anion[33,72-75]. In a series of organometallic compounds of the alkali metals, the ionic character of the bond increases on passing from lithium to sodium, potassium, rubidium, and caesium[76], as is shown in the polymerisation of dienes by a change in the structure of the polymer. In the presence of organolithium compounds, the polymers formed consist of 1,4 monomeric units; the polymers formed under the influence of organopotassium compounds contain a considerable quantity of 1,2 units[72,73]. The structure of the polydiene chain changes in the same direction if polymerisation under the influence of organolithium compounds is carried out in the presence of substances capable of forming "onium" complexes (ethers, amines, sulphides[72-75,77,78]). Hence it can be concluded that the ionic character of the lithium–carbon bond is enhanced by the coordination with lithium of electron-donor compounds, and in such solvents as tetrahydrofuran the process of polymerisation under the influence of organolithium compounds approaches in character a typically anionic polymerisation (such as, for example, polymerisation under the influence of organopotassium compounds)[74,75,77]. The influence of the counterion on the kinetics of polymerisation and the structure of the polymer shows that, in anionic polymerisation, chain growth involves not the free anion but an ion-pair or the polarised metal–carbon bond. Data on copolymerisation by an anionic mechanism are given in Table 5.[24,25,32,35,37,43,44,69,70,73,79-86]

Study of the composition of isoprene–styrene (Table 5, pair 6 [25]) and butadiene–isoprene (pair 12 [77]) copolymers shows that practically the same composition is obtained in the presence of organopotassium or organosodium compounds as in the presence of complexes of organolithium compounds with electron-donor substances. These results support the view that, under the influence of complexes of organolithium compounds, polymerisation occurs by the same mechanism as in the presence of organopotassium and organosodium compounds, i.e. by a typical anionic mechanism. However, it must be stressed that, even in tetrahydrofuran solution, chain growth by an anionic mechanism occurs in an ion-pair, and does not involve a free anion, since the rate of polymerisation of styrene in tetrahydrofuran depends on the nature of the alkali-metal ion[24].

The dependence of the relative activity of monomers on the electron density at the double bonds in the case of copolymerisation in the presence of organopotassium and organosodium compounds and of complexes of organolithium compounds with tetrahydrofuran supports the view that the active end of the growing chain is anionic in character. Actually, determinations of copolymerisation constants or of the composition of the copolymers indicate that the reactivity of the monomers in the growth reaction of a polymeric anion diminishes in the sequence

$$\underset{e=-0.33}{p\text{-chlorostyrene}} > \underset{e=-0.80}{\text{styrene}} > \underset{e=-1.05}{\text{butadiene}} > \underset{e=-1.22}{\text{isoprene}} > \underset{e=-1.81}{\text{2,3-dimethylbutadiene}},$$

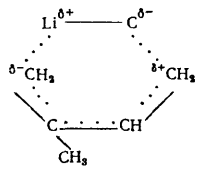
with increasing electron density on the double bonds in the monomer (with increase in e in the $Q-e$ scheme). The rate constants for the addition of various derivatives of styrene to "live" polystyrene in tetrahydrofuran solution obey the Hammett rule, with $\rho = +0.5$ having a positive value in conformity with the assumption of an anionic mechanism for chain growth. In the copolymerisation of butadiene with isoprene and with 2,3-dimethylbutadiene in tetrahydrofuran[69,70,84] or in hexane[28,29] (pairs 11 and 12 in Table 5), and also of styrene with p-methylstyrene and with p-methoxystyrene (pairs 2 and 3), the Hammett rule is obeyed by quantities representing the reactivities of the monomers towards the same active terminal unit

$$\left(\frac{1}{r_1} = \frac{k_{12}}{k_{11}}\right).$$

Instead of the σ constants, let us use the polar factor e in the $Q-e$ scheme, in order to take into consideration results obtained in the copolymerisation of dienes:

$$\log \frac{1}{r_1} = \text{const } e. \qquad (8)$$

As noted above, 1,4 polymers of dienes are formed in the presence of organolithium compounds in hydrocarbon medium, in contrast to the 1,2 and 3,4 polymers obtained under the influence of other organometallic compounds of alkali metals[74]. In discussions of this phenomenon the lithium–carbon bond has been regarded as a polarised covalent bond instead of being ionic[76]. Stearns and Forman[87] suggested a mechanism of chain growth in which the first stage involved formation of an intermediate cyclic complex with a coordinate link between $Li^{\delta+}$ and the π electrons of the double bond in the monomer, e.g. for isoprene



In the first stage the conformation of the monomeric molecule is fixed by formation of the cyclic complex, which ensures that the second stage — addition of monomer to the negatively polarised end of the chain — shall be stereospecific. In present-day terminology this mechanism of polymerisation is said to be coordinate-anionic[10,81]. With the addition of increasing quantities of an electron-donor complexing agent (or with increasing complexing power of the additive, e.g. on passing from diethyl ether to triethylamine and tetrahydrofuran), the ability of the lithium atom to form a complex with the monomer diminishes, and a transition occurs from coordinate-anionic to typically anionic polymerisation. This change in the mechanism of polymerisation produces a change in structure when isoprene is polymerised in different solvents. The relation between the activities of isoprene and styrene on copolymerisation under the influence of butyllithium changes to the same extent in the presence of different electron-donor additives[25].

Since the changes in the structure of polyisoprene and in the composition of its copolymer with styrene have the same causes, a linear correlation exists between these quantities (Fig. 2 [25]). The change in relative reactivity of the monomers on passing from copolymerisation by means of organolithium compounds in hydrocarbon medium to copolymerisation in the presence of complexes of organolithium compounds with electron-donor substances has been studied on the following pairs of monomers — styrene–butadiene (pair 5 [Table 5]), styrene–isoprene (pair 6), styrene–α-methylstyrene (pair 4), and butadiene–isoprene

TABLE 5. Copolymerisation under the influence of catalysts of anionic type.

No. of pair	M_1	M_2	Catalyst	Medium	r_1	r_2	M_1, mole %, in initial mixture	M_1, mole %, in copolymer	Ref.
1	2	3	4	5	6	7	8	9	10
1	styrene $e=-0.80$	*p*-chlorostyrene $e=-0.33$	LiC_2H_5	$N(C_2H_5)_3$	0.1±0.1	6.5±0.1	50	23	79
			LiC_2H_5	C_6H_6	—	—	50	67	79
			$NaC(C_6H_5)_3$	$(C_2H_5)_2O$	—	—	50	61	79
			LiC_2H_5	$(C_2H_5)_2O$	—	—	50	48.5	79
			Na-naphthalene	tetrahydrofuran	—	—	50	18	79
			LiC_2H_5	tetrahydrofuran	—	—	50	34.4	80
2		*p*-methylstyrene $e=-0.88$	LiC_4H_9	toluene	2.5±0.1	0.26±0.03	—	—	37
			LiC_4H_9	$C_6H_6 + (C_2H_5)_2O$	—	—	50	70	81
			"live" $(M)_n^-Na^+$	tetrahydrofuran	3.05	0.22	—	—	24
			ditto	tetrahydrofuran	5.3	0.18	—	—	85
3		*p*-methoxystyrene $e=-1.11$	LiC_4H_9	toluene	10.9±0.8	0.05±0.02	—	—	37
			"live" $(M)_n^-Na^+$	tetrahydrofuran	19	0.045			86
4		*α*-methylstyrene $e=-1.27$	LiC_4H_9	toluene	—	—	50	98	37
			LiC_2H_5	toluene	—	—	82	77.5	77
			LiC_2H_5	toluene + $(C_2H_5)_2O$	—	—	82	92	77
			LiC_2H_5	toluene + $N(C_2H_5)_3$	—	—	82	96	77
			$NaC(C_6H_5)_3$	toluene	—	—	82	94	77
			"live" $(M)_n^-Na^+$	tetrahydrofuran	21	0.003	—	—	24
5		butadiene $e=-1.05$	LiC_4H_9	n-heptane	0	7	—	—	26
			LiC_2H_5	toluene	0.1	12.5	—	—	32
			LiC_4H_9	benzene	0.05	20	—	—	37
			LiC_4H_9	benzene	0.035	10.0	—	—	73
			"live" $(M)_n^-Na^+$	benzene	0.06	3	—	—	36
			LiC_4H_9	1 M ether in benzene	0.11	1.78	—	—	43
			LiC_4H_9	1 M tetrahydrofuran in benzene	0.744	1.03	—	—	44
			LiC_2H_5	toluene + $N(C_2H_5)_3$	0.3	5.5	—	—	32
			LiC_2H_5	tetrahydrofuran	8±1	0.2±0.1	—	—	32
			NaC_2H_5	benzene	0.96	1.6	—	—	73
			$KC(CH_3)_2C_6H_5$	benzene	1	1	—	—	73
			LiC_4H_9	hexane	—	—	50	13.6	44
			LiC_4H_9	1 M ether in benzene	—	—	50	31	44
			LiC_4H_9	1 M dioxan in benzene	—	—	50	30	44
			LiC_4H_9	1 M methylal in benzene	—	—	50	31	44
			LiC_2H_5	toluene + $N(C_2H_5)_3$	—	—	50	33	32
			LiC_4H_9	1 M $(CH_3OCH_2)_2$ in benzene	—	—	50	47	44
			LiC_4H_9	1 M tetrahydrofuran in benzene	—	—	50	47	44
			LiC_4H_9	n-heptane + tetrahydrofuran	—	—	50	30	26
			$KCH_2C_6H_5$	toluene	—	—	50	67.5	82
6		isoprene $e=-1.22$	LiC_4H_9	benzene	0.14±0.02	7±0.6	—	—	30
			LiC_2H_5	toluene	0.25	9.5	—	—	83,31
			LiC_2H_5	2.5 M $N(C_2H_5)_3$ in toluene	0.8	1	—	—	31,83
			LiC_2H_5	tetrahydrofuran	40	0	—	—	31,83
			LiC_4H_9	benzene	—	—	50	11.5	25
			LiC_4H_9	monomer	—	—	50	12.5	25
			LiC_4H_9	$N(C_2H_5)_3$	—	—	50	49.5	25
			LiC_4H_9	$(C_2H_5)_2O$	—	—	50	58.2	25
			LiC_4H_9	tetrahydrofuran	—	—	50	72.3	25
			$KCH_2C_6H_5$	toluene	—	—	50	75	82
7		vinylmesitylene	"live" $(M)_n^-Na^+$	tetrahydrofuran	1060	0.004	—	—	85
8	*p*-chlorostyrene $e=-0.33$	*α*-methylstyrene $e=-1.27$	LiC_2H_5	benzene	—	—	16	26	79
			LiC_2H_5	$N(C_2H_5)_3$	—	—	16	87.5	79
9	*p*-methylstyrene $e=-0.88$	*p*-methoxystyrene $e=-1.11$	LiC_4H_9	toluene	1.93±0.03	0.72±0.02	—	—	37
10	isoprene $e=-1.22$	penta-1,3-diene	LiC_4H_9	n-hexane	17±5	0.06±0.02	20	62.8	28
			LiC_4H_9	2 M ether in hexane	—	—	20	43.4	28
11		2,3-dimethyl-butadiene $e=-1.81$	LiC_4H_9	n-hexane	17±5	0.06±0.02	—	—	28
12		butadiene $e=-1.05$		toluene	—	—	50	29.5	77
			LiC_2H_5	2 M $N(C_2H_5)_3$ in toluene	—	—	50	17.5	77
			LiC_2H_5	toluene	—	—	50	16	77
			$NaC(C_6H_5)_3$	hexane	0.47±0.03	3.38±0.14	—	—	29
			LiC_4H_9						
			LiC_4H_9	hexane, benzene, toluene, benzene soln. of tetrahydrofuran, pyridine, and $N(C_2H_5)_3$ > 0.001 M	0.5 ±0.1	3.6 ±0.3	—	—	86
			LiC_4H_9	$N(C_2H_5)_3$	0.11±0.02	3.6 ±0.6	—	—	69,84
			LiC_4H_9	tetrahydrofuran	0.13±0.02	4.5 ±0.7	—	—	69,84
13	butadiene $e=-1.05$	2,3-dimethyl-butadiene $e=-1.81$	LiC_4H_9	tetrahydrofuran	44±11	0.65±0.16	—	—	70

(pair 12). In all these cases the relative activity of the monomer having the lower electron density on the double bonds increases with the complexing power of the electron-donor additive or with its concentration (see e.g. the data on the copolymerisation of butadiene with styrene, pair 5).

In the copolymerisation of butadiene and of isoprene with styrene by means of butyllithium in hydrocarbon medium, the monomer having the higher electron density on the double bonds (isoprene with $e = -1.22$, and butadiene with $e = -1.05$) is even more active than styrene, in which

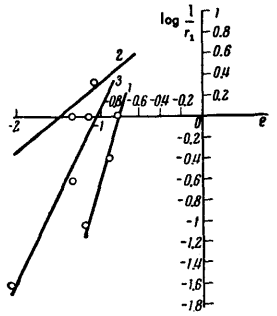


Fig. 1. Dependence, on electron density at double bonds, of reactivity of monomers in the presence of C_4H_9Li towards: 1) styrene, copolymerised with *p*-methyl- and *p*-methoxy-styrenes in toluene[37]; 2) isoprene, copolymerised with butadiene[28] and 2,3-dimethylbutadiene[29] in hexane; 3) butadiene, copolymerised with isoprene and with 2,3-dimethylbutadiene in tetrahydrofuran[68,70,84].

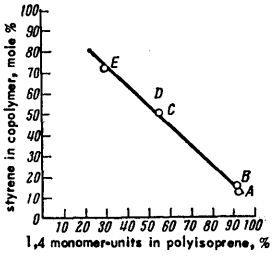


Fig. 2. Relation between structure of homopolymers of isoprene and composition of isoprene–styrene copolymers obtained from an equimolecular mixture by anionic polymerisation[25] in the presence of C_4H_9Li in: *A*) benzene; *B*) monomer; *C*) triethylamine; *D*) ether; *E*) tetrahydrofuran.

the electron density on the double bond is lower (e = -0.80), which would appear to contradict the view that a partial negative charge is present on the end of the growing chain. Actually, these results confirm the coordination nature of chain growth under the influence of organolithium compounds. The first stage — formation of a π complex with the lithium atom — should tend to produce a higher electron density on the double bonds of the monomer; the second stage — addition of monomer to the negatively polarised end of the chain — occurs more readily with monomers of lower electron density on the double bonds.

In all the cases mentioned (pairs 4–6 and 12), in conformity with this mechanism, the relative activity of the monomer of greater electron density on the double bonds increases on passing from copolymerisation under the conditions of a typically anionic process (in the presence of organopotassium compounds or of LiR in tetrahydrofuran) to polymerisation of the same monomers in the presence of organolithium compounds without electron-donor additives. The reactivity of the monomers could be changed on reaction via a cyclic complex, in comparison with polymerisation in ion-pairs, for steric reasons; but then the activity of α-methylstyrene could have been expected to decrease in comparison with styrene on passing to reaction in the ring, whereas the opposite is observed[77].

Use of the copolymerisation method to study the mechanism of polymerisation in the presence of organometallic compounds has in the first place provided evidence that the active unit in the growing chain is negatively charged, i.e. that polymerisation actually takes place by an anionic mechanism. Data on copolymerisation under the influence of organolithium compounds in various media have shown the coordinate–anionic mechanism of the action of this catalyst in a hydrocarbon solvent.

5. COPOLYMERISATION BY MEANS OF COMPLEX ORGANOMETALLIC CATALYSTS OF THE ZIEGLER–NATTA TYPE

Complex organometallic catalysts for the stereospecific polymerisation of alkenes and dienes are prepared from compounds of metals in the secondary subgroups of Groups IV–VI of the Periodic System and organometallic compounds of metals in Groups I–III.[10,88] The ionic and complex nature of these catalysts has now been proved; during growth the active unit in the chain is coordinated with the catalyst, and the act of addition of a new monomeric unit involves heterolytic cleavage of the bond between the catalyst and the terminal unit in the chain, with formation of a new polarised bond[10,75].

Study of copolymerisation enables several details of the mechanism of chain growth to be elucidated. Data on copolymerisation in the presence of Ziegler–Natta catalysts[69,70,89–128] are given in Tables 6 and 7. Investigation has been based mainly on styrene (Table 6, pairs 1–18), ethylene, propene (pair 24), and dienes (pairs 31–33).

The copolymerisation of styrene with nuclear-substituted styrenes is ideal in character, i.e. $r_1r_2 = 1$. Moreover, Wall's condition (5) is satisfied: the copolymerisation constant is equal to the ratio of the growth rate constants for the homopolymerisation of the monomers under the same conditions[129–132]: $r_2 = 1/r_1 = k_{22}/k_{11}$, so that the nature of the terminal unit in the chain does not affect the rate of addition of the monomer unit. The relative activities of *para*-substituted styrenes depend on the electron-donor power of the substituents: the copolymerisation constants obey the Hammett rule $\ln r_2 = \rho\sigma$, the reaction constant ρ being negative. Consequently monomers of higher electron density on the double bond are more active, as in cationic polymerisation. On the other hand, the higher reactivity of ethylene compared with propene, which has a higher electron density on the double bond owing to the presence of an electron-donor substituent, has previously been regarded as an argument in support of the anionic nature of the growing chain[89,90].

In order to remove the contradiction, a mechanism of chain growth has been suggested[81,93] which takes into account the complex nature of stereospecific polymerisation. As in the mechanism quoted earlier for chain

TABLE 6. Copolymerisation under the influence of a Ziegler–Natta catalyst.

No. of pair	M_1	M_2	Catalyst	Medium	r_1	r_2	Ref.
1	2	3	4	5	6	7	8
1	styrene $e=-0.80$	*p*-methylstyrene $e=-0.88$	$TiCl_4+Al(C_2H_5)$	benzene	0.90	1.15±0.08	92,118
			$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	0.84	1.19	92
			$TiCl_3+Al(C_2H_5)_3$	»	0.85	1.18	92
			$TiCl_3+Be(C_2H_5)_2$	n-heptane	0.85	1.18	92
			$TiCl_3+Al(i\text{-}C_4H_9)_3$	»	1.0±0.12	1.0±0.12	95,96
2		*o*-methylstyrene $e=-0.78$	$TiCl_4+Al(i\text{-}C_4H_9)_3$	benzene	12.5±1	0.10±0.01	92–94
			$TiCl_3+Al(i\text{-}C_4H_9)_3$	toluene	mixture of copolymers of different compositions		122
3		*m*-methylstyrene $e=-0.72$	$TiCl_4+Al(i\text{-}C_4H_9)_3$	benzene	2.0±0.1	0.50±0.1	92,93
4		2,4-dimethylstyrene	$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	7.7	0.13	92,93
5		2,5-dimethylstyrene $e=-0.84$	$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	33	0.03	92,93
6		2,6-dimethylstyrene	$TiCl_3+Al(i\text{-}C_4H_9)_3$	toluene	—	0	122
7		2,4,6-trimethylstyrene	$TiCl_4+Al(i\text{-}C_4H_9)_3$	benzene	—	0	92,93
8		*p*-ethylstyrene	$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	0.95±0.1	1.05±0.1	92–94
9		*p*-cyclohexylstyrene	$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	2.08	0.48	92,93
10		*o*-fluorostyrene	$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	5.6	0.18	92,93
11		*m*-fluorostyrene	$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	2.13	0.47	92,93
12		*p*-fluorostyrene	$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	1.50±0.1	0.60±0.1	92,93
			$TiCl_3+Al(i\text{-}C_4H_9)_3$	toluene	mixture of copolymers of different compositions		122
13		*m*-chlorostyrene $e=-0.35$	$TiCl_4+Al(i\text{-}C_4H_9)_3$	benzene	2.34	0.43	92–94
14		*p*-chlorostyrene $e=-0.33$	$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	2.20±0.2	0.50±0.1	92–94
15		*p*-bromostyrene $e=-0.35$	$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	1.75±0.1	0.55±0.1	92–94
16		*p*-methoxystyrene $e=-1.11$	$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	0.625	1.6	92–94
17		1-vinylnaphthalene $e=-1.12$	$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	3.3±0.5	0.35±0.2	92–94
18		*p*-t-butylstyrene	$TiCl_3+Al(i\text{-}C_4H_9)_3$	n-heptane	mixture of homopolymers		95,96
				toluene	mixture of copolymers		122
19		*p*-n-butylstyrene	$TiCl_3+Al(i\text{-}C_4H_9)_3$	n-heptane	mixture of homopolymers		95,96
20		propene	$TiCl_3+Al(C_2H_5)_3$	»	with 42 mole % of M_1 in mixture, 4 mole % in copolymer		97
21		5-methylhex-1-ene	$TiCl_3+Al(C_2H_5)_3$	»	mixture of two copolymers		98
22		4-methylpent-1-ene	$TiCl_3+Al(C_2H_5)_3$	»	ditto		98
23		isoprene $e=-1.22$	$TiCl_3+Al(C_2H_5)_3$	benzene	0.1	6	99
			$TiCl_4+Al(C_2H_5)_3$	»	1st fraction 0.63±0.39 2nd fraction 11±14	1.8±0.9 0.08±0.84	100
24	ethylene	propene	$VOCl_3+Al(n\text{-}C_6H_{13})_3$	n-heptane	17.95±0.27	0.065±0.02	90,104,105
			$VCl_4+Al(n\text{-}C_6H_{13})_3$	»	7.08	0.088	91,104,105
			$VCl_3+Al(n\text{-}C_6H_{13})_3$	»	6.61±0.20	0.145±0.007	101,104,105
			$TiCl_4+3Al(n\text{-}C_6H_{13})_3$	»	33.36	0.039	101,104,105
			$TiCl_3+Al(n\text{-}C_6H_{13})_3$	»	15.72	0.110	101,104,105
			$VAcac_3^a+AlCl(C_2H_5)_2$	»	15.0	0.04	107
			β-$TiCl_3+Al(C_2H_5)_3$	solvent naphtha	3.0±0.5	0.25±0.05	109
			$VO(OR)Cl_2+AlCl_2C_2H_5$	solvent naphtha	17.5	0.05	109
			$AlBr_3—VCl_3—Sn(C_6H_5)_4$	C_6H_{12}	16	0.1	110,111
			$VCl_4+Al(i\text{-}C_4H_9)_3$	C_6H_{12}	16	0.063	110
			$VCl_4+CH_3TiCl_3$	C_6H_{12}	16	0.063	110
			$VCl_4+Zn(C_6H_5)_2$	C_6H_{12}	16	0.063	110
			$VCl_4+Zn(n\text{-}C_6H_{13})_2$	C_6H_{12}	16	0.063	110
			$VOCl_3+Al(i\text{-}C_4H_9)_3$	C_6H_{12}	28	0.036	110
			$TiCl_4+Al(i\text{-}C_4H_9)_3$	C_6H_{12}	37	0.027	110
			$ZrCl_4+Al(i\text{-}C_4H_9)_3$	C_6H_{12}	61	0.016	110
			$HfCl_4+Al(i\text{-}C_4H_9)_3$	C_6H_{12}	76	0.013	110
25		but-1-ene	$VCl_4+Al(n\text{-}C_6H_{13})_3$	n-heptane	29.6±0.8	0.019±0.001	103,105
			$VCl_3+Al(n\text{-}C_6H_{13})_3$	»	29.96±0.81	0.043±0.01	103,105
26		hexa-1,5-diene	VCl_4 or $VOCl_3+AlR_3$	n-heptane	$r_1>r_2$		108
27		isoprene $e=-1.22$	$VOCl_3+Al(i\text{-}C_4H_9)_3$	tetrachloroethylene	with 90 mole % of M_1 in mixture, the copolymer contains 96 mole %		119
28	propene	but-1-ene	$VCl_4+Al(n\text{-}C_6H_{13})_3$	n-heptane	4.39	0.227	106
			$VCl_3+Al(n\text{-}C_6H_{13})_3$	»	4.04	0.252	106
29		isoprene $e=-1.22$	$TiCl_4+Al(C_2H_5)_3$	»	formation of copolymers established		118
			$TiCl_3+Al(C_2H_5)_3$	»	ditto		118
30	but-1-ene	3-methylbut-1-ene	$TiCl_3+Al(i\text{-}C_4H_9)_3$	»	8.5	0.013	120
					(empirical copolymer)		
31	butadiene $e=-1.05$	isoprene $e=-1.22$	$TiCl_4+Al(i\text{-}C_4H_9)_3$	benzene	1.0±0.05	1.0±0.05	69,123
			$TiCl_4+Al(C_2H_5)_3$	»	1.6	1.1	124
			$TiCl_4+LiC_4H_9$	»	1.6±0.3	0.8±0.2	124
			$TiI_4+Al(C_2H_5)_3$	»	1.88	0.55	124
			$CoAcac_3^a+Al(C_2H_5)_2Cl$	toluene	1.0±0.05	1.0±0.05	125
			$CoCl_2\cdot C_5H_5OH+$ $+Al(i\text{-}C_4H_9)_3Cl$	benzene	2.3±0.1	1.15±0.05	69,123
			$CoCl_2\cdot C_5H_5OH+Al(C_2H_5)_2Cl$	»	0.92	1.25	126
			$CoCl_2\cdot C_5H_5N+Al(C_2H_5)_2Cl$	»	0.99	1.37	126
			$NiCl_2\cdot C_5H_5N+Al(C_2H_5)_2Cl$	»	1.15	0.59	126
32		2,3-dimethylbutadiene $e=-1.81$	$TiCl_4+Al(i\text{-}C_4H_9)_3$	»	2.16±0.2	0.39±0.04	70
			$CoCl_2\cdot C_5H_5OH+Al(i\text{-}C_4H_9)_3Cl$	»	2.7 ±0.12	1.13±0.05	70

TABLE 6 (contd.)

No. of pair	M_1	M_2	Catalyst	Medium	r_1	r_2	Ref.
1	2	3	4	5	6	7	8
33		*trans*-penta-1,3-diene	$VCl_3 \cdot C_4H_8O + Al(C_2H_5)_2Cl$	benzene	with 92 mole % of M_1 in the mixture, the copolymer contains 69 mole %		127
			$VAcac_3^* + Al(C_2H_5)_3Cl$	»	ditto		127
			$CoCl_2 \cdot C_2H_5OH + Al(i\text{-}C_4H_9)_2Cl$	»	with 50 mole % of M_1 in the mixture, the copolymer contains 61 mole %		128

* Acac = acetylacetonate.

growth in the presence of organolithium compounds in hydrocarbon medium, chain growth is regarded as a two-stage process, in which the first stage involves formation of a monomer–active centre complex, and the second stage consists in addition of monomer to the end of the growing chain bound to the catalyst. The electron density on the double bonds in the monomers has opposite effects in these stages, and the dependence of the relative activity of a monomer on the polar effect of the substituents is determined by which of the two stages in the growth reaction is the slower. Natta and his coworkers consider that, in the stereospecific polymerisation of styrenes, chain growth takes place by an anionic mechanism, but the overall kinetics of growth is determined by the stage of formation of a π complex between the monomer and the transition metal of the active centre: this stage is favoured by a higher electron density on the double bond of the monomer.

Danusso[81] proposes that this mechanism of polymerisation should be termed "anionic polymerisation with counterion attack". As accepted previously, the term "anionic polymerisation" indicates the sign of the partial charge on the active unit in the growing polymer chain; the term "counterion attack" shows that the rate of growth is determined by interaction between the monomer and the counterion.

The proposed scheme makes it clear why the nature of the terminal unit in the chain does not affect the rate of growth in copolymerisation in contrast to cationic and anionic copolymerisation. When styrenes undergo copolymerisation and homopolymerisation in the presence of Ziegler–Natta catalysts, the rate of growth is determined solely by the stage involving formation of a complex between the monomer molecule and the transition metal, and this stage is unaffected by differences in reactivity between the terminal units formed from different monomers.

According to the mechanism of chain growth under consideration, the lower relative activity of propene and but-1-ene compared with ethylène (pairs 24 and 25 in Table 6) is due not to differences in electron density on the double bonds but to steric factors. When polar factors are decisive, differences in copolymerisation constants are due to differences in the activation energy of chain growth[20]. However, the activation energy of growth in the presence of the catalyst $(C_6H_{13})_3Al + VOCl_3$ or VCl_4 is the same for the homopolymerisation of ethylene and of propene as for their copolymerisation[105]. Consequently, the difference in activity is associated with steric factors — with the increase in steric hindrance to chain growth in the sequence ethylene–propene–but-1-ene.[10] The decisive role of steric factors in the copolymerisation of ethylene with propene (pair 24) and with but-1-ene (pair 25), as well as of but-1-ene with propene (pair 28), is indicated also by the absence of temperature variation in the copolymerisation constants of these monomers in the presence of any of the catalysts studied[90,91,101–111].

In copolymerisation of ethylene with propene[90,91,101–107,110], the atom of the transition metal present in the catalytic complex takes part in the stage of chain growth, which determines the rate of the overall process, since the copolymerisation constants vary with the nature of the compound of the transition metal. On the basis of the two-stage scheme of chain growth, however, it cannot be concluded from this variation, as is done by Carrick and his coworkers[110], that chain growth involves incorporation of monomer at the transition metal–carbon bond.

The view that in the growth reaction the position of the monomer is fixed in the reaction complex provides at the present time the most widely accepted explanation for the stereospecificity of the action of Ziegler–Natta catalysts[10]. This stereospecific action appears also in copolymerisation: in the presence of VCl_4 and $(C_6H_{13})_3Al$, ethylene forms crystalline copolymers with *cis*-but-2-ene and with cycloalkenes in which the monomer units alternate regularly, with the units of the second monomer forming a diisotactic structure[112–116,121] (Table 7). The steric selectivity of these catalysts is shown in the fact that mixtures of some monomers, in the presence of Ziegler–Natta catalysts, yield not copolymers but mixtures of homopolymers or of two copolymers differing in composition[95,96,98,100,120,122] (pairs 2, 12, 18, 19, 21–23, and 30 of Table 6).

Data on the copolymerisation of conjugated dienes (butadiene and isoprene, *cis*- and *trans*-penta-1,3-diene and 2,3-dimethylbutadiene — pairs 31–33 in Table 6) show especially clearly the difference between Ziegler–Natta coordination catalysts and ordinary cationic and anionic catalysts. Whereas when typical cationic and anionic catalysts are employed, the relative reactivity of a diene monomer is determined primarily by the electron density at its double bonds[28,29,69,70,84], in the presence of coordination catalysts the copolymerisation constants differ little among themselves, and are probably almost independent of the electron density on the double bonds in the monomer.

It has now been shown that complex catalysts based on titanium halides effect polymerisation by a coordinate-anionic mechanism[133,134], whereas those based on cobalt halides do so by a coordinate–cationic mechanism[134,135]. However, these distinctions do not lead to any substantial difference in the copolymerisation constants of the dienes in the presence of the two types of complex catalysts

TABLE 7. Copolymerisation of ethylene (M_1) with disubstituted ethylenes in the presence of Ziegler–Natta catalysts. [Polymerisation in toluene medium with vanadium tris-acetylacetonate + $(C_2H_5)_2AlCl$ as soluble catalyst, or VCl_4 + $(C_6H_{13})_3Al$ as colloidal catalyst. Copolymer formation proved by fractionation. Composition determined from content of radioactive ethylene.)

No. of pair	M_2	Catalyst	M_1, mole %, in		Ref.
			mixture	copolymer	
1	*cis*-but-2-ene	soluble	1	51	112–116
		soluble	3	82.3	121
		colloidal	1	67.5	112–116
2	*trans*-but-2-ene	soluble	1	92	112–116
		soluble	3	94.6	121
		colloidal	1	81	112–116
3	pent-2-ene	colloidal	1	26	112, 116
4	cyclopentene	soluble	1	55	112, 116, 117
		soluble	3	58.5	121
		colloidal	1	55	112, 116, 117
		colloidal	3	58	121
5	cyclohexene	soluble	3	97	121
		colloidal	3	93	121
6	cycloheptene	soluble	1	51	115, 116, 117
		soluble	3	55.5	121
		colloidal	1	63	115, 116, 117
		colloidal	3	65.5	121
7	*cis*-cyclooctene	soluble	3	90	121
		colloidal	3	92	121

(pairs 31 and 32 in Table 6). It may be supposed that the relative activity of diene monomers undergoing copolymerisation is determined primarily by steric factors. This is supported by the inability of *cis*-penta-1,3-diene (in contrast to the *trans* isomer) to polymerise or to form a copolymer with butadiene in the presence of several complex catalysts – $(C_2H_5)_2AlCl + VCl_3$ tetrahydrofuran or $VAcac_3$†,[127] $(iso\text{-}C_4H_9)_3Al + TiCl_4$, and $(iso\text{-}C_4H_9)_2AlCl + CoCl_2.C_2H_5OH$ [128] – as well as by the existence of a relation between the composition and the microstructure of the chain in copolymers obtained in the presence of catalytic systems based on compounds of cobalt and of nickel[69,70,124–126].

Data on copolymerisation in the presence of Ziegler catalysts thus show that in this process the polymer chain is neither a free anion nor a cation. The mechanism of the growth reaction is determined by the nature of the catalytic complex, in which the polymer chain occupies a definite position, and chain growth occurs as a stepwise process consisting of two stages – (1) formation of an active centre–monomer complex, and (2) addition of the monomer unit to the chain. In connection with the coordination character of chain growth, the relative activities of monomers are determined to a considerable extent not by polar but by steric factors.

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† Acac = acetylacetonate.

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THE QUANTITATIVE INTERPRETATION OF GAS CHROMATOGRAMS

L.V.Andreev, M.I.Afanas'ev,
O.G.Chabrova and M.S.Vigdergauz

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I. INTRODUCTION

When attempting a chromatographic analysis, the investigator is faced with three main types of problem. The first group relates to the choice of the best procedures and parameters for the separation process, the second to the identification of the components of the mixture to be analysed, and the third to the quantitative interpretation of the gas chromatograms.

The results of calculations of the concentration of the various constituents from the experimental chromatogram depend on correct choice and accurate measurement of the key parameter of the elution curve (particularly when the peaks are only partially resolved), on correct choice of the method of calculating the concentration, and lastly, on correct evaluation of the sensitivity of the detector towards each of the constituents.

The present review is devoted to a discussion of these problems. It is a continuation of our earlier articles[1,2], which dealt with the choice of separation procedures and with the qualitative analysis of mixtures.

A summary of published correction coefficients and peak areas for various substances and different detectors is given at the end of the review, so as to enable the reader to use these values directly in his experimental work.

Throughout this paper, it will be assumed that a differential detector is used.

II. PARAMETERS OF THE PEAK AND METHODS OF CALCULATION

When a small enough sample is eluted, a distribution of concentrations (called a layer chromatogram) is formed on the sorption layer. Further elution leads to desorption of the wanted constituent. The resulting distribution of concentrations is called an eluate chromatogram.

If the system of detector and recorder used does not distort the curve, the resulting chromatogram differs from the true eluate chromatogram only by a scale factor.

The main parameters of the chromatographic peak (Fig. 1) are[3]:

1. The height h, measured by the length of a perpendicular dropped from the peak maximum to the base line.

2. h', the length of a perpendicular dropped to the base line from the intersection of the tangents to the peak.

3. The width of the peak, which can be measured as the distance between points on the peak at a height of 0.5 ($\mu_{0.5}$), 0.75 ($\mu_{0.75}$), 0.9 ($\mu_{0.9}$), or 1/e (μ_e) of the total peak height,