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Calculation of the Individual Rate Constants for the Crossed Propagation Reaction of Binary First-Order Copolymerization

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ABSTRACT

The problem of describing quantitatively the selectivity of cationic copolymerizations leads to a new method of calculating kinetic parameters of the copolymerization. The "individual rate constants" for the binary first-order copolymerization calculated this way are well suited to describe the "dynamics of the copolymerization" and to predict copolymer characteristics, e.g., composition and microstructural parameters. By means of cationic copolymerizations of vinyl monomers, theoretical calculated copolymer characteristics and experimentally independently determined ones are compared.

INTRODUCTION

For the synthesis of macromolecular products with new properties, the copolymerization of monomers with strongly differing stereoelectronic natures should be suitable. It is well known that the properties are essentially defined by the composition of the polymers and the microstructure of the polymeric chain. The knowledge of well-defined property characteristics and the possibilities for reaction-controlled synthesis leading to such products requires investigations on the quantitative description of copolymerization behavior of two or more monomers under defined reaction conditions.

As the composition of the copolymer and the structure of the polymeric chain are in close connection with the relative reactivity of the monomers and with the selectivity of the crossed propagation reaction during the formation of the macromolecule, the derivation of parameters which are characterizing the elementary steps quantitatively is one of the central problems of kinetic research of the copolymerization.

Empirical relations between the composition of the copolymer and the concentration ratio of the comonomers in the feed are reflected by the well-known "copolymerization diagrams." These relations are quantified by the "copolymerization parameters" (CPP). Their calculation is based on the assumption that the microstructure and the composition do not change strongly with the conversion degree. Expressed by other words, these CPP are "static" in their nature.

Mirabella et al. [1, 2] reported their investigations concerning the quantitative description of copolymerization. They described in detail a Monte Carlo simulation of copolymerization [3] which considers the initiation and propagation steps and yields instantaneous and cumulative copolymer composition as a function of chain length for high conversion copolymers [2]. This method is based on the copolymerization parameters and on the integrated copolymer equation as described by Skeist [4]. The deviations between theoretical and experimental results as reported in Ref. 2 may partially have their origin in the use of the approximations $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ which need not be fulfilled in any case.

By employing corrected methods of determining copolymerization parameters as reported by Kelen and Tüdös [5], it becomes possible to evaluate data obtained at high conversion levels. But the question of reflecting the rate constant ratios k_{11}/k_{12} and k_{22}/k_{21} by copolymerization parameters r_1 and r_2 remains unsolved. In this paper we intend to deal with this problem too, i.e., with the definitional background of copolymerization parameters and their use for kinetic interpretations of copolymerizations.

Our investigations concerning the cationic copolymerization of p-substituted styrenes and other vinyl-type monomers [6, 7] showed remarkable dependence of the copolymer composition on the reaction time.

Investigating the copolymerization of α-methylstyrene and isobutene initiated by Lewis acids, we found that the composition and the microstructure (sequence lengths distribution) of the copolymer determined by ^{1}H-NMR-spectroscopy obviously depend on the conversion degree. Besides this, a competitional formation of entirely different products (not precipitable oligomers with a high degree of alternation, precipitable random copolymers, and high-molecular polyisobutene) were observable. The chemical inhomogeneity also depends on the reaction conditions and on the conversion degree.

The copolymerization of cyclopentadiene and isobutene initiated by aluminum halides has been found to be easily analyzed by ^{1}H-NMR-spectroscopy and by use of gel permeation chromatography (GPC). We found again that microstructure, composition, and chemical inhomogeneity of the product change with conversion, whereby at longer reaction time homopolymerization of isobutene is dominant.

An exact description of these "dynamics of copolymerization," i.e., the change of product composition, chemical and physical inhomogeneity, as well as microstructure (sequence lengths distribution) in dependence on the reaction time became difficult on the basis of the "classical" copolymerization parameters (CPP). Conformity between microstructure data, calculable herefrom [8] and those which had been obtained by use of experimentally independent methods, could only be expected at defined conversion degrees.

With this paper we would like to describe a method using kinetic data from the course of the copolymerization in order to permit an interpretation of the above-mentioned "dynamics of copolymerization" and to demonstrate the conformity of calculable and experimentally independently obtained microstructure data.

THE THEORETICAL PRINCIPLES

The Kinetic Model

The complete kinetic analysis of the copolymerization, i.e., the determination of the different rate constants of initiation (k_I), of the crossed propagation reaction (k_p 11, 12, 21, 22) and of the chain-limiting reactions (k_T) should characterize the time-dependent lapse of the copolymerization and with that the "selectivity" of different reaction probabilities. The meaning of the term "selectivity of the copolymerization" is therefore quite different:

1. Selective initiation (s-i). The formation of the active species from the two comonomers occurs at different rates: $k_I(M_1) \neq k_I(M_2)$.
2. Selective chain termination (s-t). The different terminal chain units have distinct tendencies for chain limiting reactions: $k_T(M_1) \neq k_T(M_2)$.
3. Selective propagation processes (s-p).

The probability P_i for including the monomer M_i into a binary copolymer consisting of M_i and M_j, i.e., the mole fraction X_i of the monomer M_i in the copolymer [9].

The conditional probabilities of a definite sequence of steps during the chain formation, i.e., the instantaneous probability dP(i/j) for the occurrence of propagation steps $\ldots M_i^{\oplus} + M_j \longrightarrow \ldots M_iM_j^{\oplus}$ at a given monomer concentration and the cumulative probability P(i/j) that an M_i unit is followed by an M_j unit in the polymeric chain [9-11].

The probabilities P_{i-j}, P_{i-j-k}, . . . for the appearance of definite monomer sequences (n-ades) [9, 10] or "cluster" [12] in the copolymer.

4. Stereoselective or stereoregular polymerization [13]. The contending of isotactical (ss-it), syndiotactical (ss-st), or atactical (ss-at) sequences (n-ades) of the copolymer.

5. Selectivity with reference to the chemical homogeneity of the product, i.e., constitutional selectivity (s-ch). Dominance of a uniform propagation process or competition of various propagating species (ions and ion pairs in ionic polymerizations), often leading to different product compositions, changes of microstructure, and molecular weight distribution (MWD).

6. Selectivity with reference to the physical homogeneity (s-ph) of the polymer. The circumstances concerning chain propagation, initiation, and termination lead to a characteristic MWD.

By assuming the properties of real copolymers to be dependent essentially on the selectivity of the crossed propagation reaction (s-p), as mentioned generally under Point 3, the dependence of the nature of the products on the reaction conditions has its root in an understanding of the different velocities of the competitive reaction steps.

The first-order model for the crossed propagation reaction of the binary copolymerization (terminal model) [14-16]:

$$\ldots M_1^{\oplus} + M_1 \xrightarrow{k_{11}} \ldots M_1^{\oplus} \tag{1a}$$

$$\ldots M_1^{\oplus} + M_2 \xrightarrow{k_{12}} \ldots M_2^{\oplus} \tag{1b}$$

$$\ldots M_2^{\oplus} + M_1 \xrightarrow{k_{21}} \ldots M_1^{\oplus} \tag{1c}$$

$$\ldots M_2^{\oplus} + M_2 \xrightarrow{k_{22}} \ldots M_2^{\oplus} \tag{1d}$$

delivers the differential equations mentioned below for the quantitatively kinetic description of the copolymerization:

$$-d[M_1]/dt = k_{11}[\ldots M_1^{\oplus}][M_1] + k_{21}[\ldots M_2^{\oplus}][M_1] \tag{2a}$$

$$-d[M_2]/dt = k_{12}[\ldots M_1^{\oplus}][M_2] + k_{22}[\ldots M_2^{\oplus}][M_2] \tag{2b}$$

$$d[\ldots M_1^{\oplus}]/dt = k_{11}[\ldots M_1^{\oplus}][M_1] + k_{21}[\ldots M_2^{\oplus}][M_1] - k_{12}[\ldots M_1^{\oplus}][M_2] \tag{2c}$$

$$d[\ldots M_2^{\oplus}]/dt = k_{22}[\ldots M_2^{\oplus}][M_2] + k_{12}[\ldots M_1^{\oplus}][M_2] - k_{21}[\ldots M_2^{\oplus}][M_1] \tag{2d}$$

The solution of these differential equation systems yields the "individual rate constants" (k_{11}, k_{12}, k_{21}, k_{22}) of the binary first-order copolymerization (IRC). The enlargement of this kinetic scheme up to the second-order model (penultimate model) [9, 17-19] or the third-order model (ante-penultimate model) [4, 20] permits a more detailed description of the crossed propagation reaction, but the mathematical formalism of the kinetic modeling is far more complicated.

In the case of the binary first-order copolymerization, the conception of selectivity can be expressed more precisely as follows:

a. $(k_{21}, k_{11}) \gg (k_{12}, k_{22})$. The homopolymerization of monomer M_1 is dominant, whereas M_2 units are rare in the polymer. This corresponds to selective homopolymerization, i.e., the polymerization runs "homoselective" (hs).

b. $(k_{11}, k_{22}) \gg (k_{12}, k_{21})$. This corresponds to a mixture of two homopolymers or to block copolymerization under appropriate conditions, i.e., the polymerization runs "block-co-selective" (b-cs).

c. $(k_{21}, k_{12}) \gg (k_{11}, k_{22})$. In this case the reaction leads to products with a high degree of alternating structure, i.e., the polymerization runs "alternating-co-selective" (a-cs).

d. $(k_{11} \approx k_{12})$; $(k_{22} \approx k_{21})$. In this case the reaction leads to random copolymerization, i.e., the polymerization runs "random-co-selective" (r-cs). The differing copolymerization tendencies of the monomers M_1 and M_2, i.e., the "co-selectivity" (cs) of the polymerization, are then given by the values of P_1 and P_2 (cumulative copolymer composition).

The Copolymerization Parameters

On the basis of differential equations (2a) and (2b) and in accordance with the steady-state model [15, 16], the copolymerization equation can be derived:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_2] + [M_1])} \tag{3}$$

The solution of Eq. (3) yields the copolymerization parameters r_1 and r_2 (CPP), often designated as "relative reactivities of the monomers" or "reactivity ratios," which according to their definition are in agreement with the IRC of the crossed propagation reaction when $r_1 \approx k_{11}/k_{12}$ and $r_2 \approx k_{22}/k_{21}$.

Calculable from r_1 and r_2 according to known relations [8, 9, 11] are the cumulative copolymerization tendencies (P_1 and P_2), i.e., the mole fractions of M_1 and M_2, respectively, in the copolymer, the cumulative conditional probabilities P(1/1), P(1/2), P(2/1), and P(2/2), as well as the "run-numbers" [21] which are in agreement with the experimentally accessible data of microstructure as, e.g., triade frequencies (P_{1-1-1}, P_{2-1-1}, P_{2-1-2}, . . .) or medium sequence lengths ($\bar{l}_1$ and $\bar{l}_2$) [9, 10, 12, 22].

From this point of view the question of determining the CPP exactly and reproducibly becomes decisively an important factor. Tidwell and Mortimer [23] claimed high requirements for methods like those with regard to comparability of experimental conditions, a mathematical method for the solution of Eq. (3), and the punctual observance of the approximations representing the basis of the chosen model.

In our former papers [6, 24, 25] we pointed out the necessity of a distinction between "kinetic" and "static" CPP, because the calculation is based on a kinetic analysis of the reaction or on the copolymerization diagram.

As the kinetic analysis in general obtains concentration-time curves for both the monomers, the "kinetic" CPP to be calculated from these data describe the total process of monomer consumption without taking into consideration the constitutive homogeneity of the product. The "static" CPP calculable from the copolymerization diagram are on the contrary quantitative parameters for the correlation between the composition of the monomer mixture and a chemical homogeneous estimated precipitable copolymer. If work is performed under constantly kept degrees of conversion of the copolymerization, these values are solutions of Eq. (3). Only under the supposition that the monomer is completely consumed for the formation of precipitable copolymer and that inhomogeneities of the second order (dependence of the composition on the conversion) can be excluded, can "static" and "kinetic" CPP become identical. There is, however, on the other side a possibility to coordinate—by means of exact product analysis and using product fractionations, extractions, etc.—the monomer consumption to the different products originating during the process of copolymerization (e.g., oligomers, precipitable copolymers, and homopolymers) and to approach in this way the problem of the description of the selectivity of the reaction.

The Individual Rate Constants (IRC)

The concentrations: $[M_1](t) := x_1(t)$; $[M_2](t) := x_2(t)$; $[...M_1^+](t) := z_1(t)$; $[...M_2^+](t) := z_2(t)$ for the first-order model of a binary copolymerization in dependence on the reaction time are described by the rate laws (2a) . . . (2d). Known are series of measurements $x_1^0, \ldots, x_1^N$ for $x_1(t)$ and $x_2^0, \ldots, x_2^N$ for $x_2(t)$, which were obtained from the process running with the unknown $k = (k_{11}, k_{12}, k_{21}, k_{22})$ as well as rough estimations of k^0 for k together with the supplementary restrictions $0 < k_{j1} < k_{j2} < k_{j3} < k_{j4}$ with $j_n \in (11, 12, 21, 22)$; $j_n \neq j_m$ for $n \neq m$; $n, m \in (1 \ldots 4)$.

Sought is an optimal parameter set k^+. For the determination of functions x(t) and z(t), the problem is at first formulated as a boundary value problem and treated by means of the "shooting method" [26a].

The numerical solution of the minimizing problem:

$$\phi(k) = \mathrm{tr}[(X(k) - X_M)^T(X(k) - X_M)] \tag{4}$$

is realized in accordance with the method of Rosenbrock [26b] with $X(k) = (x_0(t_0,k), \ldots, x_N(t_N,k))$; $X_M = (x^0, \ldots, x^N)$.

Output data are $x(t_i, k^+)$, $z(t_{,}\, k^+)$, and $k^+ = (k_{11}, k_{12}, k_{21}, k_{22})$, the "individual rate constants" of the crossed propagation reaction for the binary first-order copolymerization.

According to this method the "boundary points" of the experimental input data (digitalized concentration-time curves) should have to meet high requirements of precision, whereas the "supporting points" which are lying in the interval are allowed to be affected by errors. A criterion for the quality of the calculated parameters is the error square sum (FQS) as a scale of adaption of the calculated time curves of concentration to the experimentally determined ones.

Therefore the following points have to be observed:

1. The "individual rate constants" are only referring to the crossed propagation reaction. Initiation processes (k_I) and chain-limiting reactions (k_T) cannot be taken into consideration.

2. The IRC, k_{ij}, determined by the help of our method, must not be mixed up with the "absolute rate constants" for the elementary processes of copolymerization [27]; on the contrary, they represent, according to their nature, total constants of the monomer consumption which occurs by possible steps of chain growth. Their dimension [$\sec^{-1}$] refers to a first-order reaction with respect to the monomer.

3. The supplementary restrictions necessary for the calculation are allowed to be given as a model and can be laid down either on the basis of a plausible hypothesis about the running of the propagation reaction or on account of analogous considerations in comparison with experimentally obtained and secured findings. The conformity

of parameters to be calculated on the basis of a certain set of supplementary restrictions with experimentally obtained values permits an evaluation of the postulated model.

4. The estimation of the "starting values" k^0 will be possible in a first approach by means of the corresponding gross constants of the homopolymerization of both the comonomers and of the copolymerization parameters. Therefore the constants k_{11} and k_{22} need not be identical with the corresponding gross rate constants k_1 and k_2 of the homopolymerization, as the presence of the comonomer leads to differences in the rate in contrast with the "uninfluenced" homopolymerization.

The individual rate constants (IRC) serve for the quantitative description of the copolymerization behavior and can be compared with data which are accessible by experimentally independent methods:

$$U(t) = 1 - \frac{[M_1](t) + [M_2](t)}{[M_1]^0 + [M_2]^0} \tag{5}$$

$$dP(i/j) = \frac{k_{ij}[M_j](t)}{k_{ij}[M_j](t) + k_{il}[M_l](t)}, \qquad i, j, l \in (1, 2);\ j \neq l \tag{6}$$

$$P_i = \frac{[M_i]^0 - [M_i](t)}{([M_i]^0 + [M_j]^0) - ([M_i](t) + [M_j](t))}, \qquad i \neq j \in (1, 2) \tag{7}$$

$$P(i/j) = 1/t \int_{t=0}^{t} dP(i/j)\, dt \tag{8}$$

$$P_{i-j} = P(i/j) \cdot P_i \tag{9}$$

$U(t)$ = total conversion of the reaction at the time t

$dP(i/j)$ = "differentially" conditional probabilities, i.e., the instantaneous probability of linkage of a chain end . . .M_i^+ with the monomer M_j at the actually exisiting concentrations of monomers $[M_l](t)$ and $[M_j](t)$

P_i = composition of the copolymer formed at the time t, i.e., mole fraction of monomer M_i in the copolymer according to the cumulative copolymerization tendency of M_i

$P(i/j)$ = "integrally" conditional probabilities characterizing the copolymer existing at the time t, i.e., the cumulative probability that an M_i unit is followed by an M_j unit in the polymeric chain

P_{i-j} = frequency of dyads in the copolymer formed at the time t

The "integral" values are useful for direct comparison with corresponding experimentally independently obtained microstructure characteristics. The "differential" data permit essential conclusions on the "dynamics of copolymerization"; that means the time-dependent formation of specific monomer sequences, i.e., structural variations in the gross product.

If the crossed propagation reaction according to the first-order model is not the predominant process of the polymerization, but other processes such as formation of monomer complexes, selective initiation of one of the two monomers, or selective chain limitation are playing an important role, the deviations of the experimentally obtained data from the theoretically calculated ones give important hints on the lapse of the reaction.

Process Testing by Way of Analog Simulation of a Copolymerization

We have previously submitted a proposal concerning a method for the analog simulation of copolymerization according to the first-order model of the crossed propagation reaction [25]. Input data for the analog computer model were given "individual rate constants" (k_{11}, k_{12}, k_{21}, k_{22}), initial values for the monomer concentration ($[M_1]^0$ and $[M_2]^0$), and for the "concentration of active chain ends" ($[\ldots M_1^{\oplus}]^0$ and $[\ldots M_2^{\oplus}]^0$). Output data were curve paths of the time of running of monomer concentrations ($[M_1](t)$ and $[M_2](t)$), and active chain ends ($[\ldots M_1^{\oplus}](t)$ and $[\ldots M_2^{\oplus}](t)$) which describe the kinetics of the copolymerization. Figure 1 shows the block wiring diagram of the analog computer program for the rate laws (2a). . . (2d)

Figure 2 contains a copolymerization simulated in this way. One can see that both the monomer concentrations and the concentrations of active chain ends are functions of time.

The copolymerization simulated in this way may be used as a "testing system" for the control of the exactness of the method serving for the calculation of IRC. The input data (k_{11}, k_{12}, k_{21}, k_{22}) for the analog simulation show the meaning of "objective" IRC. From the "concentration-time curves" represented in Fig. 2, the so-called "theoretical" IRC, are calculated, and in this way the "theoretical" CPP and "kinetic" CPP (according to Ref. 25) were obtained. The data are compared in Table 1.

The estimation of the input data for the analog simulation had been

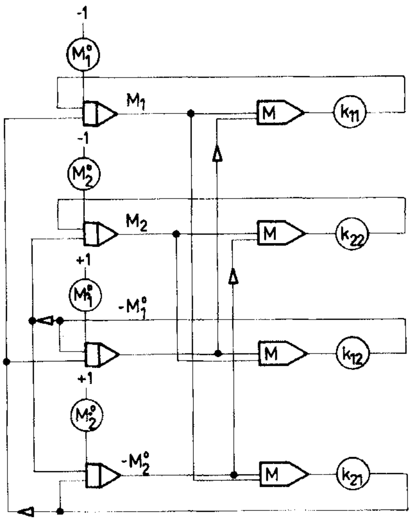


FIG. 1. Block wiring diagram for the analog computer program for the simulation of the crossed propagation reaction in the binary first-order copolymerization.

made in such a manner that their proportions corresponded with those of a cationic copolymerization of styrene and p-chlorostyrene [7]. It is shown that the theoretical IRC correspond well with the "objective" ones. Deviations may largely have their origin in faults made during the digitalization of the analog curve paths, which would correspond with the "experimental" measuring faults.

The "objective" and "theoretical" copolymerization parameters (calculated according to $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$) also correspond well with each other. The kinetic CPP (calculated according to the "trapeze rule" [25]) show remarkable deviations which seem to have their reason in the approaches used during the derivation of the copolymerization Eq. (3) and the numerical integration for the solution of this equation.

The above example of testing hints at the availability in principle of our method for the calculation of "individual rate constants." In the following, experimental parameters of cationic copolymerization are compared with the data derived in the above-mentioned way.

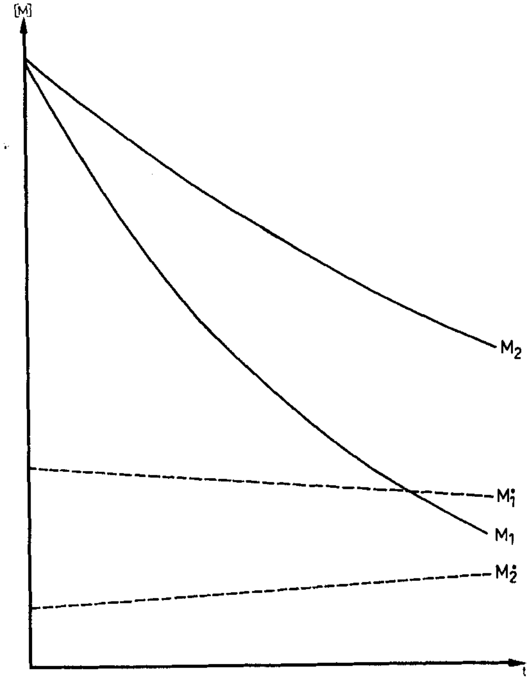


FIG. 2. The analog simulation of a random copolymerization. M_1, M_2 : concentrations of comonomers. M_1^*, M_2^*: concentrations of active chain ends (machine units).

III. RESULTS AND DISCUSSIONS

Cationic Copolymerization of Vinyl Monomers

In addition to our earlier investigations on the cationic copolymerization of vinyl-type monomers [6, 7, 28], the following systems have been taken into consideration:

MCP 1: cationic copolymerization of α-methylstyrene ($[M_1]^0 = 0.3$ mole L^{-1}) and styrene ($[M_2]^0 = 0.35$ mole L^{-1}) in methylene dichloride at 195°K, initiated by 1×10^{-4} mole L^{-1} Ph_3CSbCl_6

MCP 2: like MCP 1 initiated by 3×10^{-4} mole L^{-1} Ph_3CSbCl_6

MCP 3: cationic copolymerization of styrene ($[M_1]^0 = 0.2$ mole L^{-1}) and p-chlorostyrene ($[M_2]^0 = 0.4$ mole L^{-1}) in methylene dichloride at 273°K, initiated by 4×10^{-3} mole L^{-1} $TiCl_4$

MCP 4: cationic copolymerization of phenylvinylether ($[M_1]^0$ =

TABLE 1. Test Relating the Mode of Proceeding for the Calculation of the "Individual Rate Constants" (IRC) by Means of the Analog Simulation of a Random Copolymerization: Comparison of the "Objective" IRC with the Theoretical (calculated) Data and of the "Theoretical" Copolymerization Parameters ($r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$) with the "Kinetic" CPP Determined According to Ref. 25

k_{ij}	Analog simulation	Calculated data
k_{11}	0.7000	0.7435
k_{12}	0.3000	0.2845
k_{21}	0.9000	0.9224
k_{22}	0.4000	0.3802
r_1(theor.)	2.3333	2.6134
r_2(theor.)	0.4444	0.4122
r_1(kinet.)		3.0199
r_2(kinet.)		0.6758

0.3 mole L^{-1}) and α-methylstyrene ($[M_2]^0$ = 0.3 mole L^{-1}) in methylene dichloride at 253°K, initiated by 2.6 × 10^{-3} mole L^{-1} $SnCl_4$

MCP 5: like MCP 4, initiated by 2.5 × 10^{-3} mole L^{-1} Ph_3CSnCl

In Table 2 are shown the calculated IRC (k_{ij}), the "theoretical" CPP (r_1(th.) = k_{11}/k_{12} and r_2(th.) = k_{22}/k_{21}), the "experimental" (taken from the literature) CPP (r_1(exp.) and r_2(exp.)) as well as the gross rate constants of the homopolymerization (k_1 and k_2) of both the comonomers. The comparison of these data led us to the following conclusions:

1. From the systems MCP 1 . . . MCP 3, one observes that the monomers of higher reactivity (i.e., α-methylstyrene in MCP 1 and MCP 2, styrene in MCP 3) are preferably incorporated into the polymeric chain (one show a higher co-selectivity). Both the chain ends are favorable in the reaction with M_1 ($k_{11} > k_{12}$ and $k_{21} > k_{22}$) whereas the two monomers attack the more reactive chain end ($. . .M_2^{\oplus}$) preferably ($k_{21} > k_{11}$ and $k_{22} > k_{12}$). Our earlier statement on the selectivity of the crossed propagation reactions of the cationic copolymerization of p-substituted styrenes agrees with these results [6, 28].

2. The cationic copolymerization MCP 2, initiated by higher catalyst concentration, proceeds less selectively than MCP 1. Consequently the IRC approach one another. The higher concentration of

TABLE 2. The Results Obtained with the Kinetic Analysis of the Cationic Copolymerization of Vinyl Monomers: Individual Rate Constants (k_{11}, k_{12}, k_{21}, k_{22}), Theoretical Copolymerization Parameters (r_1(th.) = k_{11}/k_{12} and r_2(th.) = k_{22}/k_{21}), "Experimental" CPP (calculated according to Ref. 25 or according to literature data) and Gross Rate Constants of the Homopolymerization (k_1 and k_2)

Parameter	MCP 1	MCP 2	MCP 3	MCP 4	MCP 5
Individual Rate Constants					
k_{11}/sec^{-1}	2.05×10^{-6}	1.13×10^{-6}	6.38×10^{-4}	9.32×10^{-3}	1.17×10^{-3}
k_{12}/sec^{-1}	0.77×10^{-6}	0.79×10^{-6}	3.16×10^{-4}	16.29×10^{-3}	1.18×10^{-3}
k_{21}/sec^{-1}	2.47×10^{-6}	1.35×10^{-6}	11.46×10^{-4}	0.85×10^{-3}	0.52×10^{-3}
k_{22}/sec^{-1}	0.92×10^{-6}	0.94×10^{-6}	5.67×10^{-4}	1.11×10^{-3}	0.63×10^{-3}
Copolymerization Parameters					
r_1(th.)	2.663	1.429	2.018	0.572	0.99
r_2(th.)	0.375	0.700	0.494	1.306	1.21
r_1(exp.)	1.13 ± 0.08	1.13 ± 0.08	1.178 ± 0.08	0.57 [39]	-
r_2(exp.)	0.82 ± 0.003	0.79 ± 0.003	0.59 ± 0.007	1.98 [39]	-
Gross-Rate Constants of Homopolymerization					
k_1/sec^{-1}	$\sim 10^{-5}$	1.13×10^{-5}	-	$7.7 \pm 0.58 \times 10^{-3}$	$2.5 \pm 1.6 \times 10^{-3}$
k_2/sec^{-1}	No polymerization	No polymerization	-	$1.07 \pm 0.04 \times 10^{-3}$	$0.4 \pm 0.2 \times 10^{-3}$

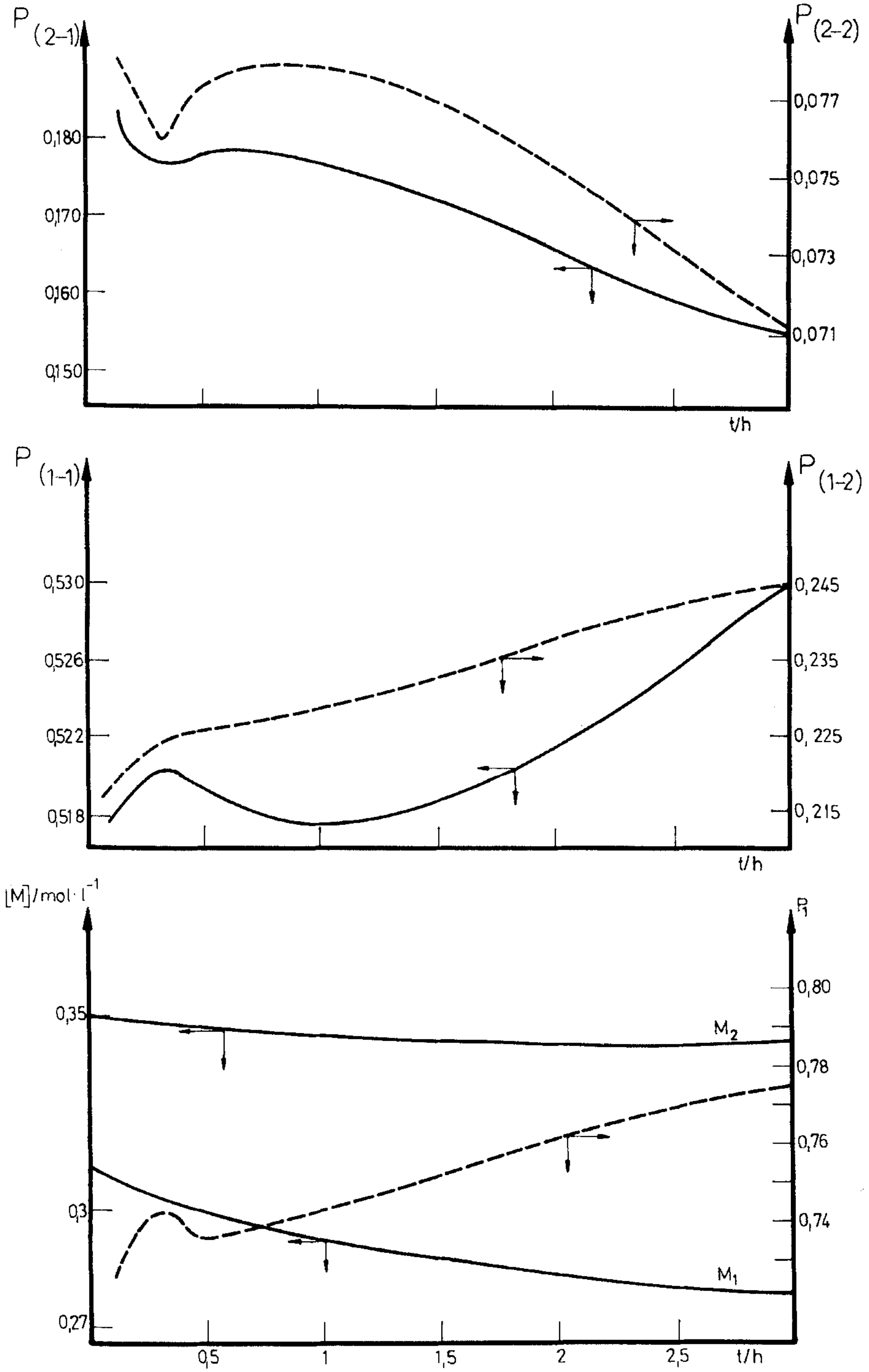


FIG. 3. Timely course for the monomer concentrations ([M]), the composition of the copolymer (P_1: mole fraction M_1 in the copolymer), and dyad frequencies P_{i-j} for the copolymerization MCP 1 (M_1: α-methylstyrene, M_2 : styrene).

initiator supports the formation of more active chain ends and thus the total reactivity of the system increases. Compared with the comonomers the active chain ends show an apparently lower co-selectivity:

k_{11}/k_{12} (MCP 1) $>$ k_{11}/k_{12} (MCP 2)

k_{21}/k_{22} (MCP 1) $>$ k_{21}/k_{22} (MCP 2)

The molecular masses and the physical inhomogeneities ($I = M_W/M_n - 1$) of the copolymers determined by means of GPC support this statement:

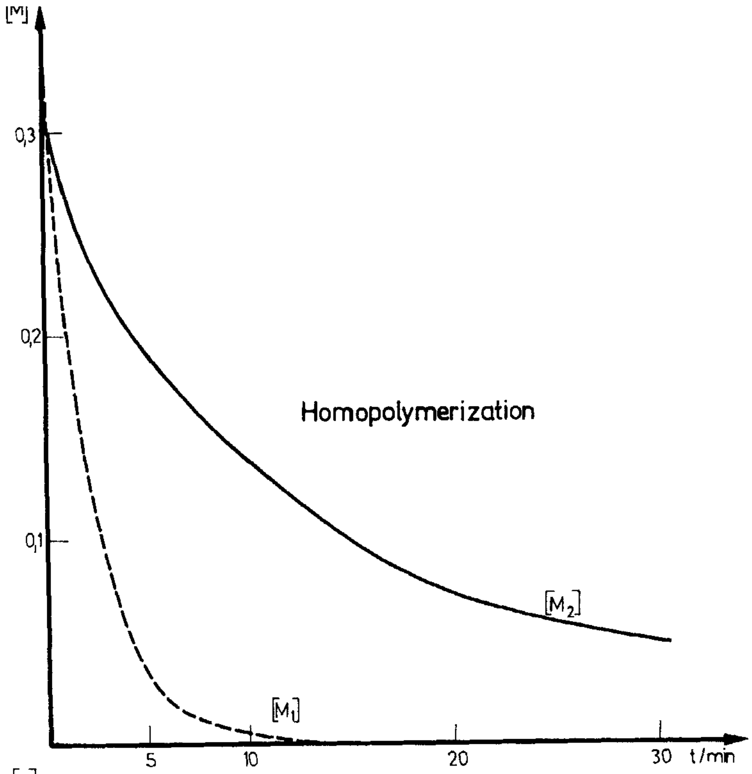
M_n (MCP 1) = 35 000 M_n (MCP 2) = 33 000

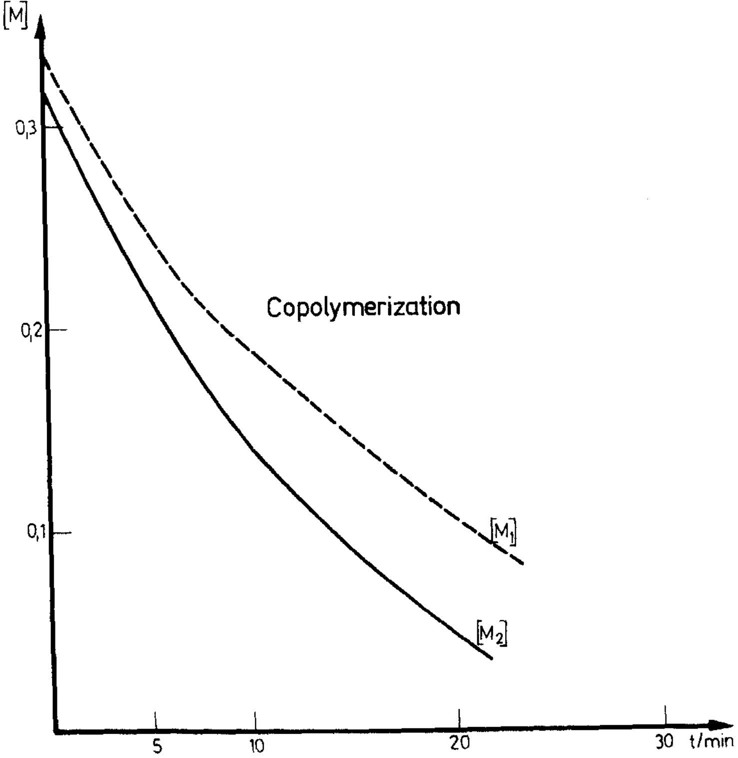
I (MCP 1) = 0.57 I (MCP 2) = 0.85

The higher inhomogeneities of MCP 2 copolymers hint at an increase of the chain-limiting reactions caused by an increase of the total reactivity.

3. In the case of initiation by stable carbenium ion salts (MCP 1, MCP 2, MCP 5), the initial phase of the polymerization shows effects which possibly may be explained by selective initiation. The dependence of the comonomer concentrations ([M]), the copolymer composition (P_1), and of the dyad frequencies (P_{1-1}, P_{1-2}, P_{2-1}, P_{2-2}) on the reaction time (Fig. 3) show that after about 0.25 hr the share of α-methylstyrene of the copolymer passes a local maximum. This can be interpreted by assuming that α-methylstyrene is preferable consumed in the initial phase of the reaction. The spectroscopically obtained rate constants for the reaction of α-methylstyrene with Ph_3CSbCl_6 at 298°K in CH_2Cl_2 yields $10.8 \pm 0.86 \times 10^{-4}$ sec^{-1} relative to $Ph_3C^{\oplus}$, whereas 3.28×10^{-4} sec^{-1} has been found for the reaction with styrene. The gross rate constants of the homopolymerization of α-methylstyrene under the conditions of MCP 2 is 1.13 $\times 10^{-5}$ sec^{-1} with reference to the monomer, whereas no polymerization of styrene could be observed under these conditions. The participation of styrene in the crossed propagation reaction should therefore chiefly be introduced by way of the crossed step: . . . α-methylstyrene$^{\oplus}$ + styrene $\longrightarrow$ . . . styrene$^{\oplus}$. By assuming the interaction between $Ph_3C^{\oplus}//SbCl_6^{\ominus}$ and that the monomer is essentially determining the rate of the initiation process (k_I), one can expect that the polymerization should be started by α-methylstyrene, i.e., selective initiation takes place and influences the copolymerization process.

4. The copolymerization of phenylvinylether with α-methylstyrene


[M]
0,3
0,2
0,1
Homopolymerization
[M2]
[M1]
5
10
20
30
t/min


[M]
0,3
0,2
0,1
Copolymerization
[M1]
[M2]
5
10
20
30
t/min

(MCP 4 and MCP 5) refers to the fact that the gross rate constants of the homopolymerization do not always permit inferences with regard to the relative reactivity of the corresponding monomers in the crossed propagation reaction and consequently also not on the selectivity of the copolymerization. In the homopolymerization the phenylvinylether shows a sevenfold gross rate constant compared with α-methylstyrene (see Table 2), whereas α-methylstyrene is the preferred monomer in copolymerization. In Fig. 4 this fact is demonstrated by the concentration-time curves for the two monomers. Plesch [29] indicated that the gross rate constant of the homopolymerization of monomers does not always allow a prediction about the reactivities of these monomers in the propagation reaction, as the interactions with the initiator leading to the chain start may be of a very different nature for monomers of distinct stereoelectronic structure.

5. The data in Table 2 allow conclusions on the "dynamics of copolymerization," e.g., on the dependence of the copolymer composition and the microstructure data on the conversion degree. Figure 5 represents correlations for copolymerization MCP 3. It is clearly evident:

> That the composition of the copolymer (P_1) alters with the reaction time.
>
> That the dyad frequencies (P_{i-j}), calculated according to Eq. (9), vary in their dependence on the conversion because the differential conditional probabilities calculated according to (6) are strongly dependent on the actual concentration ratio of monomers.

Therefore the calculation of static CPP needs to be well defined and, in general, low conversion degrees should be used for reason of mutual comparison [1, 24, 25].

The following characteristics of polymers for the polymerization MCP 3 were calculated according to (6) . . . (9):

P_1 (2.5 min) = 0.655
$\overline{l}_1 = 2.68$
$\overline{l}_2 = 1.59$
$P_{1-1} = 0.4106$
$P_{1-2} = 0.2449$
$P_{2-1} = 0.2160$
$P_{2-2} = 0.1285$

FIG. 4. Comparison of the concentration-time curves for the homopolymerization and the copolymerization of phenylvinylether (M_1) and α-methylstyrene (M_2) under the conditions of MCP 4.

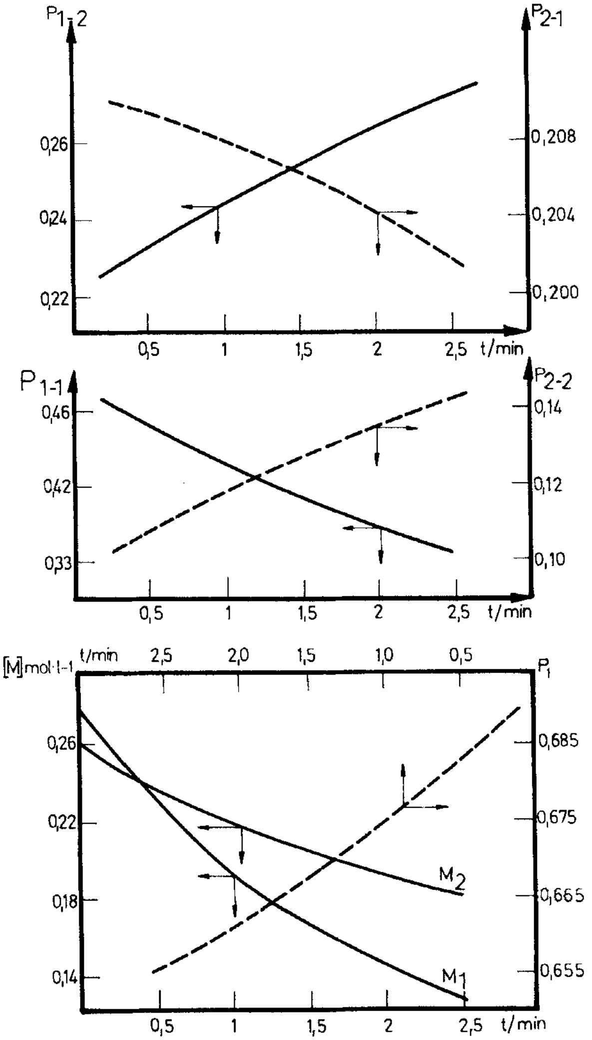


FIG. 5. The dynamics of the copolymerization of styrene (M_1) with p-chlorstyrene (M_2): timely course of the monomer concentrations ([M]), composition of copolymer (P_1: mole fraction of styrene in the copolymer), and dyad frequencies for the copolymerization MCP 3.

IR spectra of the copolymers (band at 540 cm^{-1}, intensity ratios of the bands at 700 and 760 cm^{-1}) allow the calculation of the medium lengths of styrene sequences [30]. The value of 2.8 for $\bar{l}_1$, determined experimentally in this way, is in good conformity with the theoretical predicted one ($\bar{l}_1$ = 2.68).

Results from the Cationic Copolymerization of α-Methylstyrene and Isobutene

The cationic copolymerization of α-methylstyrene and isobutene, described in detail in another paper [31], leads to polymeric products which are well characterized by ^{1}H-NMR-spectroscopy [31, 32]. Further hints regarding this polymerization are to be found in Ref. 33.

In Fig. 6 is illustrated the timely behavior of the ^{1}H-NMR-spectroscopically obtained copolymer composition (P_1) and that of the gravimetrically determined conversion of the copolymerization (U). The reaction took place in methylene dichloride ($[H_2O] = \sim 1 \times 10^{-3}$ mole L^{-1}) at 195°K. α-Methylstyrene ($[M_1]^0 = 0.4$ mole L^{-1}) and isobutene ($[M_2]^0 = 0.48$ mole L^{-1}) were initiated by 4×10^{-3} mole L^{-1} $TiCl_4$.

Figure 6 shows the formation of a considerable share of nonprecipitable oligomers on the lapse of polymerization. The similarity of the two curves generally proves the usefulness of total monomer consumption and the determination of the precipitable product for kinetic analysis of the copolymerization, but the results must be different. These concentration-time curves, which either describe the total monomer consumption or the consumption only for the purpose of formation of the precipitable polymer, are calculable from the yield and composition of the copolymer ($X(M_1) = P_1$ . . . mole fraction of M_1 in the copolymer) according to

$$[M_i](t) = [M_i]^0 - U(t)([M_i]^0 + [M_j]^0), \qquad i \neq j \in (1, 2) \tag{10}$$

By means of the kinetic curves obtained in this way, we can get the input data necessary for the calculation of the "kinetic" copolymerization parameters as well as the IRC of the crossed propagation reaction in the copolymerization in accordance with the method described above.

The necessity of distinction between kinetic and static CPP, as described above, is impressively demonstrable. According to the method chosen for their determination, entirely different parameters are obtainable (see Table 3); however, the co-selectivity (characterized by lg r_1/r_2), derivated by us formerly [28], is in good agreement if only the formation of the precipitable product is taken into consideration (compare Fig. 7 and Table 3).

The data in Table 3 characterize the kinetics of the copolymerization and are capable of serving for the calculation of the integral

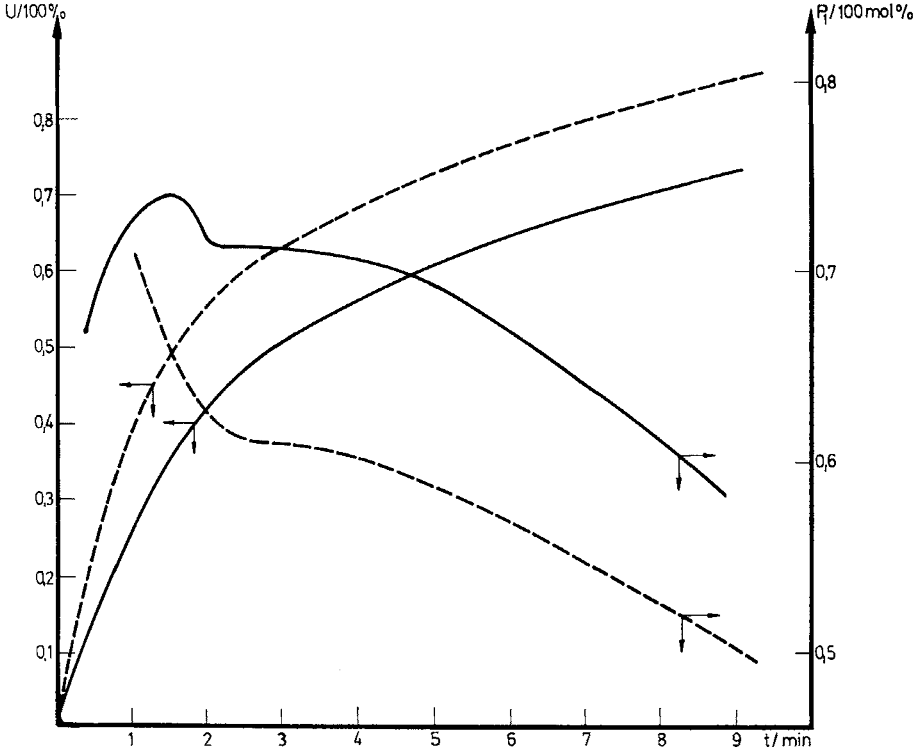


FIG. 6. Dependence of the conversion degree (U) and the composition of the copolymer (P_1: mole fraction of α-methylstyrene in the copolymer) on the reaction time for the copolymerization of α-methylstyrene (M_1) with isobutene (M_2): (- -) total conversion; (—) share of the precipitable product.

conditional probabilities stated in Table 4. This has been done on the basis of the IRC ($(P(i/j)_{IRC})$), and also on the basis of "kinetic" ($(P(i/j)_{CPP/k})$) and "static" ($(P(i/j)_{CPP/s})$) copolymerization parameters. The quantitative evaluation of the ^{1}H-NMR data by means of a computer program for peak separation [31] delivers the "experimental" values ($(P(i/j)_{exp.})$), given for comparison in Table 4. U designates the total conversion at a distinct time t (compare Fig. 6).

We conclude from Table 4:

The "static" CPP are less suited for calculation of the conditional probabilities according to Ref. 8.

TABLE 3. Results Obtained by Investigating the Cationic Copolymerization of α-Methylstyrene (M_1) with Isobutene (M_2): IRC, Theoretical, Kinetic and Static CPP for the Gross Conversion of the Reaction and the Formation of Precipitable Products

Parameters	Gross conversion	Formation of the precipitable product
	Individual Rate Constants	
k_{11}/sec^{-1}	8.358×10^{-3}	5.902×10^{-3}
k_{12}/sec^{-1}	3.220×10^{-3}	1.502×10^{-3}
k_{21}/sec^{-1}	20.880×10^{-3}	7.240×10^{-3}
k_{22}/sec^{-1}	8.357×10^{-3}	5.677×10^{-3}
	Copolymerization Parameters	
r_1(th.)	2.5958	3.9300
r_2(th.)	0.4002	0.7840
lg r_1(th.)/r_2(th.)	0.812	0.7001
r_1(kin.)	3.35 ± 0.026	2.128 ± 0.009
r_2(kin.)	0.157 ± 0.001	0.249 ± 0.001
lg r_1/r_2	1.329	0.9318
r_1(stat.)		1.06 ± 0.081
r_2(stat.)		0.159 ± 0.007
lg r_1/r_2		0.8239

The "kinetic" CPP allow a sufficiently good prediction relative to P(1/1), whereas P(2/2) is only insufficiently defined.
The values calculated on the basis of IRC correspond well with the experimentally, independently obtained ones. Accordingly, the constants k_{ij} has to be considered as a good basis for the interpretation of the "dynamics" of copolymerization.

Figure 8 illustrates the course of the "differentially" conditional probabilities dP(i/j) which means the probability that the propagation of a chain takes place in a consequence of steps:

$$\ldots M_i^{\oplus} + M_j \longrightarrow \ldots M_iM_j^{\oplus}$$

on account of the actually existing concentrations of the two comonomers at time t. Furthermore, Fig. 8 shows that the momentary

TABLE 4. Comparison of the Experimentally Independently Determined (^{1}H-NMR) Microstructure Data of the Precipitable Poly(α-methylstyrene-co-isobutene) with the Theoretically Calculated from the IRC Ones in Dependence on the Gross Conversion of the Copolymerization[a]

Conversion degree (%)	$P(1/1)_{exp}$	$P(2/2)_{exp}$	$P(1/1)_{IRC}$	$P(2/2)_{IRC}$
15.7	0.766 ± 0.038	0.503 ± 0.03	0.766	0.485
34.9	0.806 ± 0.051	0.447 ± 0.029	0.743	0.463
47.0	0.793 ± 0.078	0.494 ± 0.035	0.701	0.522
74.4	0.660 ± 0.033	0.530 ± 0.038	0.633	0.620

Calculated from CPP for a conversion of about 16%:

$P(1/1)_{CPP/k} = 0.767$
$P(2/2)_{CPP/k} = 0.230$
$P(1/1)_{CPP/s} = 0.563$
$P(2/2)_{CPP/s} = 0.160$

[a] $P(i/i)_{exp}$: calculated from ^{1}H-NMR data obtained from the product formed at the conversion U. $P(i/i)_{CPP/k}$: calculated from the kinetic copolymerization parameters according to Ref. 8. $P(i/i)_{CPP/s}$: calculated from the static CPP according to Ref. 8. $P(i/i)_{IRC}$: calculated from the IRC.

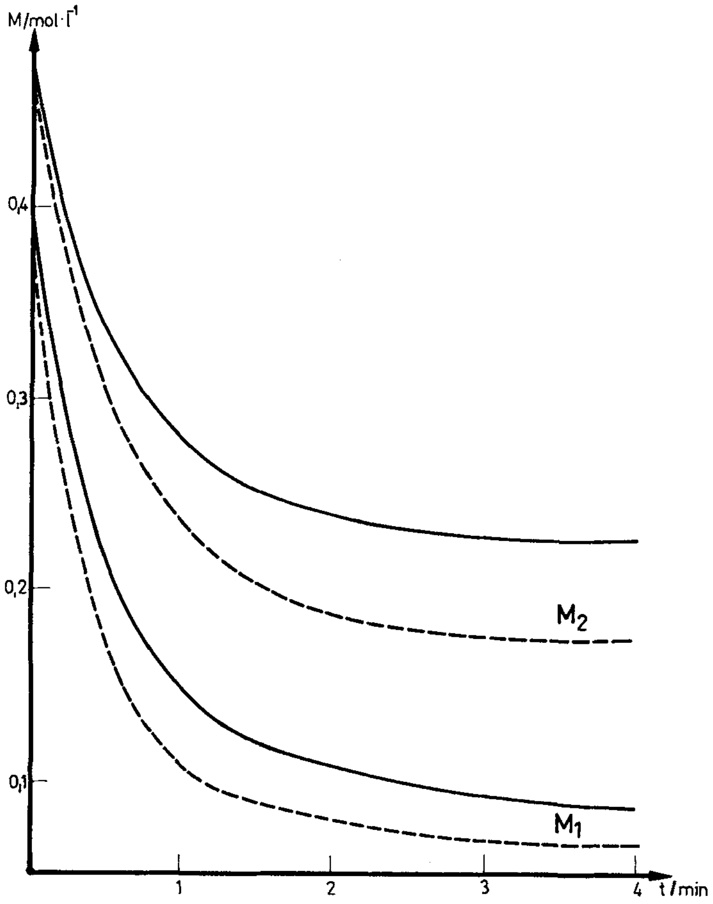


FIG. 7. Concentration-time curves for the cationic copolymerization of α-methylstyrene (M_1) with isobutene (M_2): (- -) total conversion; (—) share of the precipitable product.

probability of incorporating the reactive monomer M_1 (α-methylstyrene) into the copolymer continuously decreases the more the monomer mixture is growing poor in this monomer, or as inversely expressed, the incorporation of the less reactive monomer M_2 (isobutene) into the copolymer increases.

A comparison between the total conversion and formation of the precipitable polymer permits the assertion that the nonprecipitable oligomer constituents contain isobutene in a higher degree than the precipitable product. This can be concluded not only from the modification of the constants k_{ij} but also from the change of the conditional probabilities:

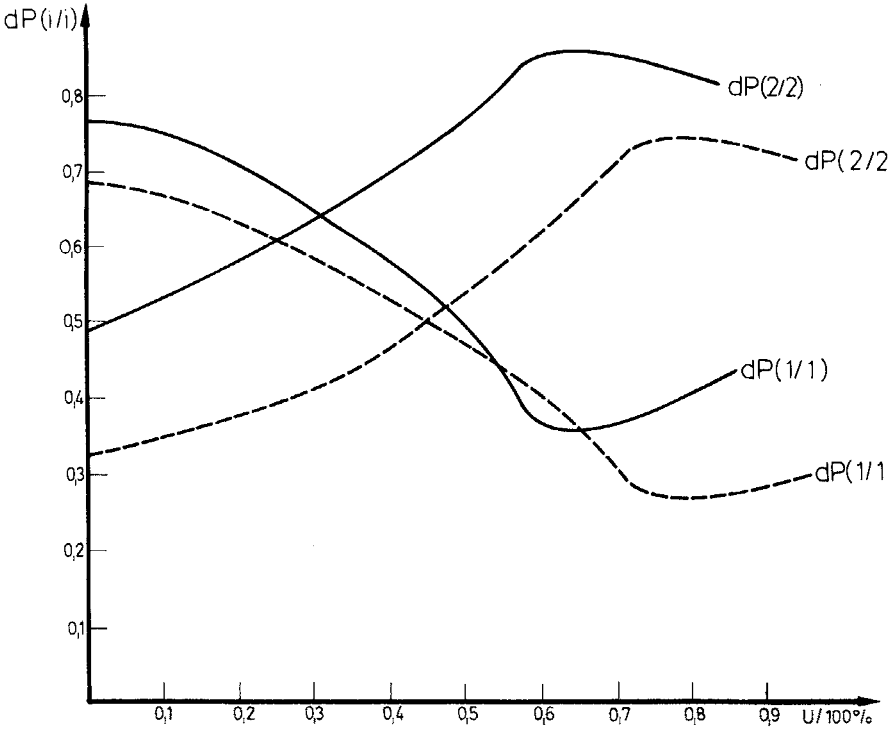


FIG. 8. Dependence of the "differential" conditional probabilities dP(1/1) and dP(2/2) on the overall conversion in the cationic copolymerization of α-methylstyrene (M_1) with isobutene (M_2): (- -) total conversion; (—) share of the precipitable product.

P(1/1) (total conversion) < P(1/1) precipitable product
P(1/2) < P(1/2)
P(2/1) > P(2/1)
P(2/2) > P(2/2)

While the precipitable polymer shows a relatively high tendency of block formation ($\bar{l}_1 = 3 \ldots 4$ and $\bar{l}_2 = 2 \ldots 2.5$), the oligomer product should be formed more strongly by alternating steps, as for the "gross product" medium sequence lengths $\bar{l}_1 = 2 \ldots 3$ and $\bar{l}_2 = 1.5 \ldots 1.8$ could be found, whereby the differences to the precipitable polymer are only traceable to the influence of the oligomers.

The dyad frequencies P_{i-j} depend on the overall conversion; that is, the probability that at a certain degree of conversion U(t) dyads i-j are found in the polymer; with an

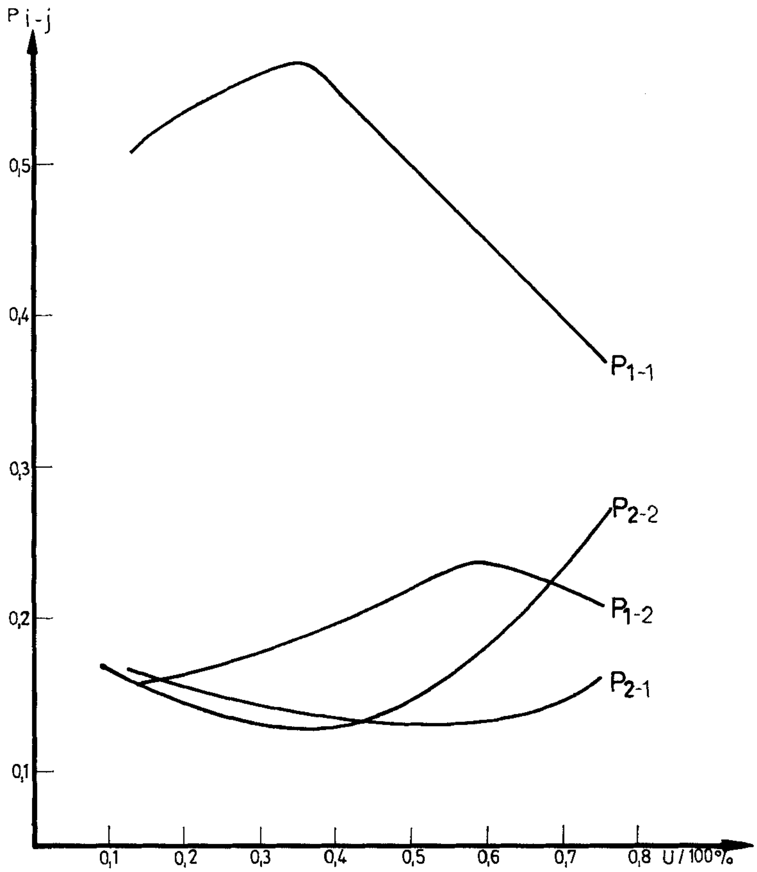


FIG. 9. Coherence between dyad frequencies (P_{i-j}) and overall conversion in the cationic copolymerization of α-methylstyrene (M_1) with isobutene (M_2) for the formation of the precipitable product.

increasing conversion the frequencies of homogeneous dyads P_{1-1} reduce, while those of the homogeneous P_{2-2} ones increase, and with that it follows that the higher the conversion, the smaller medium lengths of sequences $\bar{l}_1$ are found, but larger ones for $\bar{l}_2$ than with lower conversions (compare Fig. 9).

The appearance of extrema in the time course of dyad frequencies at still lower conversions points to the effects of selective initiation, as mentioned before.

Results from the Cationic Copolymerization of Cyclopentadiene and Isobutene

For the comparison of experimental data with those calculated, the copolymerization of 0.67 mole cyclopentadiene (M_1) with 1.454 moles isobutene (M_2) has been analyzed. Initiation occurred with 0.5 mole % $AlCl_3$ (dissolved in 220 mL 1,2-dichloroethane) which is continuously dropped in the reaction mixture (M_1 and M_2 dissolved in 200 mL heptane at 263°K).

A comparison of the ^{1}H-NMR-spectra of poly(isobutene-co-β-pinene) [34, 35] permits a clear classification of the resonances appearing between 0.7 and 1.1 ppm:

0.84 ppm = CPD-IB-CPK-triades
0.90 ppm = IB-IB-CPD-triades
0.94 ppm = CPD-IB-IB-triades
1.06 ppm = IB-IB-IB-triades

Figure 10 shows the kinetic concentration-time curves for both the monomers (isobutene followed by gas chromatography) and the composition of the precipitable product (P_1 for cyclopentadiene were taken from ^{1}H-NMR-spectroscopical analysis).

Also, the elution diagrams (GPC) show characteristic dependencies appearing as a shoulder beside the high molecular peak maximum (40 . . . 42 counts). A second low molecular peak maximum (at 47 counts) has been found with increasing polymerization time (Fig. 11). These observations obviously can be explained by an isobutene incorporation of isolated short monomer sequences into the copolymer during the first phase of polymerization. At increasing degrees of conversion, i.e., with decreasing concentration of cyclopentadiene in the solution, longer sequences of isobetene are formed as long as homopolymeric isobutene is obtained after about 10 min.

By means of a computer program factorizing the triade peak areas and by means of the equations valid for Markoff-statistics of the first order [11], it has been possible to calculate triade (P_{i-j-k}) and dyad concentrations (P_{i-j}) (Table 5) from the ^{1}H-NMR spectra of the corresponding polymers.

From the concentration-time curves the IRC were obtained:

k_{11} = 1180.00×10^{-5} sec^{-1}
k_{12} = 71.30×10^{-5} sec^{-1}
k_{21} = 8.95×10^{-5} sec^{-1}
k_{22} = 1.00×10^{-5} sec^{-1}

By use of the proposed calculation methods, the corresponding characteristics of copolymers were found (Table 5). Figure 12 contains the time course of the differential conditional probabilities.

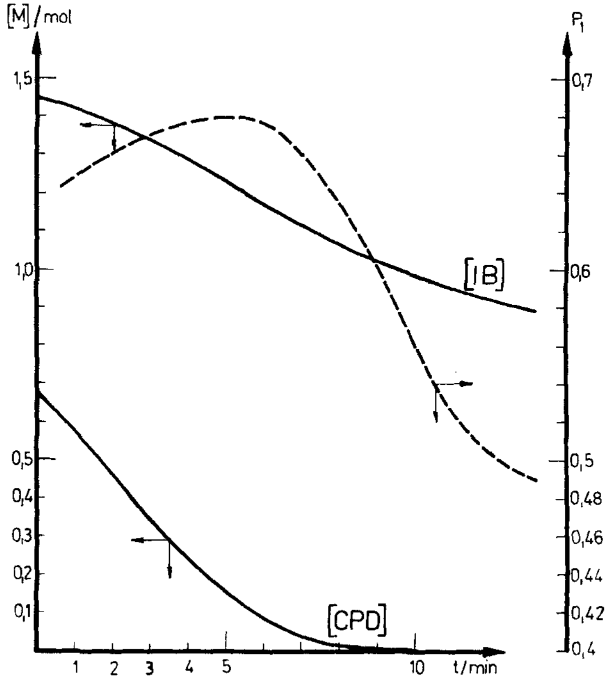


FIG. 10. Dependence of the monomer concentration ([M]) and the composition of the precipitable product (P_1: mole fraction of cyclopentadiene in the copolymer) on the reaction time for the cationic copolymerization of cyclopentadiene (M_1) with isobutene (M_2).

In Table 5, experimentally obtained and theoretically calculated integrally conditional probabilities and dyad frequencies are compared.

We would like to state the following facts:

1. The cyclopentadiene content of the copolymer (P_1) runs through a maximum which coincides with the maximum of the experimentally obtained integrally conditional probabilities (P(1/1)) at a reaction time of about 5 min.

2. The differential conditional probabilities calculated from the IRC hint that up to a reaction time of 5 min the incorporation of cyclopentadiene into the copolymer is preferred, while later on, because of the decreasing concentration of this monomer, isobutene joins the polymeric chains at a higher degree.

3. The theoretical calculated integrally conditional probabilities and dyad frequencies clearly deviate from the experimentally defined ones at low total conversion, otherwise the data show a better correspondence at increased conversion. In Fig. 13 is shown the time

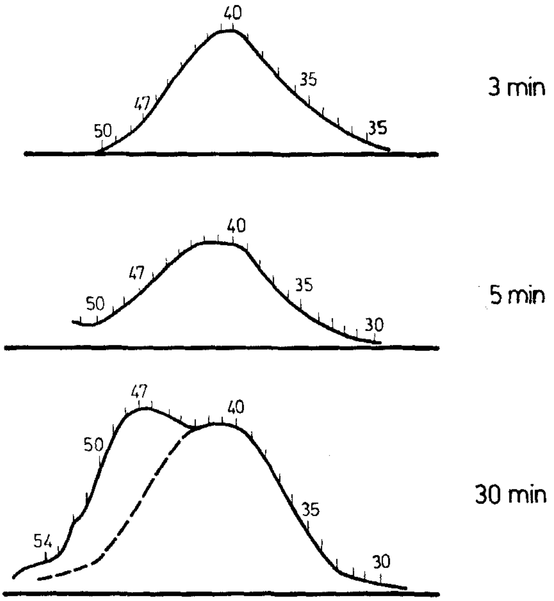


FIG. 11. Dependency of the elution diagrams (GPC) of the precipitable polymer on the reaction time for the cationic copolymerization of cyclopentadiene with isobutene.

dependence of the "concentrations of active chain ends" which are found during the course of calculation concerning the determination of the individual rate constants simultaneously.

The behavior in Fig. 13 seems to show a retardation of the cyclopentadienyl cation at the very beginning of the reaction, whereas the "concentration" of the t-butyl cation seems to remain constant. Nevertheless, cyclopentadiene is consumed far more rapidly than (as visualized by Figs. 10 and 11). This finding, if it corresponds with real behavior, may be explained by the competition of several equilibria, e.g., formation of active/inactive complexes between Lewis acids and monomers as Chmelir has mentioned [36], or the different stabilities of the intermediate carbenium ions wherefrom different reaction rates with the monomer results.

IV. COMPREHENSIVE CONCLUSIONS

The possibilities discussed in this paper concerning the quantitative description of copolymerization prove that a characterization

TABLE 5. Comparison between Experimentally Independently Determined (^{1}H-NMR) Microstructure Data and from IRC Calculated Ones for the Cationic Polymerized Poly(cyclopentadiene-co-isobutene) in Dependence on the Reaction Time

Reaction time (min)	"Integrally" conditional probabilities				Dyade frequencies							
	Calculated (IRC)		Experimental		Calculated (IRC)				Experimental (^{1}H-NMR)			
	P(1/1)	P(2/2)	P(1/1)	P(2/2)	P_{1-1}	P_{1-2}	P_{2-1}	P_{2-2}	P_{1-1}	P_{1-2}	P_{2-1}	P_{2-2}
1	0.875	0.200	-	-	0.57	0.08	0.28	0.07	-	-	-	-
2	0.86	0.22	0.61	0.25	0.57	0.09	0.27	0.07	0.40	0.26	0.25	0.09
3	0.84	0.24	0.74	0.46	0.56	0.11	0.26	0.08	0.49	0.18	0.18	0.15
5	0.79	0.32	0.77	0.50	0.54	0.14	0.22	0.10	0.52	0.15	0.16	0.16
10	0.67	0.44	0.67	0.57	0.37	0.18	0.27	0.19	0.37	0.19	0.25	0.19
60	0.56	0.53	0.55	0.60	0.27	0.20	0.25	0.29	0.25	0.21	0.21	0.33

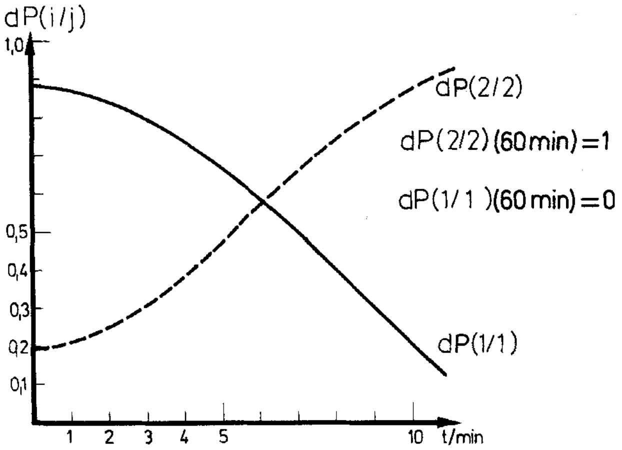


FIG. 12. The "differential" conditional probabilities dP(1/1) and dP(2/2) for the cationic copolymerization of cyclopentadiene (M_1) with isobutene (M_2) depending on the reaction time.

and prediction of copolymer properties on the basis of kinetic investigations of the polymerization reaction is possible and advantageous. The methodology presented by us for the quantification of the copolymerization by calculation of "individual rate constants" of the crossed propagation reaction for the first-order model of the binary copolymerization permits the interpretation of questions relating to the kinetics and selectivity of the reaction and the quantitative comprehension of the "dynamics of copolymer formation," whereby the following problems may be solved:

1. Calculation of quantitative data for the selectivity of the crossed propagation reaction (s-p) in binary copolymerization.
2. Model-shaped comprehension of the kinetics of the active species in the copolymerization process.
3. Calculation of microstructural aspects from kinetic data.
4. Prediction of microstructural data dependent on the reaction conditions and the conversion degree.
5. Mechanistic statements on the relation between monomer reactivity and selectivity of the crossed propagation reaction on the relations concerning the selectivity of the propagation reaction (s-p) and the initiation reaction (s-i).
6. Possibilities of optimation of the synthesis planning of copolymers of desired constitution.

Comparison with experimental data shows that the IRC for the crossed propagation reaction in a first-order copolymerization

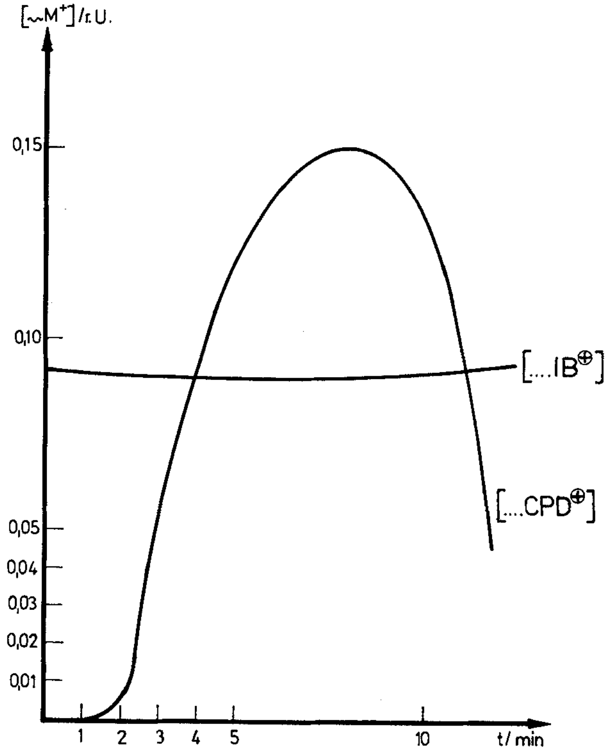


FIG. 13. Dependence of the "concentrations" of active chain ends ([. . . isobutene⊕] and [. . . cyclopentadiene⊕]) on the reaction time, calculated for the crossed propagation reaction of the cationic copolymerization of cyclopentadiene (CPD) with isobutylene (IB) according to the first-order model of copolymerization (all values are given in relative machine units = r.U.).

gives deeper insight into the course of copolymerization than classical CPP is able to do. Opposed to that is the necessity of a high computational expenditure which, however, for routine investigations will determine CPP. Derivable from CPP are important approaches for the starting values and supplementary restrictions for the calculation of IRC.

The method presented can be extended by arranging more detailed models for the crossed propagation reaction. In this way the second-order model (penultimate model) [9, 17-19] or the third-order model (ante-penultimate model) [9, 20] are in a better position to describe the influence of the structure of the chain end on the selectivity of the copolymerization than the simple terminal model. A model taking into consideration the participation of different active species in the co-propagation reaction (e.g., free ions and ion pairs) should permit it to explain better the chemical and physical inhomogeneities (s-ch, s-ph) of the product. An approximation permitting the participation of monomer complexes in the crossed propagation reaction [37, 38] is particularly apt for interpretation of copolymerization of donor monomers and acceptor monomers.

ACKNOWLEDGMENTS

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