

# Complex-radical alternating copolymerization

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## Abstract

The present review is an attempt to generalize and systematize the results accumulated in complex-radical copolymerization, as well as to analyze new aspects of alternating copolymerization of functional-substituted ethylenes as acceptor monomers with various electron-donor monomers having different types of conjugation between double bond and functional groups. The classification of mono- and bifunctional monomers is described from position of their acceptor–donor properties depending on the type of conjugation of double bond and functional groups. Phenomenon of monomer charge transfer complex (CTC) formation in radical copolymerization, cyclocopolymerization and terpolymerization reactions and its effect on kinetics and mechanisms of formation of copolymers with alternating structure are discussed in detail. In this review, new aspects of complex-radical copolymerization such as coordination effect in radical copolymerization of organotin monomers, effects of monomer CTCs, *keto–enol* tautomerism and *cis–trans* isomerism in the formation reactions of functional macromolecules with given structure and properties are described. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Monomeric charge transfer complexes; Complex-radical copolymerization; Terpolymerization; Cyclocopolymerization; Alternating copolymers; Alternating terpolymers; Kinetics; Mechanisms; Structure; Property

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## 1. Introduction

Among many various molecular complexes it is especially interesting to distinguish charge transfer complexes (CTC) of donor–acceptor monomer system (complexomers) due to their specific function as intermediates in functional macromolecules formation.

The mechanism of the study of the formation of CTC, complexomers spectra, and their action on separate stages of radical copolymerization, terpolymerization and cyclocopolymerization, are of great significance in solving the problem of controlling the chain growth, as well as planning the copolymer structure regularities, rate and degree of polymer formation reaction, and probably, steric structure which were the objective of early investigations. However, in many papers on radical copolymerization of donor–acceptor monomer systems, the role of CTC in elementary acts of chain growth reactions has been either ignored or considered inadequately.

One of the strong electron-accepting monomers able to form CTCs with various types of functional-substituted electron-donor monomers is 1,2-substituted ethylenes including maleic (fumaric) acid derivatives. The formation of a CTC in these monomer systems is the main decisive factor for determination of relative reactivities of monomers involved and for the elucidation of chain growth mechanism of complex-radical copolymerization reactions.

In several monographs [1–3] and reviews [4–9] investigations on role of monomer CTCs in radical copolymerization and peculiarities of chain growth reactions in alternating copolymerization of donor–acceptor monomers were considered and results summarized. After these publications in recent years considerable progress has been made in the field of complex-radical copolymerization and new aspects

of the mechanism of alternating chain growth reactions were revealed, and also many alternating copolymers having excellent properties were synthesized by using complex-radical copolymerization method.

The present review is an attempt to generalize and systematize the results accumulated in this interesting and important area of polymer chemistry and to analyze new aspects of mechanism of alternating copolymerization of functional-substituted ethylenes as acceptor monomers with various electron-donor monomers having different types of conjugation between double bond and functional groups.

## 2. Complex-radical alternating copolymerization

### 2.1. Classification of acceptor–donor monomers

The classification of monomers from different positions and specific classes of functional monomers were considered in several books [10–13] and reviews [14–21]. Thus, Arshady [22] classifies the monomers as structural monomers (styrene, acrylamide, dimethacrylamide, methacrylamide, acrylates, methacrylates and vinylics) and functional monomers (substituted styrenes, *N*-alkylacrylamides, alkyl and aryl acrylates and methacrylates, vinyl and allyl monomers, and maleic anhydride). This designation was employed to emphasize the relationship within and between different monomer types, and hence to better understand their homo- and copolymerization behaviors. Unfortunately, classification of functional monomers based on their position of their acceptor–donor properties was not considered in the above studies.

In general, depending on the type of conjugation of double bond and functional groups, all functional monomers can be categorized into two major groups: electron-acceptor (A) monomers and electron-donor (D) monomers. Functional substituted ethylenes, containing primary carboxyl, anhydride, ester, amide, imide and nitril fragments, include a wide range of A-monomers such as: (1) maleic anhydride and its  $\alpha,\beta$ -substituted derivatives (citroconic, dimethylmaleic and halogen-substituted maleic anhydrides), itaconic anhydride and etc.; (2) imides and *N*-substituted imides of unsaturated dicarboxylic acids (maleic and  $\alpha,\beta$ -substituted maleic acids, itaconic acid, etc.); (3) unsaturated mono- and dicarboxylic acids (crotonic, *trans*-cinnamic, maleic, fumaric acids, etc.) and their esters, nitrils and amides and (4) tetrahalogen-substituted ethylenes. Sulfur dioxide (SO<sub>2</sub>) can be also included in the above-mentioned group of A-monomers which easily copolymerize with vinyl and allyl D-monomers and form the alternating copolymers.

D-type of monomers which copolymerize with the above-mentioned A-monomers by mainly complex-radical alternating chain growth mechanism comprise also a wide range of monomers and can be divided into the following groups:

- (1) D-monomers with  $\pi$ – $\sigma$ -conjugation ( $\alpha$ -olefines, cycloalkenes, vinylcycloalkanes, allyl monomers, etc.);
- (2) D-monomers with  $\pi$ – $\rho$ -conjugation (vinyl ethers, vinyl sulfides, dimethoxyvinylene, *N*-vinylamides, *N*-vinylamines, vinylhalide, etc.);
- (3) D-monomers with  $\pi$ – $\pi$ -conjugation (vinylaromatic monomers, *trans*-stilbene, phenanthrene, acenaphthylene, inden, vinylpyridine and other vinyl-substituted heterocyclic monomers with pseudoaromatic character, phenylacetylene, etc.);
- (4) D-monomers with  $\pi$ – $\rho$ – $\pi$ -conjugation (vinyl esters, *N*-vinylcarbazole, *N*-vinylpyrrolidone, *N*-vinylsuccinimide, *N*-vinylphthalimide, etc.);

- (5) Heterocyclic monomers with  $\pi$ - $\rho$ - or  $\pi$ - $\pi$ -conjugation (furan, benzofuran, dihydrofuran, thiophen, benzothiophen, dihydropyran, *p*-dioxene, etc.);  
 (6) Elementorganic monomers of vinyl and allyl type (Si-, Ge-, Sn-, Fe-, P- and other metallorganic monomers with different types of conjugation).

Bifunctional monomers containing two D- and/or A-type of double bonds in molecule comprises the following types of monomers:

- (1) Monomers of D–D-type (divinyl and diallyl ethers, sulfides, esters, amines, and metallorganic derivatives, divinyl- and diallylarylenes, conjugated and nonconjugated dienes and cyclodienes, etc.);  
 (2) Monomers of D–A-type (vinyl and allyl esters of unsaturated mono- and dicarboxylic acids, *N*-vinyl- and *N*-allyl-substituted maleimides, etc.);  
 (3) Monomers of A–A-type (diacrylates, dimethacrylates, bis-maleimides, etc.).

## 2.2. Phenomenon of charge transfer in radical copolymerization

During the past 25 years, the radical copolymerization of various functional monomers of acceptor–donor type and synthesis of new functional polymers with given structure and properties have attracted considerable interest.

In a wide range of known molecular complexes, the CTCs from A–D monomer system are attached great importance because of their specific role in the formation reactions of functional macromolecules.

Progress in the field of radical copolymerization was considerably more thanks to discovered effect of complex-formation and possibility to control radical chain growth reactions, and also due to advanced principle about structure of monomer CTC and their relationship with kinetic parameters of reactions.

The role of monomer CTC in radical copolymerization and particularly in alternating chain growth reactions of A–D monomers were considered in particular and generalized in earlier published reviews [5–7,9,23] and monographs [1–3].

Geometry and structure of molecular A–D complexes and their relationship with mechanism of reactions were considered by Andrews and Keefer [24] and Briegleb [25], where mechanism about alternating copolymerization of some monomers also was mentioned.

It is known that molecular complex with equimolar composition is A–D system which has wave function ( $\psi$ ) in the basis state [25,26]:

$$\psi_N \approx a\psi_0(D\cdot A) + b\psi_1(D^+ - A^-)$$

Molecular complex with weak bond ( $a^2 \gg b^2$ ) is considered as resonance hybrid. E-complex in the excited state is described by following equation:

$$\psi_E = a^* \psi_1(D^+ - A^-) - b^* \psi_0(D\cdot A), \text{ where } a^* \approx a, b^* \approx b \text{ and } a^2 \gg b^2$$

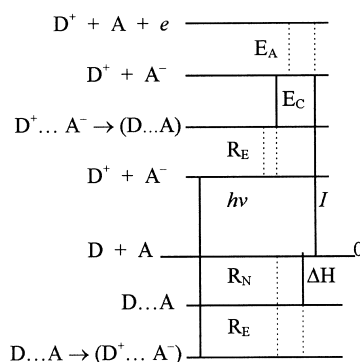
$N \rightarrow E$  transfer is accompanied by visible or UV absorption which corresponds to the electron transfer from D-monomer to A-monomer.

$\pi$ -electrons of double bond and/or functional group (COOH, COOR, C=O, CN, etc.) of A-monomers can be take part in complex-formation depending on the nature of second component (X) of  $A \cdots X$  complex, where X can be: (1) D-monomers; (2) organic compounds with electron-acceptor or electron-donor functional groups or bonds; (3) polar organic solvents and (4) acids, inorganic and organometalic

compounds of Lewis-acid-type. On the other hand, D-monomers at the same time can take part in complex-formation through other functional groups.

In this part of the present review the complex-formation in the A–D monomer systems only will be considered, since above-mentioned type of  $A \cdots X$  complexes are known long ago and are studied in detail. For example, CTC of maleic anhydride and amines are initiated by ionic polymerization of vinyl monomers [27–35] and  $A \cdots H-X$  (or Lewis acids) or  $A \cdots$ solvent complexes have important role in complex-radical homo- and copolymerization of vinyl and allyl monomers [1,3]. It was shown that the maleic anhydride  $\cdots$ tetrahydrofuran CTC can photoinitiate the radical polymerization of methylmethacrylate [33,34] and *trans*-stilbene [36]. But the maleic anhydride  $\cdots$ diethyl ether complex can initiate the cationic polymerization of isobutyl vinyl ether and vinyl carbazole [37]. The mechanism of photoinduced charge-transfer polymerization of donor–acceptor vinyl monomers are discussed in detail in a review [38].

The phenomenon of charge transfer in D–A monomer system from the point of view of interaction energy levels and their mutual transfers can be presented by the following scheme [1]:



where  $R_E$ —excited state,  $R_N$ —normal state,  $E_C$ —energy of charge transfer,  $h\nu$ —bond energy,  $I$ —potential ionization of D-monomer,  $E_A$ —affinity of A-monomer to electron and  $\Delta H$ —enthalpy of CTC formation.

CTC formation reaction is accompanied by the initiation of two new level energies: (1) more stable lower level corresponding to  $R_N$  state and (2) less stable excited level in  $R_E$  state. When light is absorbed by a CTC an electron in a definite orbit is excited and is transferred to a lower molecular orbit. The energy of this transfer as usually has an insignificant value (2–10 kcal/mol) and absorption is carried out in the visible field of spectra. As a result, the formed complexes acquire a visible color due to this reason in spite of their individual components being colorless. For transfer of electron from D-monomer orbit to orbit of A-monomer molecules of these monomers must approach each other sufficiently near and must take one's bearings so as to provide a maximum floor of corresponding orbits. Spontaneous charge transfer can be carried out in case of more active D-monomers having small value of potential ionization. Evidently, extreme case, i.e. formation of two ion-radical as a result of Coulomb interaction cannot be realized in monomer CTC systems. Formation of monomer CTC can be considered from the point of view of theory of valence as a resonance hybrid of inert and charge forms, which are transferred from one form to another as a result of interchange of charge, as shown in above-mentioned scheme. CTC have nearly non-bonded structure with insignificant conversion of donor–acceptor structure ( $D^+ \cdots A^-$ ). In normal state ( $R_N$ ).  $E_C$  depends on potential ionization of D-monomer as well as on affinity of A-monomer

for electron. Increase of  $I$  decreased force of charge transfer at  $E_A = \text{const.}$  Energy of band in CTC depend on  $I$ ,  $E_A$ ,  $E_r$  (resonance energy) and  $E_{cl}$  (Culone energy):

$$h\nu = I + E_A + E_r + E_{cl}$$

$R_N \rightarrow R_E$  transfer accompanied by increasing of  $\Delta H$  of complex-formation. Decrease of complex-formation constant ( $K_c$ ) of  $A \cdots D$  complex depends on the nature of A and D monomers and  $\Delta H$  becomes more negative (maximum increase of  $\Delta H$ ). Use of potential curves representing plot of  $E_C \rightarrow R$  (internucleus distance) also is convenient method for elucidation of charge transfer phenomenon in the D–A monomer systems [1].

First charge transfer model for copolymerization of maleic anhydride with various monomers—“electropositive and electronegative monomers can form CTC with each other. When this complex is attacked, both monomer in the complex add as a unit”, was proposed by Bartlett and Nozaki 50 years ago [39].

Zubov et al. [40], Shirota et al. [41], Sainer and Litt [42] proposed kinetic equations for determination of quantitative contribution of monomer CTC to the chain growth reactions and to the reactivity ratios of monomers, respectively. Analogous equation for complex-radical terpolymerization was considered by Rzaev et al. [43]. It was demonstrated that the monomer CTC is more reactive than either of the two monomers separately. This can be explained by principles of organic chemistry; intermediate complexes are more reactive than individual components, which in turn are more reactive than individual components in the bimolecular reactions. In opinion of authors of Ref. [42] this can be rationalized on the basis of polarizability of the complex vs. polarizability of the individual monomers. The CTC has a larger  $\pi$ -electron system, making the system as a whole highly polarizable. As such, it can interact more readily with an approaching radical of the correct polarity than an individual monomer can. The activation energy is therefore reduced. The preexponential factor may also increase in such a case as successful attack may be achieved over a wider solid angle. In copolymerization, such contact pairs may also copolymerize as a unit if they have, by chance, the correct orientations and therefore are highly polarizable. Since each monomer will usually be in contact with several molecules of comonomer, this is not impossible [42].

Kokuba et al. [44] on the basis of known experimental data of copolymerization and values of equilibrium constants of CTC formation ( $K_c$ ) for A (maleic anhydride or  $\text{SO}_2$ )–D (vinyl ethers, *N*-vinylcarbazole, *N*-vinylpyridine, *p*-dioxene, *cis*- and *trans*-2 butenes and cycloolefines) monomer systems proposed a following tentative classification of charge-transfer polymerizations:  $K_c < 0.01$  l/mol—no alternating copolymerization;  $K_c = 0.01$ – $0.1$  l/mol—alternating copolymerization in the presence of initiator;  $K_c \leq 0.15$  l/mol—spontaneous alternating copolymerization near at room temperature (the  $K_c$  value decreases with increasing solvent polarity);  $K_c = 1.0$ – $5.0$  l/mol—spontaneous ionic polymerization (the  $K_c$  value increases with increasing solvent polarity) and  $K_c = 5.0$ – $\infty$  l/mol—formation of separable, stable complexes which cannot initiate. According to the authors, by measuring the value of  $K_c$ , the mode of polymerization of the system can be predicted from such a classification, and vice versa.

### 2.3. Copolymerization of maleic anhydride

In a monograph [1] the results of studies of radical homo-, and co- and terpolymerization of maleic anhydride (MA) are presented. Periodical and patent literature in this field upto 1983 (inclusive) are

considered. Special attention is given to the explanation of the mechanism of alternating chain growth reactions on the basis of critical analysis of the contradictory views existing in the literature. The role of charge transfer complexes in the formation of copolymers with given structure and composition is stressed. The methods of preparation of poly(maleic anhydride) and its derivatives are considered. Classification of comonomers with different substitutes is given. Polymer-analogous and macromolecular reactions of maleic anhydride copolymers are analyzed in detail and full classification of inter- and intramolecular reactions is presented. Some peculiarities of structure and conformation of macromolecules, properties of anhydride-containing polymers and their major fields of application are examined. Constants of CTC-formation and copolymerization are summarized.

Much interest has been shown in the radical alternating copolymerization of MA with styrene [1,2,9,45–49] probably through formation of a CTC between initial monomers. From this monomer system, high molecular weight copolymer with alternating structure was prepared even in the absence of the initiator [50–52]. It was established that equimolar CTC was formed in the MA–styrene system [45]. However, authors of the paper [9] proposed that MA···styrene complex and other analogous type complexes play only a very small part leading to an alternation of monomer units in these systems. Moreover, the kinetics and mechanism of copolymerization of these monomer systems have been widely studied by using various models [2,46,47].

It has been demonstrated that the initial rate of 1:1 alternating copolymerization is not necessarily maximum at a 1:1 feed composition and that the position of the rate maximum is dependent on the total monomer concentration. Thus the maxima of the copolymerization rates for the MA–vinylacetate [53], MA–chloroethyl vinyl ether [54] and MA–isobutyl ether [55,56] systems shift toward 1:1 feed composition as the total monomer concentrations become larger. The initial rate of radical copolymerization of vinyl ethers and esters, and styrenes with MA is analyzed according to the simplified complex participation model.

MA is known to form an alternating copolymer with electron-donor heterocyclic monomers such as thiophene and its 2-methyl or 3-methyl derivatives [57–59], furan and 2-methylfuran [60,61] having repeating units of structures with 2,5-linkages (for thiophene and furan) and mainly 2,3-linkages across the methyl-substituted derivatives. The effect of methyl substitution on the structure and the mechanism of formation of the copolymers is studied using  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy.

MA also forms alternating copolymers with benzofuran, indol and benzothiophene under the influence of AIBN [62]. Constants of CTC formation for the all three systems are determined:  $K_c = 0.01$  (in cyclohexane), 0.28 (in chloroform) and 0.3 (in chloroform) (in l/mol), respectively. The results obtained by these authors indicate that the reactivity of the comonomers to form alternating copolymers with MA is governed by the resonance stabilization of the monomer and to a lesser extent by complex formation. They, by mistake, conclude that the formation of CTCs is not the most important factor in determining the reactivity in copolymerization of MA with above-mentioned heterocyclic monomers.

From the results of UV spectra it is suggested that spontaneous copolymerization of 8,9-benzo-2-methylene-1,4,6-thioxapiro[4,4]nonane (donor) with MA proceeds via a CTC [63].

The formation of CTC in the MA-donor monomer systems was observed and complex-radical copolymerization of MA with various electron-donor functional monomers such as *p*-dioxene [64], *p*-oxathiene [65], 2,3-dihydropyran [66], ethyl- and phenyl vinylsulfides [67], phenylvinyl alkyl ethers and thioethers [68], alkyl vinyl ethers [69–72], 2-vinyl-1,3-dioxane [72], phenylacetylene [73], ethylidene-nonbornene [74], indene [75], indol [76], thiophene [61], furan [76], allylglycidyl ether [77,78], vinyltriethoxysilane [77,79], 4-nitrylcyclohexene-1 [80], *trans*-stilbene [81], phenanthrene [82] and etc. were realized.

#### 2.4. Copolymerization of $\alpha,\beta$ -substituted maleic anhydride

The isostructural analogs of maleic acid and its derivatives such as citraconic ( $\alpha$ -methylmaleic) acid derivatives, dimethylmaleic anhydride,  $\alpha$ -chloromaleic anhydride, etc. also radical copolymerize with electron-donor comonomers with formation of alternating copolymers.

First, the synthesis of citraconic anhydride (CA) and styrene copolymer was described in Ref. [83] in 1961. Although there have been a few publications on copolymerization parameters of CA with styrene, no systematic study has been done. The detailed studies of radical copolymerization of this system were realized by Yang and Otsu [84]. Radical copolymerization of CA with styrene was carried out and studied spectroscopically. Existence of 1:1 CTC between CA and styrene was confirmed by means of UV spectroscopy. The  $K_c$  was determined as 0.098 l/mol in chloroform at 15°C. The mechanism of copolymerization was evaluated by three types of models, i.e. the classical thermal model, the penultimate model, and the complex participation model. On the basis of the experimental data and by using these models the constants of copolymerization were determined:  $r_1 = 0.00$  and  $r_2 = 0.25$  (the terminal model of Mayo and Lewis),  $r_{12} = k_{122}/k_{121} = 0.59$ ,  $r_{22} = k_{222}/k_{221} = 0.09$  and  $r_{12}/r_{22} = 6.6$  (the penultimate model) and  $r_{2c} = 0.015\text{--}0.66$  and  $r_2 = 0.026\text{--}0.42$  (the complex participation model of Seiner and Litt [42] by using value obtained of  $K_c$  and at several values of  $r_{2c}/r_{2c2} = 0.00 = 1.0$ ). From the comparison of these values Yang and Otsu concluded that the penultimate model gives a better fit for the experimental data than the thermal and complex models, indicating that the penultimate group effect is very important in this copolymerization. The complex model provides a somewhat better fit to the comparison data than the thermal model, indicating presumably that complexes also play a certain but small part in the copolymerization. The value of  $r_{12}/r_{22}$  indicates that CA is about 6.6 times more reactive toward the  $\sim M_1M_2$  radical than toward the  $\sim M_1M_2$  radical. The relatively low reactivity of CA toward the poly(St) radical with a penultimate CA unit ( $r_{12}/r_{22} = 3.7$ ) for the MA–St system [9] seems to be attributed to steric and dipolar repulsion.

It was shown that the copolymerization of CA with styrene proceeded rapidly to give the copolymers having  $M_n$  in the range of  $(7.4\text{--}15.0) \times 10^4$ . The rate of copolymerization was found to increase with an increase in the molar fraction of CA in the monomer mixture, and the  $M_n$  of the copolymers have a maximum [CA] value at about 60 mol%. In addition, it was observed that the copolymerization proceeded slowly even in the absence of AIBN, to give a high molecular weight ( $>500\ 000$ ) copolymer [84].

The copolymerization of dialkyl citraconates and the isomeric mesaconates with vinyl acetate, as well as isobutyl vinyl ether, have been performed and found to give alternating copolymers [85].

It is known that the  $\alpha,\beta$ -dimethylmaleic anhydride copolymerize with alkyl vinyl ethers [86–88]. However, this acceptor monomer does not copolymerize with styrene [89,90].

The copolymers which approach alternating character but are of low molecular weight were prepared by copolymerization of  $\alpha,\beta$ -dimethylmaleic anhydride with ethylene at very low pressure of ethylene [84].

#### 2.5. Copolymerization of N-substituted maleimides

N-substituted maleimides as electron-acceptor monomers have been reported to copolymerize alternatingly with a variety of electron donor vinyl comonomers such as styrene [91–98],  $\alpha$ -methylstyrene [99,100], alkyl (2-chloroethyl) vinyl ethers [93,101], cyclohexyl vinyl ketone and its derivatives (in the



enol forms) [102,103], isobutylene [95], butadiene-1,3 [104] and 2-vinylpyridine [95], by a free-radical and/or complex-radical mechanism. These alternating copolymers have some unique properties such as high and superior thermal stabilities [95,105,106], fire resistances [107–111], photo-, X-ray and E-beam sensitivities [98,102,105,112], as well as catalytic and chiroptical activities [91,113–117].

Various *N*-substituted (R) maleimides (R = C<sub>6</sub>H<sub>11</sub>, *p*-C<sub>6</sub>H<sub>4</sub>-X, where X = H, CH<sub>3</sub>, OCH<sub>3</sub>, F, Cl, CF<sub>3</sub>, CN, COOEt and OOCCH<sub>3</sub>) have been shown to alternately copolymerize with several vinyl ethers [118–120]. Copolymerization conditions as temperature, solvent, total monomer concentration and the donor–acceptor character of the comonomer, favoring the formation of a CTC invariably gave higher *cis:trans* stereochemical ratios at the succinimide units in the resulting copolymers. The results are interpreted as indicating that copolymer succinimide unit stereochemistry is dependent on the fraction of maleimide monomer in complex form and that the CTC participates significantly in the propagation steps of the copolymerization.

In the copolymerization of  $\alpha$ -methylstyrene with maleimide and *N*-phenylmaleimide, the resulting copolymers were found to have a high alternating structure regardless of the ratio of comonomers in the feed. It was found that the copolymerization of  $\alpha$ -methylstyrene with maleimide proceeds predominantly through participation of the CTC ( $K_c = 0.03$  l/mol). However in the system of  $\alpha$ -methylstyrene-*N*-phenylmaleimide the reaction proceeds predominantly by the addition of free monomers ( $K_c = 0.02$  l/mol) [99,100].

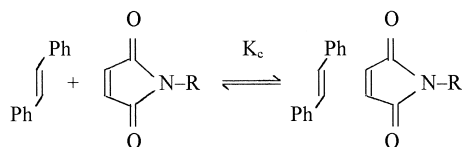
The free-radical copolymerization of styrene with *N*-phenylmaleimide is dominated by alternating copolymerization with the participation of monomer CTC in both initiation and chain growth [9,121–126].

It was shown that in the copolymerization of *N*-alkylmaleimides (Alkyl = Me, Et, *n*-Pr, *iso*-Pr, *tert*-Bu, *n*-Hex) with  $\alpha$ -methylstyrene, the rate of polymerization decreases with an increase in the bulkiness of alkyl groups [126,127]. During the course of the studies on the copolymerization of maleimidocholesterylhexanoate, maleimidocholesterylbenzoate and *N*-(benzo-15-crown-5)maleimide with  $\alpha$ -methylstyrene, it was found that copolymerization proceeds under the participation of CTCs, yielding alternating copolymers [117,128].

The results of a series of complex-radical alternating binary and ternary copolymerization of donor–acceptor monomer systems including *trans*-stilbene, maleic anhydride and *N*-phenylmaleimide were reported, previously [43,81,96,97,129,130].

Several authors also studied the radical alternating copolymerization of other *N*-substituted imides donating vinyl monomers systems: *N*-(4-substituted phenyl)itacoimides (R = CH<sub>3</sub>, Cl, OCH<sub>3</sub>, OOC-CH<sub>3</sub> and COOC<sub>2</sub>H<sub>5</sub>)–styrene [131–133], *N*-alkylcitraconimides–styrene [133–135],  $\alpha$ -methylstyrene [136] and vinyl acetate [137].

In Ref. [138], the effects of *N*-substituents (H, C<sub>2</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>5</sub>) on the charge transfer complex (CTC) formation and copolymerization reactivities in the Stb(donor)-*N*-substituted maleimides, (MI, EtMI and PhMI acceptor monomers) system, are examined and discussed, and thermal properties of resulting alternating copolymers are presented. The equilibrium constants of 1:1 complexes between Stb (donor) and maleimides (acceptors) of the following general structure

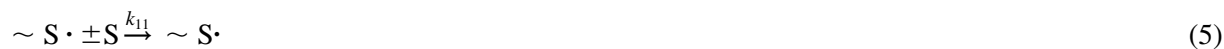


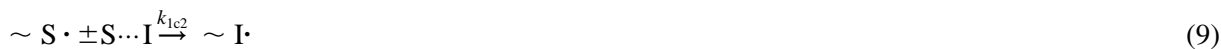
where R = H, C<sub>2</sub>H<sub>5</sub> or C<sub>6</sub>H<sub>5</sub>, are determined by <sup>1</sup>H-NMR method of Hanna–Ashbaugh equation [139]. The concentration of acceptor monomers (imides) in different mixtures with Stb at [imide] ≪ [Stb] was constant at 0.1 mol/l. On the base of <sup>1</sup>H-NMR spectra of free MI (δ<sup>f</sup> = 5.57 ppm), EtMI (δ<sup>f</sup> = 5.75 ppm) and PhMI (δ<sup>f</sup> = 5.73 ppm) and their different mixtures with Stb the chemical shifts of imides protons are determined. A comparative analysis of <sup>1</sup>H-NMR spectra of initial monomers revealed that the chemical shift of CH group is affected by the transfer from H-atom to C<sub>2</sub>H<sub>5</sub> or C<sub>6</sub>H<sub>5</sub> substituent in the imide molecule. The introduction of C<sub>2</sub>H<sub>5</sub> or C<sub>6</sub>H<sub>5</sub> group into the maleimide molecule resulted in a displacement of the CH = chemicalshift (Δ = 0.16–0.18 ppm) to a weaker field, which stipulated for change of π-electron density of imide double bond, which had an effect on the tendency of the imide acceptor monomers for complex-formation reaction with Stb (donor). From these data the complex formation constants (K<sub>c</sub>) for Stb···MI, Stb···EtMI and Stb···PhMI complexes are calculated. The values obtained for K<sub>c</sub> of the complexes are 0.114 (0.005) (Stb···MI), 0.053 (0.003) (Stb···EtMI) and 0.177 (0.006) (Stb···PhMI) (in l/mol) at 37°C in C<sub>6</sub>H<sub>6</sub>-d<sub>6</sub>. In fact, if one compares K<sub>c</sub> values obtained for complexes, it is clear that K<sub>c</sub>(Stb···MI) is greater than K<sub>c</sub>(Stb···EtMI). However, analogous change for K<sub>c</sub> of Stb···MI and Stb···PhMI complexes do not take place, which can be explained by supplementary effect of π-electrons of N-phenyl ring on complex formation reaction.

All copolymers are close to an equimolar composition, irrespective of composition of the initial monomer mixtures. Since neither Stb (S) nor imides (I) homopolymerize in selected copolymerization conditions, the monomer systems can be characterized by the following elementary reactions of chain propagation allowing for free monomer and for those bound in CTC:



The constants of copolymerization for three monomer pair systems studied are calculated in accordance with classical terminal model equations of Fineman–Ross (FR) [140] and Kelen–Tüdös (KT) [141], as well as terminal complex model equation of Seiner–Litt (SL) [42], involving chain growth reactions of (1) and (2), and afterwards (5–10):





The reactivity ratios of the studied pair of monomers are calculated with the FR, KT and SL equations in the following forms, respectively:

$$F(f - 1)/f = r_1 F^2/f - r_2 \quad (11)$$

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \quad (12)$$

$$(y - 1) = r_{1c}/r_{1c1} + (r_{1c}/K_c)\chi \quad (13)$$

where  $F = M_1/M_2$ ,  $f = m_1/m_2$ ,  $\eta = (F^2/f)/(\alpha + F^2/f)$ ,  $\xi = [F(f - 1)/f]/(\alpha + F^2/f)$ ,  $\alpha = \sqrt{(F^2/f)_{\min} \cdot (F^2/f)_{\max}}$ ,  $y = (1 + r_{12}F)/(1 + r_{21}F^{-1})$ ,  $\chi = 1/M_2[1 - (y - 1)/r_{12}F]$ ,  $r_{1c} = (r_{1c1} + r_{1c2})/(r_{1c1}r_{1c2})$  for the condition of  $k_{1c} = k_{1c1} + k_{1c2}$ .

The constants of copolymerization obtained and parameters of  $Q_2$  and  $e_2$  for imide comonomers have following values: Stb–MI— $r_1$  0.006;  $r_2$  0.064,  $Q_2$  1.73 and  $e_2$  2.56; Stb–EtMI— $r_1$  0.021,  $r_2$  0.014,  $Q_2$  0.59 and  $e_2$  2.47; Stb–PhMI— $r_1$  0.04,  $r_2$  0.25,  $Q_2$  0.29 and  $e_2$  1.94; As evidenced from these data, the tendency for alternation increases in the row of MI > EtMI > PhMI which can be explained with the change of polarizability of  $\pi$ -electron systems of imide cycles connected with the effect of *N*-substituted ethyl and phenyl groups decreasing electron-acceptor properties of maleimide double bond. This fact observed is confirmed by values of  $K_c$  for CTC of Stb··-imides.

$Q_2$  and  $e_2$  values properly calculated for imides studies by using of Alfrey–Price  $Q$ - $e$  scheme [142], which correlate with energy of localization, order and  $\pi$ -electron density of maleimide double bonds. These parameters decrease with transfer from MI to its *N*-ethyl and *N*-phenyl derivatives. PhMI is the most active comonomer in copolymerization with Stb. The values of copolymerization constants of  $r_{1c}$  ( $k_{11}/k_{1c}$ ) 0.028, 0.052 and 0.189,  $r_{1c1}$  ( $k_{11}/k_{1c1}$ ) 1.08, 3.59 and 13.46 and  $r_{1c2}$  ( $k_{11}/k_{1c2}$ ) 0.029, 0.053 and 0.129 for Stb–imides system are obtained by taking into consideration of distribution of  $K_c$  on the relative activity of monomers confirms the fact that chain growth proceeds primary by addition of Stb··-imides complexes in growing macroradical of  $\sim$ Stb· with the imide side.

## 2.6. Copolymerization of unsaturated dicarboxylic acid derivatives

It was known that radical copolymerization of dialkyl maleates and fumarates with electron-donating monomers was proceeded by the mechanism of alternating copolymerization [143–147], similarly as maleic anhydride.

Alternating copolymerization of esters of unsaturated dicarboxylic acids with electron-donor vinyl monomers including dialkyl fumarates (maleates)–styrene(St) [148], diethyl fumarate–vinyl acetate [149], diethyl fumarate(maleate)-*N*- and 9-vinylcarbazole [150–152], isopropyl perfluorohexyl(octyl)-ethylfumarates–St [153], dialkyl fumarate–vinyl monomers [154], dimethyl fumarate–2-vinyl naphthalene [155], alkyl fumarates–vinyl and allyl monomers [156], diethyl itaconate–St [157] and alkyl citraconates–isobutyl vinyl ether (vinyl acetate) [85,158] acceptor–donor systems were investigated. It was shown that the CTC mechanism is mainly realized in these monomer systems.

It follows from the research of Yang and Otsu [85] that dibutyl itaconate ( $M_1$ ) and mesaconate ( $M'_1$ ) as acceptor monomers copolymerize in alternating manner with vinyl acetate ( $M_2$ ) in the condition of higher concentrations of  $M_1$  in monomer feed ( $r_1 = 0$  for both monomers and  $r_2 = 0.58$  and  $0.03$ , respectively). It was found that the reactivity of  $M'_1$  (*trans*-isomer) toward  $\sim VA \cdot$  macroradical was about 20 times higher than of  $M_1$  (*cis*-isomer), similarly for *cis*- and *trans*-dichloroethylenes, and diethyl fumarate (maleate) [142,159].

Overall copolymerization rate coefficients in the *n*-butyl itaconate–methylmethacrylate system have been analyzed by Madruga and Garcia [160] on the basis of terminal and penultimate effects on the chain growth. It was found that these parameters as well as the copolymer composition were not affected by total monomer concentration.

Copolymerization of some dialkyl itaconates with styrene has been carried out and it was found that all itaconates studied were electron-accepting and conjugative monomers [161–164].

Radical-initiated alternating copolymerization of the diethyl itaconate– $SnCl_4$  complex with styrene was carried out by Nakamura et al. [165]. On the basis of kinetic and ESR studies they concluded that the alternating copolymerization proceeded via free-monomer propagation mechanism.

Complex-radical alternating copolymerization of diethyl fumarate (or fumaronitrile) with *N*-vinylcarbazole were observed by Shirota et al. [166,167]. According to authors the polymerization rates of the *N*-vinylcarbazole–fumaronitrile system were approximately 10 times quicker than those of the system containing fumaronitrile. This study also assumed the participation of monomer CTCs in the propagation reactions.

Fumaronitrile provides alternating copolymer with styrene and copolymerization behavior of fumaronitrile–styrene system was discussed in terms of the complex [7,168] and penultimate [169] model. Recently, Braun et al. [170] found that the fumaronitrile–styrene system copolymerizes according to the penultimate mechanism to a significant degree. They explained this to be due to strongly polar fumaronitrile unit in the penultimate position which influences the reactivity of terminal unit of the growing  $\sim St \cdot$  macroradical.

It was known that when dimethyl cyanofumarate was mixed with *p*-methoxystyrene, spontaneous radical copolymerization took place [171]. Authors of this work suggested that copolymerization was initiated by the tetramethylene biradical. This argument was supported by a kinetic study, competition between cycloaddition and copolymerization, trapping and a lack of the solvent effect.

Effect of CTC on the copolymerization of fumaronitrile with vinylphenyl ester was observed [172]. The kinetic of radical alternating copolymerization of this pair monomers was studied by IR spectroscopy and quantum-chemical method. It was shown that the interaction of the double bond of fumaronitrile with the  $\pi$ -system of benzene ring in a planar conformation of ester leads to the lower reactivity of monomers in the complex as compared to that of free monomer molecules.

## 2.7. Copolymerization of tetra-substituted ethylenes

Tetracyanoethylene belongs to the class of the strong acceptor monomers and easily copolymerizes with various donor vinyl monomers.

Radical copolymerization of cyanoethylene dicarboxylate with 2-chloroethyl vinyl ether was studied by Butler et al. [173]. In this study it was shown that in the copolymerization of this monomer pair the alternating structure of copolymer is obtained rather than the expected complex addition structure. However, it was follows from the research of Boutevin et al. [174] that in the case of chlorotrifluoroethylene–2-chloroethyl

vinyl ether system the polarizability of tetra-substituted ethylene monomer is not as important as the other usual monomers.

Radical alternating copolymerization of chlorotrifluoroethylene (A, acceptor monomer) belonging to the tetra-substituted ethylenes with various vinyl ethers (donor monomers) such as 2-chloroethyl vinyl ether (I), ethyl vinyl ether (II), 2,3-epoxypropyl vinyl ether (III), and 2-acetoxyethyl vinyl ether (IV) was carried out [174]. By using  $^{19}\text{F}$ -NMR method and Hanna and Ashbaugh equation [128] the CTC-formation constant for  $\text{II}\cdots\text{A}$  complex was determined to be 1.4 l/mol at 20°C in  $\text{CHCl}_3\text{-d}_1$ . This study noted that the structure of the complex with high value of  $K_c$  described above exhibits a maximum of steric hindrance between the vicinal carbons due to both the chlorine and ether groups; the distribution of electronic charges from the donor to the three fluorine atoms of the acceptor was close together in the CTC. Constants of copolymerization and  $Q_1$  and  $e_1$  parameters for the monomer pairs studied were also determined:  $r_1 = 0.011$  and  $r_2 = 0.005$  for  $\text{II-A}$  pair,  $r_1 = 0.008$  and  $r_2 = 0.002$  for  $\text{I-A}$  pair,  $Q_1 = 0.026$  and  $e_1 = 1.56$  for chlorotrifluoroethylene monomer. On the basis of results obtained from the copolymerization of A with vinyl ethers and cotelomerization of A with  $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{SH}$  (model system), and from the high constant of charge transfer observed, it was concluded that a mechanism by propagation of acceptor–donor complex is realized in the monomer systems studied [174].

### 3. Coordination effect in radical copolymerization of organotin carboxylate monomers

It has been known [8,175,176] that in many functional organotin monomers of carboxylate type the tin atom is in a coordination state and tend to form complexes with various electron-rich compounds, primarily with monomers containing electron-donor functional groups. However, the long time intra- and intermolecular coordination complexes including also monomer CTC of organotin monomers and their role in elementary acts of radical polymerization and copolymerization reactions has been either ignored or considered inadequately. First, the coordination effect of tin atom was discovered in free-radical copolymerization of trialkyl( $\text{C}_{1-4}$ )stannylmethacrylates with maleic anhydride [8,177–179]. It is shown that electron-acceptor monomer pair of this system forms CTC with intermolecular coordination of tin atom and carbonyl group ( $-\text{Sn}\cdots\text{O}=\text{C}-$ ) and easily copolymerize in presence of free radicals by the mechanism of alternating chain growth [1,8,179]. Similar effects with  $-\text{Sn}\cdots\text{O}-$  and  $-\text{Sn}\cdots\text{Cl}-$  coordination were observed in spontaneous polymerization of organotin epoxides and in radical copolymerization of organotin maleates, methacrylates and cinnamates with vinylchloride [8,180–182]. The results of studies of coordination effects in formation and cross-linking reactions of organotin macromolecules are discussed and generalized in a review article [8].

In recent years considerable development has been made in the field of radical and complex-radical copolymerization of organotin functional monomers. The results of these studies are discussed in following parts of this review.

#### 3.1. Organotin (metha)acrylates

Copolymerization of tri-*n*-butylstannyl acrylate (TBSA) with methyl- (MMA), propyl- (PMA) and butylmethacrylates (BMA), and acrylonitril (AN) in toluene at 70°C using AIBN as initiator led to monomer reactivity ratios as follows:  $r_1 = 0.395 \pm 0.013$  and  $r_2 = 2.18 \pm 0.058$  for the pair TBSA–MMA;  $r_1 = 0.314 \pm 0.017$  and  $r_2 = 1.684 \pm 0.033$  for the pair TBSA–PMA;  $r_1 = 0.197 \pm 0.012$  and

$r_2 = 1.668 \pm 0.028$  for the pair TBSA–BMA and  $r_1 = 0.24 \pm 0.004$  and  $r_2 = 0.997 \pm 0.007$  for the pair TBSA–AN [183], which were determined by KT-method. The  $r_1 r_2$  values obtained for the said systems indicated that the copolymers should have random distributions of the monomer units and the tendency towards alternation increases with increasing length of the alkyl chain of the methacrylic acid ester, in agreement with previous studies on copolymerization of tri-*n*-stannyl methacrylate with methacrylic and acrylic esters [184,185] and on alternating copolymerization of trialkyl(C<sub>1–4</sub>)stannyl methacrylates with maleic anhydride [8,177–179].

The kinetics of copolymerization reactions of tri-*n*-butylstannyl 4-acryloyloxybenzoate (TBSAB) with AN, alkyl(C<sub>1–4</sub>) acrylates (MA, EA and BA), MMA and St were studied [186]. The ternary copolymerization of TBSAB, AN and alkyl acrylates (or St) also were studied [187]. The determination of unitary, binary and ternary azeotropics of various systems studied was easily handled by a computer program. The results obtained show that there is no ternary azeotropic composition for any terpolymer system studied.

The binary and ternary copolymerization of di-(tri-*n*-butylstannyl)itaconate with acrylic acid esters, St, and AN were studied [188]. Also, the kinetics of copolymerization of TBSA and TBSMA with itaconic acid (IA) or dimethylitaconate (DMI) have been investigated [189]. Results of ternary radical copolymerization of TBSA or TBSMA with IA or DMI and AN show that the ternary azeotropic composition for TBSMA–IA–AN, TBSA–IA–AN and TBSA–DMI–AN systems were 39.0:26.1:34.9, 1.7:10.5:37.8 and 0.30:66.3:33.4 mol%, respectively. Also “pseudo-azeotropic” regions were identified where the deviation between monomer feed and polymer compositions is very small [188].

Radical copolymerization of *p*-acryloyloxy-tri-*n*-butylstannyl benzoate (ABSB) with allyl methacrylate (AMA), *N*-vinyl pyrrolidone (VP) and vinylacetate (VA) were investigated [190]. The monomer reactivity ratios for the said pairs and  $Q$  and  $e$  parameters for ABSB have been found to be  $r_1 = 0.28 \pm 0.02$  and  $r_2 = 0.89 \pm 0.04$  (ABSB–AMA),  $r_1 = 0.074 \pm 0.01$  and  $r_2 = 0.4 \pm 0.01$  (ABSB–VP) and  $r_1 = 0.92 \pm 0.01$  and  $r_2 = 0.99 \pm 0.01$  (ABSB–VA),  $Q = 0.456$  and  $e = 0.64$ . These values obtained indicate that the copolymers of ABSB with said electron-donor comonomers should give copolymers with strong tendency to alternation.  $Q$  and  $e$  values for ABSB are in good agreement with the known values for esters of acrylic acid. Unfortunately, in this work the cause of alternation of monomer units in copolymers, which did not take place in the case of organic isostructural analogs of ABSB, was not explained. This fact can be early explained by specific role (coordination effect) of tin atom, which have a tendency to complex-formation with functional fragments of comonomers.

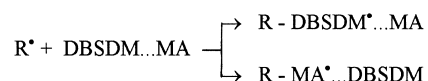
The structure of the di-*n*-butylstannyl dimethacrylate (DBSDM) is noted for coordination interactions between tin atoms and the carbonyl group, as confirmed by data of IR spectroscopic investigations [191]. In the spectra of pure DBSDM the carbonyl group appears in the range of  $1540 \text{ cm}^{-1}$  in the form of widened band, which corresponds to the coordination-combined form of the organotin carboxylate group. In an octane solution of DBSDM this absorption band is displaced by  $1580 \text{ cm}^{-1}$ , which is evidence of the presence of intermolecular bonds of tin atoms and carbonyl oxygen. However, subsequent dilution does not markedly shift this band to a higher region ( $1620\text{--}1640 \text{ cm}^{-1}$ ), typical of the free carbonyl group in organotin carboxylates.

The fact observed is due to intramolecular coordination-combined particles being contained in the structure of DBSDM molecules, as well as intermolecular particles. Mössbauer spectra of DBSDM are characterized by an asymmetric doublet of quadrupole fission with parameters of isomeric shift  $\delta = 1.67$  and quadrupole fission  $\Delta = 4.29 \text{ mm/s}$ . It follows from ratio  $\delta/\Delta$  that tin atom in the DBSDM molecule examined has a coordination number of 6 [191].

The regularities of complex-radical copolymerization of DBSDM with maleic anhydride (MA) that are due to the tendency of organotin methacrylate for coordination interaction with MA and cyclization, as well due to the influence of the above factors on the reactivity ratio of comonomers and on the mechanism of alternating propagation involving the same, are discussed in the work [192]. It is shown that the copolymer composition with a wide variety of starting monomer ratios is close to stoichiometric ones.

The copolymerization constants obtained by KT-method are  $r_1 = 0.084 \pm 0.005$  and  $r_2 = 0.026 \pm 0.001$ . The value of  $K_c$  for DBSDM...MA complex determined by  $^1\text{H-NMR}$  method based on analysis of spectra of free monomers and their mixtures with  $[\text{MA}] \gg [\text{DBSDM}]$  (a coordination complex, involving tin and anhydride carbonyl groups) and  $[\text{MA}] \ll [\text{DBSDM}]$  (a CTC, involving multiple donor–acceptor bonds).  $K_c = 0.24$  and  $0.054 \text{ l/mol}$  are derived for coordination and charge transfer complexes, respectively [192].

From the kinetic studies of homo- and copolymerization at the initial stage of conversion at various total concentrations of monomers and AIBN initiator and at temperature, some kinetic parameters were found to be as follows:  $n = 1.18$ ,  $m = 0.53$ ,  $E_a = 59.5 \text{ kJ/mol}$  (for homopolymerization reaction of DBSDM) and  $n = 1.45$ ,  $m = 0.54$ ,  $E_a = 64.9 \text{ kJ/mol}$  (for copolymerization reaction). The relatively low  $E_a$  value for the system under study, as compared with ordinary homo- and copolymerization reactions, seems to be due to monomer complexes, involved in the initiation reactions:



Radical copolymerization of DBSDM with MA also leads to cyclic structures, as evidenced by iodometric titration, FTIR, and NGR (Mössbauer) spectroscopy. The  $E_a = 13.1 \text{ kJ/mol}$  and Mössbauer parameters such as isomer shift  $\delta = 1.54$  (and quadrupole splitting  $\Delta = 3.60 \text{ mm/s}$  for the copolymerization and copolymer, respectively, differ from  $E_a = 9.6 \text{ kJ/mol}$ ,  $\delta = 1.43$  and  $\Delta = 3.29 \text{ mm/s}$  for homopolymerization and homopolymer, which may be accounted for by the effect of complex bonded monomer, highly reactive towards the  $\sim\text{DBSDM}^{\cdot}$  macroradical.

The propagation reactions of alternating radical copolymerization, taking into account cyclization and complexing effect may be represented as follows:



The kinetic data are indicative of strong dependence of initial copolymerization rate on MA content in the starting mixture at different overall concentration of monomers. The position of  $v_{\max}$  on all the curves corresponds to stoichiometric composition of the monomer mixture. The rate constant ratios for propagation, involving free and complex bonded monomers, were found to be:  $k_{1c}/k_{12} = 0.9$  and  $k_{2c}/k_{21} = 2.4$ . The obtained value of  $k_{1c}/k_{12}$  close to unity indicates that the free MA before interacting with the  $\sim$ DBSDM $\cdot$  macroradical forms a coordination complex with its tin-containing portion, while the complex bonded monomer adds more readily to the growing  $\sim$ MA $\cdot$  radical, than the free DBSDM. It was inferred from these results that radical copolymerization of DBSDM with MA proceeds by complex mechanism with the predominant effect of intramolecular cyclization on the propagation and formation of alternating copolymer with cyclic and linear unsaturated units in the macromolecular chain [192].

Mechanism of radical copolymerization of DBSDM with vinylacetate (VA) also were examined [181]. Constants of copolymerization and complex-formation of the monomer pair examined, and also some kinetic parameters of copolymerization were determined:  $r_1 = 0.029 \pm 0.03$  and  $r_2 = 0.33 \pm 0.035$  (by KT-method),  $K_c = 0.27 \pm 0.02$  l/mol (by  $^1\text{H-NMR}$  method using chemical shifts of Sn-CH<sub>2</sub> protons in TBSDM  $\ll$  VA mixtures),  $n = 1.56$ ,  $m = 0.53$ ,  $E_a = 82.1$  kJ/mol,  $k_{1c}/k_{12} = 1.2$  and  $k_{2c}/k_{21} = 4.2$ .

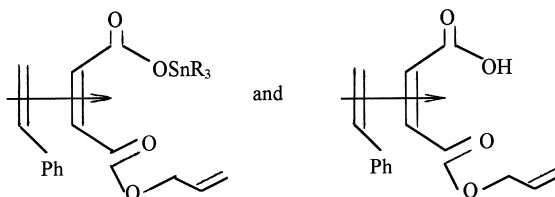
It follows from data of IR and  $^1\text{H-NMR}$  spectroscopy of free monomers and their mixtures with considerable excess of VA (DBSDM : VA = 1 : 20) that in a mixture of monomers IR spectra show the appearance of a new band at  $575\text{ cm}^{-1}$ , which corresponds to the pentacoordination state of the tin atom; in the  $^1\text{H-NMR}$  spectrum of this mixture a shift is observed in signals of the Sn-CH<sub>2</sub> group from 0.875 ppm for DBSDM to 0.825 ppm for its mixture with VA [191].

### 3.2. Organotin allylmaleates

The copolymerization of tri-*n*-butylstannylallyl maleate (TBSAM) and monoallyl ester of maleic acid (MAM) with styrene (St) has been studied [193]. It has been shown that in the monomer systems investigated, alternating copolymerization occurs and the equimolar composition of the copolymers formed does not depend upon the initial monomer ratio. By using the FR-method of "linearization", the values of the copolymerization constants for the above-mentioned pairs of monomers were determined:  $r_1 = 0.018 \pm 0.005$  and  $r_2 = 0.12 \pm 0.01$  for the pair TBSAM-St and  $r_1 = 0.076 \pm 0.01$  and  $r_2 = 0.11 \pm 0.015$  for the pair MAM-St. Values of the polarizability parameter  $e_1$  and the specific reactivity  $Q_1$  were calculated in accordance with the Alfrey-Price scheme for TBSAM  $e_1 = 1.67$  and  $Q_1 = 1.11$ , for MAM  $e_1 = 1.39$  and  $Q_1 = 1.6$ , respectively.

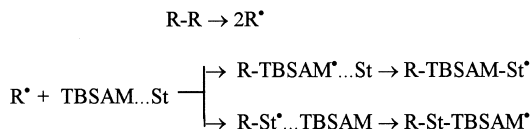
$^1\text{H-NMR}$  has been used to determine the equilibrium constants for the formation of CTC by use of the known equation [139]. The values of  $K_c$ , namely 0.396 l/mol in the deuterated acetone or methylethyl ketone at  $35 \pm 0.5^\circ\text{C}$  for the TBSAM $\cdots$ St complex, 0.256 l/mol for the MAM $\cdots$ St complex were found. The observed difference in the values of  $K_c$  is caused by the contribution which is made by the tri-*n*-butylstannyl groups to complex-formation and is determined by the penta-coordination condition of the tin atom, in a manner similar to the effect described previously in the system tri-*n*-butylstannyl methacrylate-maleic anhydride [8,177–179]. Because of this, the internal multiple bond in the TBSAM attains more electron-acceptor character and, as a consequence of this, the transfer of an electron from St to TBSAM is comparatively readily accomplished. The data obtained enable the following structures to be assigned to the CTC [193].





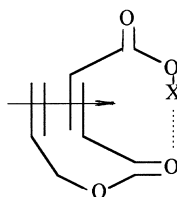
It has been established that the stability of the complexes has a substantial effect on the penta-coordinated state of the tin atom [193].

It follows from the data of the kinetic investigations how the magnitude of the dependence the initial rate of copolymerization on the monomer concentration and the concentration of the initiator, benzoyl peroxide, that the order with respect to the monomer,  $m$ , for the system TBSAM–St is equal to 1.2 and for the system MAM–St, 1.14; the rate of copolymerization has an order of reaction with respect to the initiator,  $n$ , that is equal to 0.55 and 0.53, respectively. The values of activation energy  $E_a$ , found from the graphs of the  $\log k$  as a function of  $1/T \times 10^3$ , are equal to 44.6 and 77.0 kJ/mol respectively. For the system TBSAM–St, the comparatively high value of  $m$  and the correspondingly low values of  $E_a$  make it possible to suggest that the complexes formed participate in the initiation reaction, the contribution made to this reaction by the TBSAM $\cdots$ St complex being greater than that made by the MAM $\cdots$ St complex. Initiation with the participation of these CTC may be characterized by the following elementary acts [193]:



For both pairs of monomers, the dependence of the copolymerization rate on the composition of the polymer mixture for various overall concentrations has an extreme value at the equimolar composition of the reacting monomers. At all the monomer concentrations investigated, the rate of copolymerization of TBSAM with St is less than the rate of copolymerization of MAM with St. Steric factors, caused by the bulky tri-*n*-butylstannyl group, could be expected to have a considerable effect on the rate of copolymerization. It follows, however, from the values of  $K_c$  that these factors do not affect the stability of the TBSAM $\cdots$ St complex. In order to assess the quantitative contribution made by CTC to radical chain propagation reactions the data of kinetic investigation and known equation [1,37] were used. From these data the following values of the ratio between the constant for the chain growth of the complexed monomer and that of the free monomer were obtained: for the system TBSAM–St  $k_{1c}/k_{12} = 15.9$  and  $k_{2c}/k_{21} = 6.4$ , and for the system MAM–St  $k_{1c}/k_{12} = 64.4$  and  $k_{2c}/k_{21} = 2.5$ . The reactivity of the CTC is considerably greater than the reactivity of the free monomer, the contribution of the TBSAM $\cdots$ St complex to radical chain growth being 2.5 times greater than that of the MAM $\cdots$ St complex in the reaction between these complexes and the growing macroradicals  $\sim\text{St}\cdot$ . These complexes are found to make a predominant contribution to the reactions with the growing macroradicals  $\sim\text{TBSAM}\cdot$  and  $\sim\text{MAM}\cdot$ . The comparatively low value of  $k_{1c}/k_{12}$  for TBSAM–St system is explained by the additional stabilization of the growing TBSAM $\cdot$  macroradical by the tri-*n*-butylstannyl group [193].

The paper [194] discusses some kinetic aspects and the mechanism of radical copolymerization of TBSAM and MAM with an electron acceptor monomer – maleic anhydride (MA). The formation from the monomer pairs of CTC is confirmed by the data of  $^1\text{H-NMR}$  spectroscopy. On introducing the  $\text{R}_3\text{Sn}$  group into the MAM molecule the protons of the  $-\text{CH}=\text{CH}-$  bond become non-equivalent and their signals are transformed to the spectrum of AB type ( $J_{cis} = 9.0$  Hz) with displacement of the chemical shifts of these protons to the strong field. The observed displacements allow one to calculate the  $K_c$  of CTC:  $K_c = 0.214$  (TBSAM $\cdots$ MA) and  $K_c = 0.101$  l/mol (MAM $\cdots$ MA), the comparatively high value of  $K_c$  for TBSAM $\cdots$ MA complex may be explained by the influence of the penta-coordinated tin increasing the susceptibility of TBSAM molecule to complex with MA. From the donor–acceptor properties of the multiple bonds of the monomers (allyl-donor and olefin  $-\text{CO}-\text{CH}=\text{CH}-\text{CO}-$  acceptor) one may assume the formation and participation in chain growth intramolecular CTC also of the type



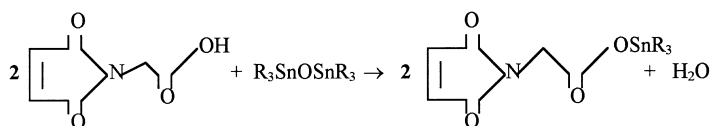
where  $\text{X} = \text{H}$  and  $\text{R}_3\text{Sn}$ ).

Using the FR-equation and kinetic data the values of the copolymerization constants and  $n$ ,  $m$  and  $E_a$  parameters were calculated:  $r_1 = 0.083 \pm 0.005$ ,  $r_2 = 0.01 \pm 0.002$ ,  $n = 0.52$ ,  $m = 1.55$  and  $E_a = 74.1$  kJ/mol for the pair MA–TBSAM and  $r_1 = 0.04 \pm 0.006$ ,  $r_2 = 0.05 \pm 0.005$ ,  $n = 0.53$ ,  $m = 1.25$  and  $E_a = 117.6$  kJ/mol for the pair MA–MAM. However these values do not allow for the contribution of the CTC to the radical reactivity of the monomers. Therefore the experimental findings obtained were treated according to the SL-equation which together with attachment of the growing macroradicals of the free monomers takes into account the attachment of the complex-bound monomer (C) giving the following values of the copolymerization constants:  $r_{12} = 0.083$ ,  $r_{21} = 0.099$ ,  $r_{2c} = 0.008$ ,  $r_{2c1} = 0.023$  and  $r_{2c2} = 0.09$  for the system MA–TBSAM;  $r_{21} = 0.05$ ,  $r_{2c} = 0.022$ ,  $r_{2c1} = 0.027$  and  $r_{2c2} = 0.11$  for the system MA–MAM. For the quantitative characterization of the participation of the complex-bound monomers in the radical chain growth reaction, kinetic method was used based on determination of the ratios of the rate constants of chain growth through the CTC ( $k_{1c}$  and  $k_{2c}$ ) and free monomers ( $k_{12}$  and  $k_{21}$ ):  $k_{1c}/k_{12} = 1.25$  and  $1.75$  and  $k_{2c}/k_{21} = 16.4$  and  $46.6$  for the system MA–TBSAM and MA–MAM, respectively. The high values of these ratios for both system favor the complex mechanism of chain growth. The complex-bound monomers make a considerable contribution to the reactions with the participation of the macroradicals containing the terminal TBSAM and MAM units. Despite the high value of  $K_c$  for the coordination-bound complex MA $\cdots$ TBSAM ( $-\text{Sn}\cdots\text{O}=\text{C}-$ ) its contribution to radical chain growth is less than that of the complex MA $\cdots$ MAM which may be explained by spatial factors due to the organotin fragments [194].

### 3.3. Tributylstannyl- $\alpha$ -(N-maleimido)acetate

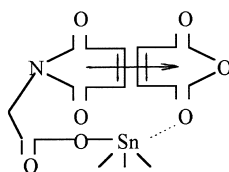
In view of structural symmetry, steric factors and the high positive polarity of the vinyl group,  $\alpha$ -(N-maleimido)acetic acid (MIA) does not form homopolymers in the presence of radical initiators,

but is fairly readily alternating copolymerized with styrene (St)—an electron-donor monomer ( $r_1 = 0.11$  and  $r_2 = 0.09$ ) by KT-method [141,195]. The addition into the molecule of MIA of an electron-acceptor group  $-\text{Sn}(n\text{-C}_4\text{H}_9)_3$  with a strong positive induction effect, by the interaction with hexabutyl-distannoxane



results in a redistribution of electron density in the molecule so that synthesized tri-*n*-butylstannyl- $\alpha$ -(*N*-maleimido)acetate (TBSMI), unlike monomer MIA, shows a high tendency for homopolymerization by a radical mechanism, while copolymerization with St results in the formation of a random copolymer ( $r_1 = 0.004$  and  $r_2 = 1.65$ ). As a result of copolymerization of TBSMI with an electron-acceptor monomer of MA a product of regularly alternating structure is formed ( $r_1 = 0.16$  and  $r_2 = 0.02$ ) [195].

Analysis of  $^1\text{H-NMR}$  spectra of monomer mixtures allows to calculate  $K_c$  for complexes  $\text{MA}\cdots\text{TBSMI}$  and  $\text{AMI}\cdots\text{St}$ , which are 0.005 and 0.21 l/mol, respectively. The low value of  $K_c$  for the  $\text{MA}\cdots\text{TBSMI}$  complex may be explained by the effect of pentacoordinated tin on the electron-donor from the multiple bond of the imide ring, which is confirmed to be the shift observed in the FTIR spectra of the monomer mixture of absorption bands of Sn–C and C=O bonds ( $\nu_{\text{Sn-C}}$  535 and  $\nu_{\text{C=O}}$  1625  $\text{cm}^{-1}$ ). In spectra of free monomers these bands are seen in the range of 505–1596  $\text{cm}^{-1}$ , respectively.



Using the SL-equation [42] with well-known values of  $r_1$  and  $r_2$  enabled us consider the effect of complex-formation on copolymerization constants:  $r_{2c} = 0.011$ ,  $r_{1c1} = 0.011$  and  $r_{2c2} = 0.09$  for St–AMI system, and:  $r_{1c} = 0.005$ ,  $r_{1c1} = 0.022$  and  $r_{1c2} = 0.07$  for TBSMI–MA system. Results suggest the simultaneous participation of CTC in elemental chain growth of alternating copolymerization, which includes the addition of both free monomers and their complexes to macroradicals for the case, when one of the monomers cannot undergo homopolymerization [195].

As a result of kinetic investigations of radical copolymerization the orders concerning the initiator, AIBN,  $n$  and  $m$  were determined:  $n = 0.51$  and  $m = 1.71$  (MIA–St) and  $n = 0.52$  and  $m = 1.50$  (TBSMI–MA), effective activation energies  $E_a = 76.6$  and 67.0 kJ/mol, respectively, which are somewhat lower than for conventional radical processes without monomer CTC [195].

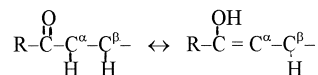
The type of dependence of the rate of copolymerization on the composition of reaction mixture varies: for systems MIA–St and TBSMI–MA curves pass through maximum rate,  $\nu_{\text{max}}$ , whereby in the first case dilution of the reaction mixture results in a shift of the  $\nu_{\text{max}}$  value from 55 to 48 mol% of MIA; for the second system the position of  $\nu_{\text{max}}$  is unchanged and is observed with an equimolar ratio of monomers, while for the system TBSMI–St a continuous reduction of the rate of copolymerization takes place with

an increase in the content of TBSMI in the monomer feed. The different character of kinetic curves observed is due to the form of copolymerization in the system examined: the extremum form of curves is typical of alternating copolymerization, which takes place in systems MIA–St and TBSMI–MA, while the conventional dependence of rate on the composition of the reaction mixture is typical of random copolymerization of TBSMI with St. Since MIA under these conditions does not form homopolymers and TBSMI takes part very poorly in homopolymerization, basic reactions of propagation are possible in the MIA–St system with free and complex-bound monomers, while in the TBSMI–MA system reactions of macroradicals with a complex may chiefly take place. This is, apparently, due to higher ordering of the TBSMI··MA complex, compared with the MIA··St complex. For a TBSMI–MA system  $k_{2c}/k_{21} = 160.0$  and  $k_{1c}/k_{12} = 87.5$ , i.e. CTC is much more active than free monomers in reactions with similar macroradicals, which suggests a complexed mechanism of chain propagation in alternating copolymerization of TBSMI with MA. Alternating copolymerization of MIA with St is characterized by the following parameters:  $k_{12}/k_{21} = 0.52$  (i.e. reactions of addition of free monomer MIA to a St radical are dominant among reactions of free monomer addition),  $k_{2c}/k_{21} = 9.07$  and  $k_{1c}/k_{12} = 1.54$ . Comparison of values of  $k_{12}/k_{21}$  and  $k_{1c}/k_{12}$  indicates that the rate constant of addition of a complex-bound monomer to a macroradical with a St terminal unit is somewhat higher than the rate constant of interaction of free MA with a similar radical. This difference is very significant in the case of free and complex-bound St. It may be assumed that alternating copolymerization takes place by a mixed mechanism; among reactions of CTC with a growing radical, predominant are those of complex-bound St with MIA and among reactions of free-monomer, addition-reactions of MIA with St radical [195].

#### 4. Effect of *keto–enol* tautomerism

##### 4.1. Keto–enol tautomerism in monomer systems

An important characteristic of carbonyl-containing organic compounds (aldehydes, ketones, ketoesters, etc.) is an unusual activity of  $\alpha$ -hydrogen atoms on carbon atoms adjacent to the C=O group, and it can be assumed that tautomerism is the basis for the chemistry of these compounds.

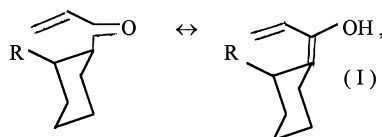


For simple monocarbonyl compounds such as acetaldehyde, acetone and cyclohexanone, the amount of the *enol* form present at equilibrium is very small, i.e. extremely small, 0.00015 and 1.2%, respectively [196]. The activity of  $\alpha$ -hydrogen atoms, hence and tautomerism depends on the type of carbon atom (primary or secondary), solvents, pH of reaction phase, temperature, etc.

The slow keto–enol proton tautomerization in the acetaldehyde–vinyl alcohol ( $K = [\text{enol}]/[\text{keto}] \approx 3 \times 10^{-7}$  at 25°C) has been reported by Capon et al. [197]. By taking advantage of stabilizing electron donor–acceptor interactions the free radical copolymerization of enolic tautomer of acetaldehyde with maleic anhydride proved to be successful [198]. This investigation of these reactions demonstrated that equimolar amounts of maleic anhydride and O–D vinyl alcohol (D is deuterium) were consumed in the formation of polymer, suggesting that an alternating one to one copolymerization.

The role of different types of tautomers as monomers and polymerization initiators including





where R = H, CH<sub>3</sub>.



Low-intensity bands appearing in the FTIR spectra of the above-mentioned vinyl ketones in the form of doublets in the 3630 and 3550 cm<sup>-1</sup> regions are associated with intermolecular-(I) and intramolecular-bound (II) OH groups. Thanks to the mobility of the hydrogen atom in the  $\alpha$ -position of the cycle the vinylcyclohexyl ketone (VCHK) molecule is in the equilibrium state of the *keto* and *enol* forms as a result of which in the FTIR spectrum a weak doublet is observed in the region 3610–3630 cm<sup>-1</sup> characteristic of the molecularly bound hydroxyl group. The absorption band at 1620 cm<sup>-1</sup> corresponds to the C=C bond and the peaks of different intensity at 1680 and 1700 cm<sup>-1</sup> characterize the absorption of the carbonyl groups present, respectively, in the *trans* and *cis* positions in relation to the conjugated multiple bond [103].

In the usual <sup>1</sup>H-NMR spectrum of *enol* form of the VCHK does not show up because of the overlap by its powerful and complex signals from the protons of the cyclohexane ring. Therefore, to detect the *enol* form, the <sup>1</sup>H-NMR spectra of VCHK in presence of the paramagnetic reagent Eu(fod)<sub>2</sub> (partially fluorinated ligand 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione) was recorded. As to be expected the introduction of Eu(fod)<sub>2</sub> leads to heavy shift of the proton of the *enol* form to the weak field with appreciable widening of the resonance line (3.1–3.4 ppm). It may be assumed that the C=O groups of the *trans-S*-form undergo *enol* conversion since in the case of the *cis-S*-conformation such a transition is energetically less advantageous [103].

#### 4.2. Vinylcyclohexylketones–maleic anhydride

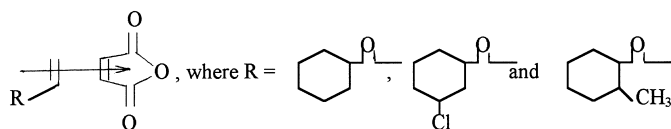
Polymers and copolymers of vinyl ketones are of major interest in regard to the preparation of reactive and photosensitive polymer film-forming materials with a broad set of commercially good properties.

It is known that vinylphenyl(methyl)ketones enter into radical copolymerization reaction with MA. However, it appears from the data in Ref. [206] that no alternating copolymerization takes place, and that statistical copolymers enriched with vinyl ketone units are formed. Despite this, when cyclohexyl derivatives of vinyl ketones were copolymerized it was found that regularly alternating copolymers of 1:1 composition were obtained [103,205].

The relationship between structural features of cyclohexane derivatives of vinyl ketones and their readiness to form CTC with MA were investigated. In addition, a study was made of the quantitative contribution of monomeric CTC to radical reactions of chain propagation.

The formation of CTC between the vinyl ketones and MA is substantiated by the results of <sup>1</sup>H-NMR

analysis of the spectra of the pure monomers and their mixtures at different ratios. The data obtain show that CTC are formed between the initial monomers:



Changes occurring in chemical shifts of MA protons in mixtures of MA and vinyl ketones with an excess of  $K_c$  for complexes which were as follows:  $K_c = 0.05 \pm 0.01$  for VCHK $\cdots$ MA,  $K_c = 0.11 \pm 0.02$  for VCCHK $\cdots$ MA and  $K_c = 0.04 \pm 0.01$  l/mol for VMCHK $\cdots$ MA. Comparing these values, it is seen that the  $\gamma$ -chlorocyclohexyl substituent increases the stability of the complex with MA, whereas the methyl group incorporated in the  $\beta$ -position of the cyclohexane ring very slightly reduces the value of  $K_c$ . It is surmised that vinyl ketones enter the composition of complexes with MA in the form of structures I and II. The latter structure probably accounts for their donor properties. In addition, it appears that the *enol* form II is further stabilized on account of formation of an intramolecular bond of type  $-\text{OH}\cdots\text{Cl}-$ , which increases the complexing constant  $K_c$ .

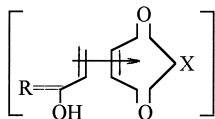
Copolymerization of vinyl ketones ( $M_1$ ) with MA may be characterized by the following propagation reactions a allowing for free and complex-bound monomer:



In cases where alternating copolymers are formed Eqs. (19) and (21) may be neglected.

It is shown that the experimental curves plotted for the copolymerization rate vs. the MA concentration have a maximum, and on dilution of the reaction system there is a marked displacement of the maxima towards reduced VCHK. Changes observed in the position of the maxima accompanying a reduction in the total concentration of monomers is attributable to both free monomers and complex-bound monomers participating in chain growth reactions. Results of kinetic study and use known equations [37] allows to evaluate the quantitative contribution of complexes to propagation reactions:  $k_{21}/k_{12} = 6.59$ ,  $k_{1c}/k_{12} = 10.95$  and  $k_{2c}/k_{21} = 3.64$ . It follows from the value of  $k_{21}/k_{12}$  that the reactivity of macroradical  $\sim\text{VCHK} \cdot$  with respect to MA is lower than that of  $\sim\text{MA} \cdot$  with respect to VCHK. The values of  $k_{1c}/k_{12}$  and  $k_{2c}/k_{21}$  show that it is very probable that the complex with respect to  $\sim\text{MA} \cdot$  is three times that with respect to the macroradical having a VCHK terminal unit. The found ratios of rate

Table 1

Values of  $K_c$  for the CTC of VCHK with maleic anhydride derivatives [102,103]

R	X	$K_c^a$ (l/mol)	
		25°C	45°C
Cyclohexyl	–O–	$0.05 \pm 0.01^a$	$0.075 \pm 0.015$
$\alpha$ -Methylcyclohexyl	–O–	$\sim 0$	
$\beta$ -Methylcyclohexyl	–O–	$0.042 \pm 0.01$	–
$\alpha$ -Chlorocyclohexyl	–O–	$\sim 0$	
$\delta$ -Chlorocyclohexyl	–O–	$0.11 \pm 0.02$	$0.180 \pm 0.02$
Cyclohexyl	$C_6H_5-N <$	$0.021 \pm 0.002$	$0.042 \pm 0.005$
Cyclohexyl	$p-CH_3-C_6H_5-N <$	$0.018 \pm 0.003$	$0.035 \pm 0.0025$
Cyclohexyl	$p-CH_3O-C_6H_5-N <$	$0.014 \pm 0.001$	$0.026 \pm 0.002$
Cyclohexyl	$p-NO_2-C_6H_5-N <$	$0.026 \pm 0.002$	$0.052 \pm 0.005$
$\beta$ -Methylcyclohexyl	$C_6H_5-N <$	$0.023 \pm 0.002$	–
$\delta$ -Chlorocyclohexyl	$C_6H_5-N <$	$0.071 \pm 0.005$	–
$\delta$ -Chlorocyclohexyl	$C_6H_5-N <$	$0.055 \pm 0.004$	–

constants of elementary steps (18), (20), (22) and (23) suggest that the reactivity of the monomers increases when they are bound in complexes. The “displacement of the maximum” of the copolymerization accompanying a change in the total monomer concentration, as well as the found values of rate constant ratios to provide a basis for calculating statistical parameters of copolymerization. It is shown that as the reaction system is diluted and the MA concentration in the monomer mixture increases, the probability of propagation through addition of the complex decreases on account of a reduction in the concentration of VCHK $\cdots$ MA in the initial mixture. At the same time the position of  $\nu_{max}$  approximates to an equimolar monomer composition, which is due to increased probability of VCHK transition to the *enol* form, which is responsible for a purely complex-based type of propagation mechanism [103].

In view of the results obtained, it can be concluded that regularly alternating chain propagation in the radical copolymerization of VCHK with MA is due to transition of VCHK molecule to an *enol* form, which favors formation of CTC with MA, and takes place by “mixed” mechanism with complex-bound monomers playing a dominant role.

#### 4.3. Vinylcyclohexylketones-N-substituted maleimides

Studies of the radical copolymerization of VCHK with *N*-substituted maleimides are of special theoretical and practical interest, partly for the determination of the effect of the nature of the electron-acceptor monomer on the course of the radical copolymerization of the studied monomers and partly in connection with the possibility of preparing reactive and photosensitive polyfunctional polymers [102,103].



Table 2

Complex-radical copolymerization of vinylcyclohexyl ketones ( $M_1$ ) with maleic acid derivatives ( $M_2$ ): solvent—MEK, initiator—BP (0.5%),  $[M] = 1 \text{ mol/l}$ ,  $60^\circ\text{C}$

Monomer feed	Composition of reaction mixture (mol %)		AN (mg KOH/g)	N(Cl) (%)	Composition of copolymers (mol%)		$[\eta]$ benzene at $25^\circ\text{C}$ (dl/g)	$T_{\text{soft}}$ ( $^\circ\text{C}$ )	
	$[M_1]$	$[M_2]$			$m_1$	$m_2$			
VCHK–MA	25	75	478	–	49.68	50.32	0.17	126	$r_{1c} = 0.007$
	50	50	466	–	50.79	49.21			$r_{1c1} = 0.020$
	75	25	464	–	50.94	49.06			$r_{1c2} = 0.008$
VCHK–PMI	30	70	–	4.13	48.35	51.65	0.10	152	$r_{1c} = 0.005$
	50	50	–	4.47	50.25	49.75			$r_{1c1} = 0.010$
	70	30	–	4.64	54.12	45.88			$r_{1c2} = 0.009$
VCHK–TMI	30	70	–	3.91	47.64	52.36	0.09	155	$r_{1c} = 0.002$
	50	50	–	4.27	50.45	49.55			$r_{1c1} = 0.010$
	70	30	–	4.47	55.21	44.79			$r_{1c2} = 0.019$
V– $\delta$ -CCHK–MA	30	70	368	14.10	47.06	52.94	0.11	118	$r_{1c} = 0.016$
	50	50	415	13.12	50.15	49.85			$r_{1c1} = 0.004$
	70	30	436	12.53	55.44	44.56			$r_{1c2} = 0.006$

Complex formation between VCHK and *N*-phenylmaleimide (PMI) was studied by the  $^1\text{H-NMR}$  method, and the complex equilibrium constant was determined:  $K_c = 0.021$  l/mol. Analogous method was used for determination of  $K_c$  for VCHK–maleic acid derivatives (anhydride and imides) pairs, results of which are summarized in Table 1.

Analysis of the IR spectra of VCHK and mixtures of it with MA and maleimides in chloroform show that the addition of the maleic acid derivatives appreciably changes the form and considerably increases the intensity of the doublet at  $3610\text{--}3630\text{ cm}^{-1}$  as a result of the stabilization of the *enol* form although in the VCHK–imides systems this effect is more weakly marked. Similar changes occur in the IR spectra of equimolar mixtures of methyl and chlor-substituted VCHKs with MA [102,103].

The considerable lowering of the  $K_c$  value of the VCHK···PMI complex as compared to other system (for example VCHK–MA) is evidently connected with the weaker electron-acceptor strength of PMI. On the other hand, the arrangement in space of the comonomer molecules giving maximum molecular orbital overlap of the vinyl group of VCHK and of the benzene ring of PMI leads to a larger distance between the double bonds and evidently may also result in weakening of complex formation.

With the disappearance of the conjugation between the multiple bond and the carbonyl group the vinyl group of the *enol* form is characterized by higher electron density thanks to which VCHK and its derivatives are capable of forming CTC with anhydride and imides of maleic acid belonging to monomers of the acceptor type. From comparison of the tabulated data it follows that an appreciable influence is exerted on the  $K_c$  values both by the electron-acceptor nature of the maleic acid derivatives and the presence of conjugation between the substituted cyclohexyl fragment and the vinyl group. The observed anomaly in change of the complexation constants may be explained by increase in the fraction of the *enol* form of the vinyl ketones with rise in temperature.

From the experimental findings and the structural features of the vinyl ketones of the cyclohexane series it may be assumed that the *keto–enol* tautomerism is due to the high mobility of the hydrogen atom in the  $\alpha$ -position of the cycle and they form part of the intermolecular complexes with the maleic acid derivatives in the *enol* form of the *trans-S*-conformation. It was found that by radical copolymerization of the studied monomers, copolymers of equimolar composition are formed. The copolymerization constants both of the free and the complex-bound monomers for PMI–VCHK pair were determined:  $r_1 \sim 0$ ,  $r_2 = 0.08$ ,  $r_{2c} = 0.005$ ,  $r_{2c2} = 0.01$  and  $r_{2c1} = 0.009$ . The order with respect to initiator—benzoyl peroxide ( $n$ ) and to the monomers ( $m$ ) were also determined:  $n = 0.5$  and  $m = 1.12$ . By the “shift of rate maximum” kinetic method, participation of donor–acceptor complexes in the chain growth reaction could be quantitatively determined:  $k_{12}/k_{21} = 1.84$ ,  $k_{1c}/k_{12} = 22.01$  and  $k_{2c}/k_{21} = 4.75$ .

Table 2 presents information on the complex-radical copolymerization of the vinyl ketones with anhydride and imides of maleic acid and indicates some characteristics of the copolymers synthesized. It will be seen that in all the cases presented alternating copolymers are of composition close to 1:1 form.

The dependencies of the copolymerization rates on the compositions of the monomer mixtures at  $[\text{M}] = \text{const}$  for all studied monomer systems are described by curves with a maximum of the value of the rate which also characteristic of alternating copolymerization.

The results obtained may be interpreted with reference to the possibility of attachment of the free and complex-bound monomers to the growing macroradicals. In this connection the SL-equation was applied to the system studied in which one of the monomers is not homopolymerized enabling one to find the ratios of the rate constants of attachment of the free monomers and CTC to homonymous macroradicals and to demonstrate the considerable rise in the reactivity of the CTC (by several orders) as compared with the free monomers [102,103,205].

## 5. Effect of charge transfer complex in alternating terpolymerization

Copolymerization of multi-component systems, in complexity and variety of kinetic aspects, is one of most challenging problems of polymer chemistry. Investigations on radical polymerization of these systems with the participation of donor–acceptor monomers are believed to allow one to understand: (a) how the copolymer composition can be planned; (b) how spatial and molecular microstructure can be planned. This should allow the creation of novel reactive copolymers with given composition and special properties.

In a theoretical sense, the study of ternary copolymerization is important for modelling processes by means of which it would be possible to describe the main growth step quantitatively.

Ternary monomer systems containing maleic acid derivatives as electron-acceptor monomers and vinyl monomers as electron-donor monomers differ from other multi-component monomer systems in that radical terpolymerization occurs via both free and complexed monomers; the kinetics of these systems can be regarded a copolymerization of two complexomers [1,43,129,130,206–211].

Study of radical polymerization of ternary systems with above-mentioned A-type monomers enables valuable information to be obtained about the mechanism of chain growth in alternating copolymerization of donor–acceptor monomers.

### 5.1. *trans-stilbene–maleic anhydride–styrene*

A study was made of radical copolymerization of *trans*-stilbene ( $D_1$ , donor-I), styrene ( $D_2$ , donor-II) and maleic anhydride (A, acceptor) [43]. The monomers studied form a system of donor-I–donor-II–acceptor, which is characterized by the presence of two complexes with similar constants of complex-formation:  $K_c = 0.21$  l/mol for  $D_1 \cdots A$  [81] and  $K_c = 0.29$  l/mol for  $D_2 \cdots A$  [213]. In dual systems with the participation of these monomers alternating copolymerization takes place by “complex” ( $D_1 \cdots A$ ) and “mixed” ( $D_2 \cdots A$ ) mechanisms [81,212]. Therefore, to explain the role of complexomers  $D_1 \cdots A$  and  $D_2 \cdots A$  ternary copolymerization of these monomers and kinetic investigations were carried out under conditions which ensure complex-formation to a maximum extent: with constant concentration of A (50 mol%) and low transformations of monomers into copolymers (<10%). It follows from results obtained that a marked change in the content of  $D_1$  and  $D_2$  within a wide range with constant content of A in the initial reaction mixture, hardly affects the composition of copolymers obtained, which is close to 1:1:2 ( $D_1:D_2:A$ ).

Constants of copolymerization of complexomers  $D_1 \cdots A$  and  $D_2 \cdots A$  determined by FR-method, taking into account constants of complex-formation  $K_c$  for both complexes ( $r_1 K_1 / K_2 = 0.676$  and  $r_1 K_2 / K_1 = 0.327$ ), proves that they show a marked tendency to undergo alternating copolymerization. Kinetic investigations enabled us to establish that ternary copolymerization is carried out by a radical mechanism ( $n = 0.5$ ) and a second-order reaction for the monomer ( $m = 2.0$ ). It is shown that the dependence of the rate of ternary copolymerization on the composition of the initial reaction mixture with different overall concentrations of monomers have the extremal form and constant value  $v_{\max}$  with 50 mol% of complexomer  $D_2 \cdots A$  in the monomer mixture. Such a maximum in the rate is generally inherent to alternating complex-radical copolymerization and can be easily explained within the bounds of the cross-growth mechanism of polymer chains.

Based on the fact that under conditions of ternary copolymerization  $D_1$  and A are not polymerized and

the addition of  $D_2$  to a similar radical with low transformations of monomers is unlikely, the following reactions of chain growth may be derived [43].

*Free monomer propagation*



*Complex-monomer propagation*



Under conditions of alternating ternary copolymerization reactions (28) and (31) may be ignored and the following equations adopted:

$$k_{13}[D_1 \cdot][A] = k_{31}[A \cdot][D_1] \quad (34)$$

$$k_{23}[D_2 \cdot][A] = k_{32}[A \cdot][D_2] \quad (35)$$

$$k_{1c2}[D_1 \cdot][A \cdots D_2] = k_{2c1}[D_2 \cdot][A \cdots D_1] \quad (36)$$

$$k_{3c1}[A \cdot][D_1 \cdots A] = k_{3c2}[A \cdot][D_2 \cdots A] \quad (37)$$

To explain the mechanism of chain growth and treat results of alternating copolymerization of  $D_1$ ,  $D_2$  and  $A$  and to determine the quantitative effect of complexomers  $D_1 \cdots A$  and  $D_2 \cdots A$  in accordance with

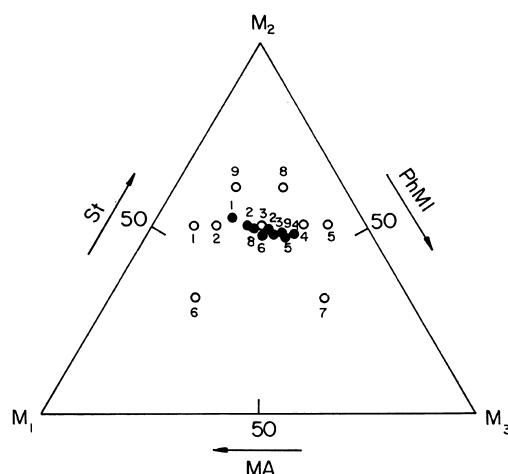


Fig. 1. The diagram of monomer and copolymer compositions for ternary system of MA–St–PMI: initial monomer mixture (–O–) and copolymer composition (–●–).

the above-mentioned condition, following general kinetic equation was proposed:

$$2f/(K_1 + K_2) = \frac{(k_{1c2} + k_{2c1})}{(k_{13} + k_{23})} F + \frac{(k_{3c1} + k_{3c2})}{(k_{31} + k_{32})}, \quad (38)$$

where  $f = a/b$ ,  $F = [D_1 \cdots A]/[D_2 \cdots A]$ ,

$$a = (u_{in}/k_0)^{0.5} \frac{(K_1 + K_2)[(k_{31} + k_{32})(k_{1c2} + k_{2c1})F^2 + (k_{13} + k_{23})(k_{3c1} + k_{3c2})F]}{(k_{13} + k_{23}) + (k_{31} + k_{32})F}$$

$$b = (u_{in}/k_0)^{0.5} \frac{2(k_{13} + k_{23}) + (k_{31} + k_{32})F}{(k_{13} + k_{23}) + (k_{31} + k_{32})F}$$

Values of  $\beta_1 = (k_{1c2} + k_{2c1})/(k_{13} + k_{23}) = 35.29$  and  $\beta_2 = (k_{3c1} + k_{3c2})/(k_{31} + k_{32}) = 10.05$  were determined diagrammatically from the dependence of  $2f/(K_1 + K_2) \rightarrow (F)$ . It follows from a comparison of  $\beta_1$  and  $\beta_2$  values that reactions of addition of complexes to growing radicals predominate in macromolecular chain propagation, namely the total of rates of addition of A in the complex-combined state to macroradicals  $\sim D_1 \cdot$  and  $\sim D_2 \cdot$  is 35-fold higher than that of free A and rates of addition of complexes  $D_1 \cdots A$  and  $D_2 \cdots A$  to growing radicals with an anhydride end unit exceeds the rate of addition of free  $D_1$  and  $D_2$  10 times. Furthermore, it is obvious that complexes  $D_1 \cdots A$  and  $D_2 \cdots A$  have the main effect on the mechanism of chain propagation; these complexes are added to radicals with donor end groups at a dominant rate.

Therefore, experimental results obtained enable ternary copolymerization of *trans*-stilbene, styrene and maleic anhydride to be regarded as alternating copolymerization of two complexomers with a marked effect (quantitative) on the mechanism of chain propagation [43].

## 5.2. Maleic anhydride–*trans*-stilbene(styrene)– N-phenylmaleimide

The complex-radical terpolymerization of the donor–acceptor monomer system maleic anhydride

(acceptor  $A_1$ ), *trans*-stilbene (donor D) and *N*-phenylmaleimide (acceptor  $A_3$ ), which cannot be homopolymerized by radical mechanism, has been of interest for a long time; it is chosen as the object of the investigation of work [129]. In this study the effect of a possible participation of a CTC on the alternating terpolymerization of maleic anhydride, *trans*-stilbene or styrene and *N*-phenylmaleimide is also investigated.

### 5.2.1. Free monomer propagation mechanism

It is known that there are nine types of possible growth reactions that determine the composition of a ternary copolymer product [143]. Since  $A_1(M_1)$ , D( $M_2$ ) and  $A_3(M_3)$  in the  $A_1$ -D(*trans*-stilbene)- $A_3$  ternary system cannot add to their own radicals or to each other, and D also is not homopolymerizable, the following equations for terpolymer composition were derived [129]:

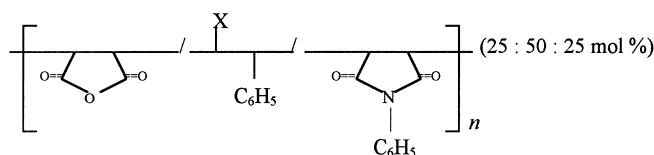
$$m_1/m_2 = \{1 + (k_{23}/k_{21})[M_3]/[M_1]\}^{-1} \quad (39)$$

$$m_2/m_3 = 1 + (k_{21}/k_{23})[M_1]/[M_3] \quad (40)$$

$$m_1/m_3 = (k_{21}/k_{23})[M_3]/[M_1] \quad (41)$$

where  $m_1$ ,  $m_2$  and  $m_3$  are the contents of  $A_1$ , D and  $A_3$  units in the terpolymer in mol%.

Ternary copolymerization of  $A_1$ , D and  $A_3$  and their kinetic investigation were carried out not only under most probable complex formation conditions (content of D monomer: D = 50 mol%), but also with a range of other ratios of comonomers in the feed. It is found that the considerable change in the feed composition is only weakly reflected in the composition of the obtained copolymers (Fig. 1); the mole ratio of monomer units in all products is found to be almost constant and near to 1:2:1.



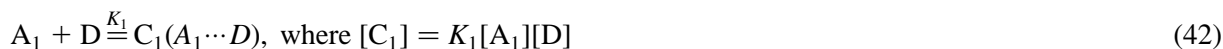
where  $x = 0.37$ – $0.57$ ,  $y = 2.0$ , and  $z = 1.62$ – $1.43$ .

It was shown that the data calculated by using above-mentioned equations and found for the D content in the terpolymers are very close to each other, while for  $A_1$  and  $A_3$  great differences are evident. From  $[M_1]/[M_3]$  vs.  $m_1/m_3$  plots by least squares analysis the values of  $k_{21}/k_{23}$  for  $A_1$ -D(*trans*-stilbene)- $A_3$  system were estimated to be 0.094, showing that  $A_3$  has a much higher activity than  $A_1$  towards the  $\sim$  D-macroradical.

### 5.2.2. Complex mechanism

Two kinds of complexes  $A_1 \cdots D$  ( $C_1$ ) and  $A_3 \cdots D$  ( $C_3$ ), exist, because an equimolecular (1:1) complexes with constants complex-formation  $K_c = 0.21$  l/mol for  $A_1 \cdots D$  complex [81] and  $K_c =$

0.13 l/mol for  $A_3 \cdots D$  (*trans*-stilbene) complex [213] are formed:



Assuming binary copolymerization between  $C_1$  and  $C_3$ , the above equations are substituted into the Mayo–Lewis (ML) [214] or KT-equations [141] of copolymerization to give following modified equations:

$$\frac{d[C_1]}{d[C_3]} = \frac{d[A_1]}{d[A_3]} = \frac{[m_1]}{[m_3]} = \frac{r_1(K_1/K_3)[A_1] + [A_3]}{r_2(K_3/K_1)[A_1] + [A_3]} \quad (44)$$

$$\eta = [r_1(K_1/K_3) + r_2(K_3/K_1)/\alpha]\xi - r_2(K_3/K_1)\alpha \quad (45)$$

which makes it possible to determine the modified monomer reactivity ratios:  $r_1(K_3/K_1) = 0.03$  and  $r_1(K_3/K_1) = 0.08$  for the  $A_1 \cdots D(M_1)$  and  $A_3 \cdots D(M_3)$  pairs ( $D$  is *trans*-stilbene).

The applicability of Eqs. (44) and (45) to the alternating ternary copolymerization of monomer systems studied can be judged from the experimental data of composition of copolymers ( $f_{\text{exp}} = 0.82\text{--}1.09$ ) and calculated by Eq. (44) using the complex-formation constants found and the copolymerization constants of complexomers ( $f_{\text{calc}} = 0.91\text{--}1.17$ ); where the ratios  $f = m_1/m_2$  and  $[A_1]/[A_3] = 0.43\text{--}4.0$ . The fit between  $f_{\text{exp}}$  and  $f_{\text{cal}}$  values demonstrates that the ternary copolymerization is realized by an alternating copolymerization of two complexes. On the other hand, that the values of  $m_1/m_3$  are approximately equal to 1 is an induction of the equimolar ratio of complexomers in the macromolecules, i.e. the composition of the ternary copolymers can be formally described by the equation relating to an alternating copolymerization.

Based on the fact that in the terpolymerization of  $A_1$ ,  $A_3$  and  $D$  no homopolymers are produced, the following chain growth reactions can be derived:





On condition that an alternating ternary copolymerization reaction occurs, steps (50) and (55) may be ignored, and at the stationary state the following equations can be adopted:

$$k_{12}[\sim A_1 \cdot][D] = k_{21}[\sim D \cdot][A_1] \quad (56)$$

$$k_{23}[\sim D \cdot][A_3] = k_{32}[\sim A_3 \cdot][D] \quad (57)$$

$$k_{1c3}[\sim A_1 \cdot][C_3] = k_{3c1}[\sim D \cdot][C_3] \quad (58)$$

$$k_{2c1}[\sim D \cdot][C_1] = k_{2c3}[\sim D \cdot][C_3] \quad (59)$$

If it is assumed that the ternary copolymerization is carried out at a stage close to alternating copolymerization of two complexomers, the equation of the rate of copolymerization, under consideration of the constants of complex-formation, is applicable for evaluating the overall effect of complexes on radical chain propagation. To prove the characteristic CTC participation in the terpolymerization mechanism quantitatively, Eq. (38) was used along with the complex-radical alternating copolymerization model [7]. The ratio of the constants for the addition of  $A_1 \cdots D$  (*trans*-stilbene or styrene) and  $A_3 \cdots D$  (*trans*-stilbene or styrene) complexes and the free monomers to the propagation centre, values of  $\beta_1 = (k_{1c3} + k_{3c1})/(k_{12} + k_{32}) = 12$  and  $\beta_2 = (k_{2c1} + k_{2c3})/(k_{31} + k_{23}) = 115$  for  $A_1$ -D (*trans*-stilbene)- $A_3$  system, were determined. These data show that CTC is more active than free monomers by some orders of magnitude in the chain growth reactions. As it follows from a comparison of  $\beta_1$  and  $\beta_2$  values, the addition of  $A_3 \cdots D$  to the growing radical  $\sim D \cdot$  predominates in the chain growth; the complexes  $A_1 \cdots D$  and  $A_3 \cdots D$  are added to macroradicals with donor end-groups at a dominant rate. These play an essential part in the elementary terpolymerization reactions, leading to the formation of macromolecules with nearly alternating structure, i.e.  $A_1 : D : A_3 = 1 : 2 : 1$  [129].

### 5.3. Phenanthrene–maleic anhydride–*trans*-stilbene

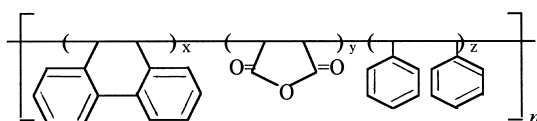
Much interest has been shown in the radical copolymerization of maleic anhydride (M) with vinyl and vinylenic aromatic monomers, such as styrene,  $\alpha$ -methyl/and  $\alpha$ -acetoxystyrenes/and vinyltoluene [1,2,9],  $\beta$ -isopropenyl-naphthalene [215], phenanthrene [82], stilbene [81] and others [1,2,9], which produce alternating copolymers, probably via formation of CTC of donor–acceptor type between M and the above monomers indicated. A number of systematic studies were carried out only for the terpolymerization of M, styrene, and donor- or acceptor-type monomers such as acrylics [216–218], vinyltriethoxysilane [79], unsaturated epoxides [219,220], 4-nitrylcyclohexene-1 [80], stilbene [43], 2-chloroethyl vinyl ether, conjugated dienes [221], citroconic anhydride [222], and certain maleimides [223].

In Ref. [130], the results of initial data of authors on free radical terpolymerization of a donor (phenanthrene, P)–acceptor (M)–donor (*trans*-stilbene, S) monomer system are being presented. Any



three of monomers cannot homopolymerize. The complex-formation of M with P and S, the radical terpolymerization, and the determination of terpolymer composition were carried out and were investigated by  $^1\text{H-NMR}$ , FTIR and chemical analysis methods, respectively. The mechanism of the terpolymerization reaction was evaluated by the free monomer propagation and the CTC participation models. Moreover, radical terpolymerization of P, M, and S was also studied to compare the relative reactivities of P and S towards the  $\sim \text{M}\cdot$  macroradical. The terpolymerization was carried out in *p*-dioxane and/or toluene at  $70^\circ\text{C}$  in the presence of BP used as the initiator.

The structure and composition of the terpolymers synthesized were determined by FTIR spectroscopy and chemical analyses (for M unit content). As analytical bands  $1770\text{ cm}^{-1}$  ( $\nu_{\text{C=O}}$  of anhydride group),  $764\text{ cm}^{-1}$  ( $\delta_{\text{CH}}$  in S for mono-substituted benzene), and  $820\text{ cm}^{-1}$  ( $\delta_{\text{CH}}$  in P for di-substituted benzene) were used. The structure of terpolymers, obtained at a wide range of the changes of P and S contents in monomer feed, can be present in the following total form:



where  $x = 0.38\text{--}0.57$ ,  $y = 2.0$  and  $z = 1.62\text{--}1.43$ .

### 5.3.1. Free monomer propagation model

Since, under the condition used, no homopolymerization of feed monomers and no addition of P and S to the growing macroradicals of  $\sim \text{S}\cdot$  and  $\sim \text{P}\cdot$  is expected to occur, respectively, then chain growth of free monomers in the terpolymerization of P, M, and S consider. It can be described by four equations in spite of nine equations of chain growth reactions used for analysis of classical terpolymerization. By the kinetic analysis of the chain growth reaction after application of stationary state condition, one obtains:  $m_1/m_2 = (k_{21}/k_{23})[\text{P}][\text{S}]$ , where  $m_1$  and  $m_3$  are the instantaneous representation of structural units of P and S monomers in the terpolymer, respectively.

It is shown that a change made in the content of P and S within a wide range with constant content of M in the initial monomer mixture, affects the  $m_1/m_3$  ratio in terpolymers to a lesser extent. The average value of  $k_{21}/k_{23}$  is calculated as 0.28 for P–M–S system in toluene (heterogeneous phase), which indicated that the S is 3.6 times more reactive than the P toward the  $\sim \text{M}\cdot$  macroradical. The lower reactivity of P as compared with the monomer S is considered as a result of the steric effect, which can be conditioned by fixing *cis*-conformation of P molecule. The S monomer has more advantageous *trans*-conformation for chain growth. On the other hand, average value of  $k_{21}/k_{23}$  is calculated as 0.46 for P–M–S system in dioxane (homogeneous phase), it follows that dioxane is a more suitable solvent for reactions studied in which the macromolecules with higher contents of monomer S rings are formed. The changes observed for (P/S) ratio in terpolymers can be explained by the effect of solvent on radical copolymerization of P, M, and S. As it is known, dioxane, styrene (through aromatic fragment) [224], or benzene [45] form  $\pi$ -complexes with M, for which the following complex-formation constants were found:  $K_c$  (dioxane...M) = 0.8,  $K_c$  (dioxane...styrene) = 0.05, and  $K_c$  (benzene...M) = 0.158 l/mol, respectively. Similar complexes seem to be formed in the P–M–S–solvent (dioxane and toluene) systems, which do not take place in chain growth reactions.

### 5.3.2. Complex propagation model

The monomers (P, M and S) form a system of donor (P)–acceptor (M)–donor (S), which is characterized by the presence of two CTC with the equilibrium constants of  $K_c = 0.37 \pm 0.02$  l/mol for  $M \cdots P$  complex and  $K_c = 0.34 \pm 0.015$  l/mol for  $M \cdots S$  complex at 35°C in dioxane. The observed difference in the values of  $K_c$ , which is conditioned by the structural peculiarities of donor monomers, causes the formation of terpolymers with different ratios of P and S monomer rings. On the other hand, a change of M in the monomer feed leads to the formation of terpolymers with constant content of M rings (close to a 50 mol%). By using of ratio  $A^{820}(P)/A^{764}(S)$  as function of terpolymer composition (data of FTIR analysis), the extreme curves with maximum values of absorbance ratio at P : M = 1 : 1 and M:P (or S) = 2:1 compositions are obtained. It is shown that maximum values of  $A^{820}/A^{764}$  correspond to more probable form of CTC in monomer feed [130].

The obtained results from the kinetic point of view allow one to approximate terpolymerization to binary copolymerization of two complexing monomers, i.e.  $M \cdots P (M_1)$  and  $M \cdots S (M_2)$ . Then elementary acts of chain growth with participation of monomer CTC can be described by the following reactions:



Therefore, to determine the relative activity of  $M \cdots P$  and  $M \cdots S$  complexing monomers, terpolymerization was carried out under conditions that ensure complex-formation to a maximum event: with constant concentration of M (50 mol%) and low conversion ( $\leq 10\%$ ). Analysis of constants of copolymerization of FR- and KT-methods [140,141] taking into account constants of complex-formation ( $K_1$  and  $K_2$ ), proves that the  $M \cdots S$  complex is more active in the radical copolymerization as compared with  $M \cdots P$  complex:  $r_1(K_1/K_2) = 0.24 \pm 0.021$  and  $r_2(K_2/K_1) = 0.73 \pm 0.05$  by FR-method [140], and  $r_1(K_1/K_2) = 0.28 \pm 0.02$  and  $r_2(K_2/K_1) = 0.67 \pm 0.05$  by KT-method [141].

## 6. Bifunctional monomers: effects of complex-formation, cyclization and *cis-trans* isomerism

Bifunctional monomers with two polymerizable double bonds of the donor–acceptor type are very attractive, both for development of a complex-radical copolymerization theory and for synthesis of the polyfunctional macromolecules with a given composition, structure, and properties.

Radical cyclopolymerization of bifunctional monomers containing two multiple bonds of different nature, in particular, allyl esters of unsaturated mono- and di-carboxylic acids has been studied in some

detail [225–227]. Yet few publications [228,229] have been devoted to radical copolymerization of the monomers of this series with no regard for the influence of complexing on the cyclization reactions and alternating chain propagation. These monomers belonging to the category of bifunctional monomers with heteronomous multiple bonds of the donor–acceptor type, readily enter into radical homo- and copolymerization with the formation of polyfunctional macromolecules of cycloliner structure. The mechanism of radical homo- and copolymerization is essentially interpreted in terms of the susceptibility of bifunctional monomers towards cycloformation at the stage of chain growth without reference to the donor–acceptor interactions of the  $\pi$ -electrons of the double bonds of monomers of an inter- and intra-molecular nature [229–231].

It has been demonstrated that complex-radical copolymerization of bifunctional monomers such as allyl esters of maleic, fumaric, acrylic,  $\alpha$ -(*N*-maleimido)acetic and *trans*-cinnamic acids proceeds successfully via formation of alternating copolymers with unsaturated and cycloliner structure [95,191–195,232–236].

### 6.1. Inhibition of allyl resonance by charge transfer complexes

Earlier investigations have shown that kinetic regularities of alternating copolymerization of maleic anhydride (acceptor, A) with allyl monomers affording high-molecular-weight products are reasonably intelligible considering the formation of CTCs in initial monomer mixture leading to inhibition of degradative chain transfer [1,78,237–244].

Some peculiarities and mechanism of complex-radical alternating copolymerization of allyl alcohol and allyl glycidyl ether with A were discussed [78]. Complex-formation between allyl monomers studied and A is conformed by data of  $^1\text{H-NMR}$  spectroscopy:  $K_c = 0.16$  l/mol for allyl alcohol (AA)···A complex and  $K_c = 0.11$  l/mol for allyl glycidyl ether (AGE)···A complex at 35°C in  $\text{CHCl}_3\text{-d}_1$ . Dependence of initial rate of copolymerization on the monomer ratios have extremal character with maximum points corresponding to equimolar ratio of donor–acceptor monomers. By using kinetic method the ratio of chain growth constants rates were determined:  $k_{1c}/k_{12} = 8.0$  and  $26.0$  and  $k_{2c}/k_{21} = 10.0$  and  $30.8$  for AGE–A and AA–A systems, respectively. It was shown that complex-formation and alternating copolymerization (the orders by initiator and by monomers equal  $n = 0.5$  and  $m = 1.2$ , respectively) offers an efficient method for inhibition of allyl chain rupture, i.e. degradative chain transfer.

The mechanism of radical alternating copolymerization of A with allyl chloracetate (ACA) was studied [244]. The formation of CTC between comonomers with complexing constants  $K_c = 0.052 \pm 0.0025$  l/mol was found. It should be noted that for ACA efficient chain transfer accounts for 65–86% of transfers, whereas this value for allyl acetate is 24% [245]. Consequently, the introduction of chlorine atom into the molecule causes the reactivities of allylic radicals to be enhanced.

The dependence of copolymer composition on initial monomer ratio shows that the A and ACA monomers have a significant trend toward alternation. In the range of 20–60 mol% A in the initial mixture, the composition of copolymers varies little and is close to the equimolar one. These data along with the SL-equation [42] allow one to determine the copolymerization constants considering the addition of growing macroradicals together with free monomers and complex-bound monomers:  $r_{12} = 0.088$ ,  $r_{2c} = 0.046$ ,  $r_{2c1} = 0.016$ ,  $r_{2c2} = 0.017$  and  $r_{21} = 0.006$ .

The kinetic parameters for the copolymerization reaction of A with ACA are found:  $n = 0.5$  (the order with respect to the initiator, BP) and  $m = 1.3$  (the order with respect to the total concentration of monomers). As can be seen from these values the principal factor responsible for increasing copolymerization of

Table 3

Copolymerization of allyl(metha)acrylates ( $M_1$ ) with maleic anhydride, styrene and vinylacetate ( $M_2$ ): solvent—MEK, initiator—AIBN  $(3.1 - 3.9) \times 10^{-3}$  mol/l,  $[M] = 0.7 - 2.3$  mol/l,  $60^\circ\text{C}$

[ $M_1$ ] in monomer mixture (mol %)	AN (mg KOH/g) <sup>a</sup>	Composition of copolymer (mol %)		Mole fraction of structural units in copolymers $f^b$				$k_{\text{cycl}}/k_{12}$ (mol <sup>-1</sup> ) <sup>c</sup>
		$m_1$	$m_2$	$f_a$	$f_v$	$f_l$	$f_{\text{cycl}}$	
<i>Allylacrylate–maleic anhydride</i>								
70	480	54.9	45.1	0.064	0.092	0.156	0.844	3.72
50	516	51.5	48.5	0.057	0.100	0.157	0.843	6.21
30	542	49.0	51.0	0.052	0.119	0.171	0.829	7.80
<i>Allylmethacrylate–maleic anhydride</i>								
70	495	50.5	49.5	0.059	0.092	0.151	0.849	3.68
50	505	50.5	50.5	0.051	0.113	0.164	0.836	5.97
30	520	46.1	53.9	0.043	0.124	0.167	0.833	8.40
<i>Allylmethacrylate–styrene</i>								
70	–	54.3	45.7	0.158	0.021	0.179	0.821	4.59
50	–	52.8	47.2	0.144	0.032	0.176	0.824	5.27
30	–	50.1	48.9	0.122	0.053	0.175	0.825	7.40
<i>Allylmethacrylate–vinylacetate</i>								
70	–	53.4	46.6	0.131	0.160	0.291	0.709	1.68
50	–	50.5	49.5	0.126	0.176	0.302	0.698	2.80
30	–	48.7	51.3	0.100	0.181	0.281	0.719	4.12

<sup>a</sup> The acid numbers for the AA–M and AMA–M alternating copolymers of composition 1:1 are equal respectively to 533 and 499 mg KOH/g.

<sup>b</sup>  $f$  is fractions of allyl  $f_a$ ; vinyl  $f_v$ ; linear  $f_l = f_a + f_v$ ; and cyclic  $f_{\text{cycl}}$  fragments.

<sup>c</sup> Calculated from the formula  $k_{\text{cycl}}/k_{12} = [M_2]f_{\text{cycl}}/f_l$  at  $[M_2] = 0.69\text{--}1.61$ .

degradative chain transfer owing to the presence of CI substituent in molecule and participation of CTCs in the chain growth reactions. For the quantitative estimation of contribution of complex-bound monomers to the growth reaction the known kinetic method of analysis [40] was used and the following values were determined:  $k_{12}/k_{21} = 3.03$ ,  $k_{1c}/k_{12} = 4.22$  and  $k_{2c}/k_{21} = 2.78$ . The value obtained for relation of crossing growth ( $k_{12}/k_{21}$ ) points to a prevalent role of chain growth reaction via additions of free ACA to  $\sim A\cdot$  macroradical. Other values obtained suggest that complex-bound monomers are added to macroradicals having ACA and A links on ends. The chain growth reaction with participation of  $\sim A\cdot$  macroradical and ACA $\cdots A$  complex prevails in this case. The probability of chain growth via complex addition,  $P(C) = 0.25\text{--}0.31$ , is, as could be expected, always less than 1, i.e. chain growth proceeds by a “mixed” mechanism. At a constant value of  $M$ ,  $P(C)$  depends on the monomer mixture composition. In this manner, during the radical alternating copolymerization of A with ACA in dilute solutions (in benzene) the “free-monomer” mechanism is realized, and in concentrated solutions “mixed” mechanism of chain growth takes place [243].

Analogous inhibition of degradative chain transfer by CTCs were observed in complex-radical copolymerization of several bifunctional monomers with allyl group in molecule such as allyl(metha)acrylates [232], monoallylmalete [123,124], methylallyl maleate (fumarate) [233] and allyl *trans*-cinnamate [234,235].

## 6.2. Allyl(meth)acrylates

It is known that the structure of the polymers of allyl esters of acrylic (methacrylic) acid at the early stages of polymerization when the presence of units with transverse bonds in insignificant is characterized by the presence of fragments with linear and cyclic structures ( $\gamma$ - and  $\delta$ -lactones) [234,235]. The formation of the analogous cyclic structures in alternating copolymers of allyl(meth)acrylates (AA and AMA) with maleic anhydride (M), styrene (St) and vinylacetate (VA) synthesized over a wide ratio interval of comonomers (Table 3) is confirmed by the methods of chemical analysis and the spectral data [232]. In this work the role of the monomer CTC in the radical alternating cyclocopolymerization is established by the methods of kinetic and spectral investigations. It is shown that allyl(meth)acrylates display a tendency toward complexing with the comonomers indicated and to cyclization in reactions forming copolymers of cycloliner structure.

The good solubility, in the usual organic solvents, of the copolymers produced at the early stages of the process (yield  $\leq 15\%$ ) and the considerable fall in unsaturation as compared with the theoretical point to the cycloliner structure of the copolymers is distinguished by the character of the unsaturated side groups: in AA–M, AMA–M and AMA–VA these are essentially vinyl and in AMA–St allyl fragments.

Intermolecular complexing is confirmed by the  $^1\text{H-NMR}$  data from which were determined the equilibrium constants of complex-formation were determined  $K_c = 0.038 \pm 0.025$ ,  $0.22 \pm 0.02$ ,  $0.11 \pm 0.01$  and  $0.25 \pm 0.02$  l/mol for the AA $\cdots$ M, AMA $\cdots$ M, AMA $\cdots$ St and AMA $\cdots$ VA complexes, respectively.

For the quantitative characterization of the reactions involving cyclic and linear macroradicals in the systems of monomers studied, the effective ratio of the rate constant of the intramolecular cyclization reaction to that the bimolecular chain growth reaction leading to the formation of a linear radical, were used (Table 3).

From the values of ratio  $k_{\text{cyc}}/k_{12}$  presented in Table 3 it follows that with increase in the concentration of the comonomer  $[\text{M}_2]$  in the initial mixture the susceptibility to cyclization of allyl(meth)acrylates increases as compared with their cyclization in conditions of homopolymerization:  $k_{\text{cyc}}$  for poly(AMA) is 2.42 [246].

The activation energies of the cyclization  $E_a$  found are comparable with that of the elementary reaction of chain propagation and the influence of the character of the vinyl comonomer on their values is obvious  $E_a = 28.89$ , 28.67, 38.26 and 40.22 kJ/mol, respectively, in the systems AA–M, AMA–M, AMA–St and AMA–VA.

Thus, one of the possibilities of influencing the mechanism of the propagation reaction with a set ratio of linear and cyclic fragments, besides change in the ratio of the components, is selection of the comonomers  $\text{M}_2$  as is confirmed by the quite good correlation of the values of  $k_{\text{cyc}}/k_{12}$  and  $E_a$  found with the content of the cyclic structures in the copolymers studied.

The currently known kinetic scheme of alternating copolymerization [240] presupposing the participation both of free monomers and their CTCs in the elementary activities of propagation in the case of bifunctional monomers (allyl)A– $\text{M}_1$ –V(vinyl) must allow for the stage of intramolecular cyclization and, consequently, the possible participation in the chain growth reaction of radicals of linear and cyclic structure.

### Free monomer propagation



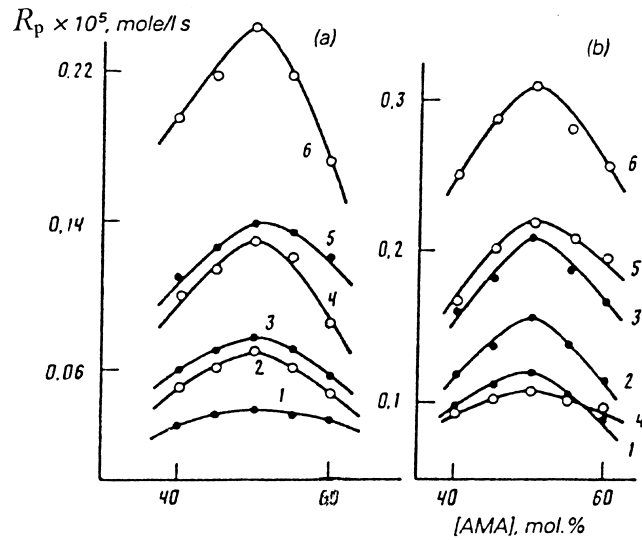


Fig. 2. Dependence of the rate of copolymerization on the composition of the monomer mixture and the total concentration of monomers in the various systems: (a) – allylmethacrylate–Maleic anhydride (1,3,5),  $[M] = 0.7(1)$ ,  $1.0(3)$  and  $1.3 \text{ mol/l}(5)$ ; allylacrylate–maleic anhydride (2, 4 and 6),  $[M] = 1.0(2)$ ,  $1.3(4)$  and  $1.6 \text{ mol/l}(6)$ ; (b) allylmethacrylate–styrene (1–3),  $[M] = 1.7(1)$ ,  $2.0(2)$  and  $2.3 \text{ mol/l}(3)$ ; allylmethacrylate–vinylacetate (4–6),  $[M] = 0.7(4)$ ,  $1.0(5)$  and  $1.3 \text{ mol/l}(6)$ .

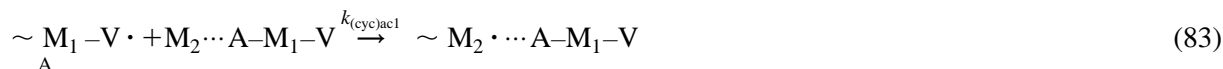
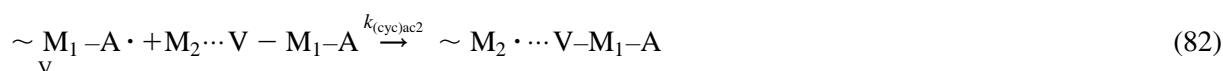
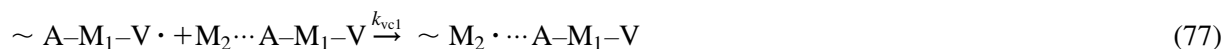
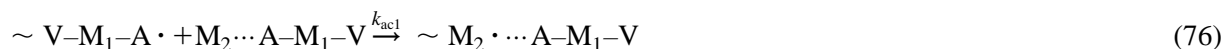


#### Chain growth via cyclization



#### Complex propagation





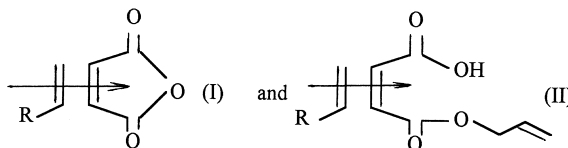
One of the features of alternating copolymerization with the participation of CTCs is the extremal nature of the dependence of the rate of copolymerization on the composition of the reaction mixture. As follows from kinetic data obtained (Fig. 2) such a dependence operates in the system studied in the interval 30–70 mol% of the electron-donor comonomer in the initial monomer mixture.

From the results of kinetic and spectral investigations it was established that complex-formation in monomer systems studied is the main factor ensuring the reaction at the stage of alternating cyclo-copolymerization with the formation of copolymers containing lactone and linear-unsaturated fragments in the macromolecular chain [232].

### 6.3. Monoallylmalate

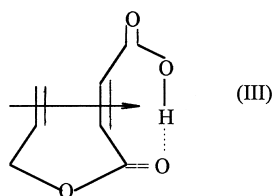
The kinetics and mechanism of radical copolymerization of monoallyl ester of maleic acid (MAM) with styrene (St) [193] and maleic anhydride (M) [194] have been studied. It has been shown that, in the monomer systems investigated, alternating copolymerization occurs and the equimolar composition of the copolymers formed does not depend upon the initial monomer ratio. Constants of copolymerization, parameters  $Q$  and  $e$ , equilibrium constants for the formation of the CTCs and some kinetic parameters of reaction were determined, and also the quantitative contributions made by the monomer CTCs to the radical chain propagation reactions have been found. Results of these studies were considered and discussed in the Section 3.2 of present review, where the comparison of these data with the results on the copolymerization of its organotin derivative was carried out.

$^1\text{H-NMR}$  has been used to determine the equilibrium constants ( $K_c$ ) for the formation of CTC by use of the Ketelaar equation [247]. The values of  $K_c$ , namely 0.256 l/mol and 0.101 l/mol in the deuterated acetone or methylethyl ketone at  $35 \pm 0.1^\circ\text{C}$  for the  $\text{MAM}\cdots\text{M}$  and  $\text{MAM}\cdots\text{St}$  complexes, respectively, were found.

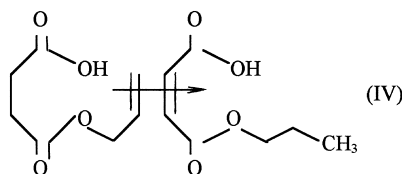


where  $\text{R} = \text{CH}_2\text{OOCCH}=\text{CHCOOH}$  and  $\text{R}^1 = \text{C}_6\text{H}_5$ .

From the donor–acceptor properties of the multiple bonds of the monomers (allyl-donor and olefin –  $\text{CO}-\text{CH}=\text{CH}-\text{CO}-$  acceptor) one may assume the formation and participation in chain growth also of the intramolecular CTC of the type



This confirms the possible formation of the structure (II) the model system monoallylsuccinate–monopropylmaleate. From the  $^1\text{H-NMR}$  spectra of these monomers, containing one double bond in molecule, in the free state and mixtures for different ratios the values of complexing constant  $K_c = 0.06 \pm 0.01$  l/mol, were estimated.



Consequently, it may be assumed that the formation of the lactone fragments is connected with the possible realization of the intramolecular chain growth reaction through the stage of complexing.

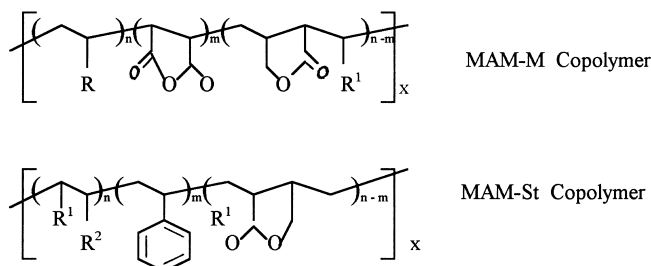
It has been shown that in the monomer systems investigated alternating copolymerization occurs and the equimolar composition of the copolymers formed does not depend upon the initial monomer ratio. By using the FR-method, the values of the copolymerization constants for the above-mentioned pairs of monomers were determined:  $r_1 = 0.05 \pm 0.005$  and  $r_2 = 0.04 \pm 0.006$  for the pair  $\text{MAM}-\text{M}$  and  $r_1 = 0.076 \pm 0.01$  and  $r_2 = 0.11 \pm 0.015$  for the pair  $\text{MAM}-\text{St}$ . Values of the polarizability parameter  $e_1$  and the specific reactivity  $Q_1$  were calculated in accordance with the Alfrey–Price scheme for  $\text{MAM}$   $e_1 = 1.39$  and  $Q_1 = 1.6$ . However these values do not allow for the contribution of the CTC to the radical reactivity of the monomers. Therefore the experimental findings obtained were treated according to the SL-equation which together with attachment of the growing macroradicals of the free monomers takes into account the attachment of the complex-bound monomer (C) giving the following values of the copolymerization constants:  $r_{12} = 0.05$ ,  $r_{1c} = 0.022$ ,  $r_{1c1} = 0.027$  and  $r_{1c2} = 0.11$  for the system  $\text{MAM}-\text{M}$ .



Using kinetic data the values of  $n$ ,  $m$  and  $E_a$  parameters were calculated:  $n = 0.53$  and  $0.52$ ,  $m = 1.25$  and  $1.14$ , and  $E_a = 117.6$  and  $77.0$  kJ/mol for the pair MAM–M and MAM–St, respectively.

For the quantitative characterization of the participation of the complex-bound monomers in the radical chain growth reaction, kinetic method was used [43] based on determination of the ratios of the rate constants of chain growth through the CTC ( $k_{1c}$  and  $k_{2c}$ ) and free monomers ( $k_{12}$  and  $k_{21}$ ):  $k_{1c}/k_{12} = 46.6$  and  $k_{2c}/k_{21} = 1.75$  for the system MAM–M and  $k_{1c}/k_{12} = 64.4$  and  $k_{2c}/k_{21} = 2.5$  for the MAM–St system. The high values of these ratios favor the complex mechanism of chain growth. The complex-bound monomers make a considerable contribution to the reactions with the participation of the macroradicals containing the terminal MAM units.

In the FTIR spectra of the poly-(MAM) together with the main band  $1735$  ( $\nu_{C=O}-COOCH_2CH=CH_2$ ),  $1710$  ( $\nu_{C=O}-COOH$ ) and  $1650$  ( $\nu_{C=C}-CH=CH-$ ) ( $cm^{-1}$ ), and a new absorption band at  $1772$   $cm^{-1}$  ( $\nu_{C=O}$ ) appears characteristic of the cyclic lactone structure [188]. The spectra of the MAM–M and MAM–St copolymers contain the characteristic absorption bands  $1845$  and  $1775$   $cm^{-1}$  ( $\nu_{C=O}$  anhydride),  $1715$   $cm^{-1}$  ( $\nu_{C=O}-COOH$ ),  $930$ ,  $995$  and  $3080$   $cm^{-1}$  ( $\delta_{CH=CH_2}$  and  $CH=$  of allyl group) and  $1650$   $cm^{-1}$  ( $\nu_{C=C}$  allyl or vinylenic group). As is clear from the spectra the band of the C=O group of the lactone overlaps with the anhydride band, which complicates the demonstration of the formation of analogous cyclic structures in the macromolecules of the copolymers studied. However, the observed considerable deviation of the total degree of unsaturation from theoretical value for the copolymers of equimolar composition (unsaturation 50 mol%) may serve as confirmation of the presence of intramolecular cyclic fragments in the chain of macromolecules



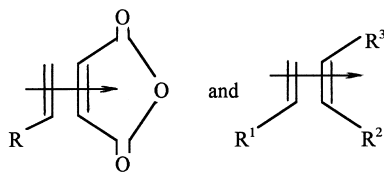
where  $R = CH_2OOCCH=CHCOOH$ ,  $R^1 = COOH$ ,  $R^2 = COOCH=CH_2$ ,  $n = 26.8$ – $31.5$  and  $m = 50$ .

#### 6.4. Methylallylmaleate (fumarate)

Taking into account the influence of the *cis*–*trans* effect the authors of work [233] discuss the patterns of the complex-radical cyclopolymerization of methylallyl esters of maleic (*cis*-MAM) and fumaric (*trans*-MAF) acids with maleic anhydride (acceptor, A) and styrene (donor, D). The different behavior of the fumaric and maleic multiple bonds in the reactions of complexing and cyclization has been recorded. It was established that the synthesized alternating cycloliner copolymers are distinguished by the content and structure of the cyclic fragments in the macromolecule and also by the character of the unsaturation of the side reactive groups.

As to be expected in the monomer systems studied where the donor–acceptor interaction comes about with the participation of the allyl bond, the influence of the *cis*- and *trans*-forms of the monomers is weakly reflected in the  $K_c$  values which are close in magnitude and equal to  $0.19 \pm 0.01$  l/mol for the *trans*-MAF $\cdots$ A complex and  $0.17 \pm 0.01$  l/mol for the *cis*-MAM $\cdots$ A complex. When complexing

involves fumaric and maleic bonds C=C with different degree of screening this leads to a fairly appreciable difference in the values  $K_c = 0.3 \pm 0.015$  l/mol for the *trans*-MAF···D complex and  $0.21 \pm 0.01$  l/mol for the *cis*-MAM···D complex (Table 4).



where  $R = \text{CH}_2\text{OOCCH}=\text{CHCOOCH}_3$  in maleic and fumaric monoesters,  $R^1 = \text{C}_6\text{H}_5$ ,  $R^2 = \text{COOCH}=\text{CH}_2$  and  $R^3 = \text{COOCH}_3$ .

From comparison of the  $K_c$  values found stems the following set of changes in  $K_c$ : *trans*-MDF···D > *cis*-MAM···D > *trans*-MAF···A > *cis*-MAM···A.

It was established that the residual unsaturation of the copolymers obtained including both “allyl” and “vinyl” unsaturation markedly deviates from the unsaturation of the hypothetical linear alternating copolymer containing in each comonomer unit one C=C bond in the side fragments of the macromolecule. The content of the cyclic fragments  $f_{\text{cyc}}$  in the *trans*-MAF-A(or D) copolymers is lower but of the linear containing multiple  $f_1$  higher than in the *cis*-MAM-A(or D) copolymers, unsaturation of an “allyl” with A and a “vinyl” character being observed in copolymers with D (Table 4).

Judging from the values of the cyclization constant  $k_{\text{cyc}}$  characterizing the ratio of the rate constant of the formation of the cyclic radical (intramolecular propagation) to that of its conversion to the radical of the linear structure (intermolecular propagation) [195] the *cis*-monomer displays a greater capacity for cyclization in radical copolymerization with A and D (Table 4). According to the FTIR data the *trans*-MAF–D copolymer contains a large number of unreacted double bonds in the form of side allyl groups (absorption bands at 940 and 990  $\text{cm}^{-1}$ ) and a cyclic lactone structure (1740 and 1780  $\text{cm}^{-1}$  for  $\nu_{\text{C=O}}$  in six- and five-membered lactone cycles).

The copolymers synthesized, the composition of which is close to equimolar over a wide interval of comonomer ratios, are distinguished by a high degree of alternation of the monomer units as witnessed in the copolymerization constants (Table 4) obtained by KT- and SL-methods taking account  $K_c$  of the complexes *trans*-MAF–A(or D) and *cis*-MAM–A(or D) equal to the values shown in Table 4.

The dependence of the copolymerization rate on the composition of the reaction mixture and the total concentration of monomers (Fig. 3) is of an extremal character which is, in general, peculiar to alternating copolymerization and the absence of the dilution effect—constancy of the position of the

Table 4

Constants of complex-formation ( $K_c$ ), cyclization ( $k_{\text{cyc}}$ ) and copolymerization ( $r_1$ ,  $r_2$ ,  $r_{1c}$ ,  $r_{1e1}$  and  $r_{1e2}$ ) for the *trans*-MAF–A (or D) and *cis*-MAM–A (or D) systems

Monomer pair	$K_c$	$f_1$	$f_{\text{cyc}}$	$k_{\text{cyc}}$	$r_1$	$r_2$	$r_{1c}$	$r_{1e1}$	$r_{1e2}$
<i>trans</i> -MAF–A	0.19	0.56	0.44	2.45	0.082	0.061	0.0078	0.09	0.0085
<i>cis</i> -MAM–A	0.17	0.65	0.35	1.77	0.097	0.112	0.085	0.074	0.010
<i>trans</i> -MAF–D	0.30	0.29	0.71	0.79	0.03	0.023	0.010	0.124	0.011
<i>cis</i> -MAM–D	0.21	0.36	0.64	0.54	0.036	0.03	0.0053	0.076	0.0057

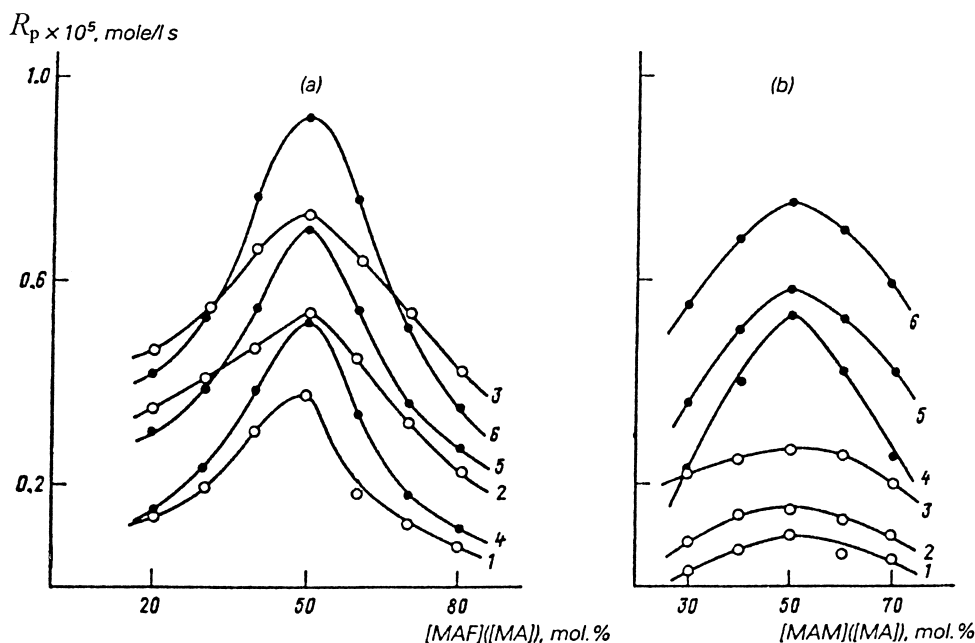


Fig. 3. Dependence of copolymerization rate on the composition of the reaction mixture and the total monomer concentration in different systems. (a) *trans*-MAF-D (1–3); *trans*-MAF-A (4–6); (b) *cis*-MAM-D (1–3); *cis*-MAM-A (4–6).  $[M] = 1.0$  (1); 1.5 (2); 2.0 (3, 4); 2.5 (5); and 3.0 mol/l (6). Solvent, benzene. Initiator, AIBN.  $T = 60^\circ\text{C}$ .

independent of  $[M]$  indicates either free monomer or a complex-mechanism ensuring alternation of the monomer units.

The order of initiator equalling 0.5 for the systems *trans*-MAF(*cis*-MAM)–A testifies to the suppression of degradation chain transfer to the monomer as a result of intermolecular complexing as it was shown previously for maleic anhydride–allyl glycidyl ether system [78]. The values of the order by monomers  $m = 1.5$  (*trans*-MAF–A); 1.07 (*cis*-MAM–A) and 1.2 (*trans*-MAF–D and *cis*-MAM–D) were also found. The closeness of the order by monomers to unity gives grounds for postulating the “dissociative” model of attachment of the CTC to the growing radicals [233].

### 6.5. Allyl- $\alpha$ -(*N*-maleimido)acetate

The alternating copolymers of allyl- $\alpha$ -(*N*-maleimido)acetate (AMI) with maleic anhydride (A) and styrene (D) were prepared in benzene or MEK at  $70^\circ\text{C}$  by using of AIBN as initiator and their structures were determined by FTIR and chemical analyses (iodometric and potentiometric titration for determination of unsaturation and acid number of copolymers [248]. The participation simultaneously of allyl (donor) and vinylene (acceptor) groups in the molecule of AMI ensured intramolecular reaction in the chain growth steps with formation of macromolecules of cycloliner structure. In the spectra of homo- and copolymers new band at  $1720\text{ cm}^{-1}$  for C=O group of cyclic lactone appeared. Fig. 4 indicates that the increase of temperature of the reaction and conversion of AMI–A copolymer leads to decrease of the noncyclic units that can be explained by the participation of side allyl groups in the intramolecular reaction. On the contrary, no such dependence is observed in the AMI–D system is conditioned by high

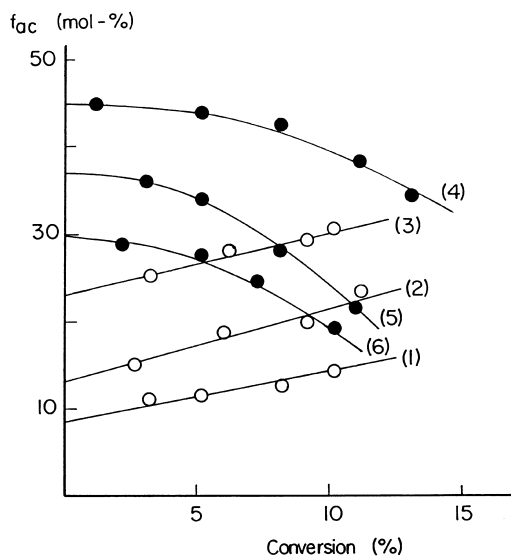


Fig. 4. Plots for the content of linear fragments  $f_{ac}$  in D-AMI (1–3) and AMI-A (4–6) copolymers vs. conversion and temperature: 50°C (1 and 4), 60°C (2 and 5) and 70°C (3 and 6).

reactivity of D monomer towards vinylene group of imide cycle and also by effect of gel-formation in the initial stages of copolymerization [248].

It is obvious from Fig. 4 that  $f_{ac}$  values for zero conversion increase markedly with temperature increase and increase with conversion in the D-AMI system. This fact observed can be explained by predominant participation of side allyl groups in the intramolecular reaction and also by effect of gel-formation in the initial stages of copolymerization. On the contrary no such dependence is observed in the AMI-A system, which may be accounted by high reactivity of A monomer towards allyl group than towards cyclized growing macroradical.

From the dependence of  $\log k_{cyc} \rightarrow 1/T$  for D-AMI and AMI-A systems studied, the values  $E_a = 46.0$  and  $27.2$  kJ/mol for cyclization reactions were determined. On comparing these values it is obvious that the cyclization reaction is more advantageous in the AMI-A system, which may be accounted for by the effect of monomeric CTC, highly reactive towards the  $\sim A\cdot$  macroradical.

The evaluation of the overall kinetics of copolymerization was done on the basis of copolymerization rate measurements for equimolar D/AMI or AMI/A mixtures in MEK at 70°C and at different concentrations of monomers and initiator. The values of rates with total concentration of monomers of 1.5 mol/l and AIBN concentration ranging from  $2.5 \times 10^{-3}$  to  $7.6 \times 10^{-3}$  mol/l permitted us to calculate the order  $n$  with respect to the initiator.

The measurements at different total concentrations of monomers ranging from 0.5 to 2.0 mol/l and at constant concentration of AIBN ( $5.47 \times 10^{-3}$  mol/l), the order of which is given with respect to the total concentration of monomers,  $m$ . The values these parameters are presented in Table 5. As can be seen from the values of  $n$  ( $\sim 0.5$ ) and  $m$  the principal factor responsible for increasing copolymerization of degradative chain transfer (allyl resonance) is the participation of complexing allyl groups in the chain growth and cyclization reactions.

The effective energy of activation  $E_a = 52.7$  kJ/mol for copolymerization reaction, derived from

Table 5  
Kinetic parameters of complex-radical cyclocopolymerization of AMI with D (styrene) and A (maleic anhydride)

Parameters	D-AMI	AMI-A
Constant of complex-formation $K_c$ (l/mol) in $\text{CH}_3\text{COOH-d}_4$ at $35 \pm 0.1^\circ\text{C}$	$0.20 \pm 0.01$	$0.05 \pm 0.005$
Constant of cyclization $k_c \times 10^5$ (l/mol s) <sup>a</sup>	1.71	0.66
$R_p \times 10^5$ (l/mol s) <sup>a</sup>	0.59	0.48
$k_p \times 10^5$ (l/mol s) <sup>a</sup>	3.35	3.84
Orders to initiator ( $n$ ) <sup>a</sup>	0.52	0.50
And to $[\text{M}]_{\text{total}}$ ( $m$ ) <sup>a</sup>	2.40	1.30
<i>Constant of copolymerization</i>		
by KT-method:		
$r_1$	$0.13 \pm 0.01$	$0.037 \pm 0.002$
$r_2$	$0.048 \pm 0.002$	$0.052 \pm 0.002$
by SL-method:		
$r_{1c}$		
$r_{1c1}$	$10.52 \pm 0.5$	$1.64 \pm 0.1$
$r_{1c2}$	$0.65 \pm 0.5$	$0.12 \pm 0.01$
Parameters of Alfrey-Price:		
$Q$ (AMI)	2.88 (imide)	0.018 (allyl)
$e$ (AMI)	1.24 (imide)	-0.20 (allyl)
Ratios of constants of chain growth rates:		
$k_{12}/k_{21}$ ( $\alpha$ )	0.20	0.62
$k_{1c}/k_{12}$ ( $\beta_1$ )	0.60	29.8
$k_{2c}/k_{21}$ ( $\beta_2$ )	4.8	9.1

<sup>a</sup> These parameters were calculated by the equation:  $R_p = k_p[\text{M}]^m$ ;  $[\text{AIBN}]^n$  in the following copolymerization conditions:  $[\text{M}]_{\text{total}} = 1.5$  mol/l,  $[\text{AIBN}] = 5.47 \times 10^{-3}$  mol/l,  $[\text{M}_1]/[\text{M}_2] = 1$ , solvent—MEK  $60^\circ\text{C}$ .

the  $\log k_p$  vs.  $1/T$  plot (where  $T = 50, 60$  and  $70^\circ\text{C}$ ) and constant of initial rate of copolymerization ( $k_p$ ) obtaining by using the dependence of  $R_p = k_p \times [\text{M}]^m \times [\text{AIBN}]^n$  for the AMI–D pair differ from  $E_a = 80.4$  kJ/mol for AMI–A system, which may be explained by different mechanism of initiation and cyclization in the monomer systems studied, and the effect of complex bonded monomers.

The alternating chain growth reactions, taking into account cyclization and complexing effects may be represented as follows:

for AMI–D system



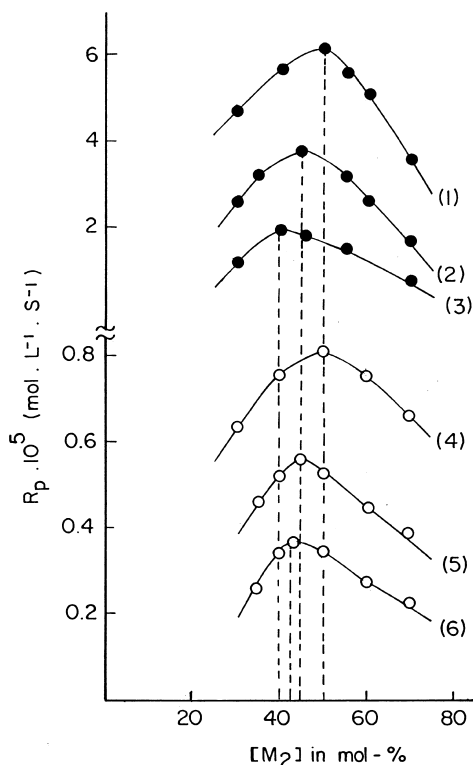


Fig. 5. Plots for initial copolymerization rates of AMI with A and D vs. monomer composition at total monomer concentration:  $[M]_{\text{total}} = 1.0(1), 1.5(2)$  and  $2.0(3)$  for D-AMI and  $0.5(4), 1.0(5)$  and  $1.5(6)$  for AMI-A systems.

for AMI-A system



From the structural peculiarities of bifunctional monomer studied containing two polymerizable groups of allyl (donor) and imide (acceptor) character one may suppose that the formation of following types of equimolecular (1:1) CTC in the monomer systems with its participation [248]:



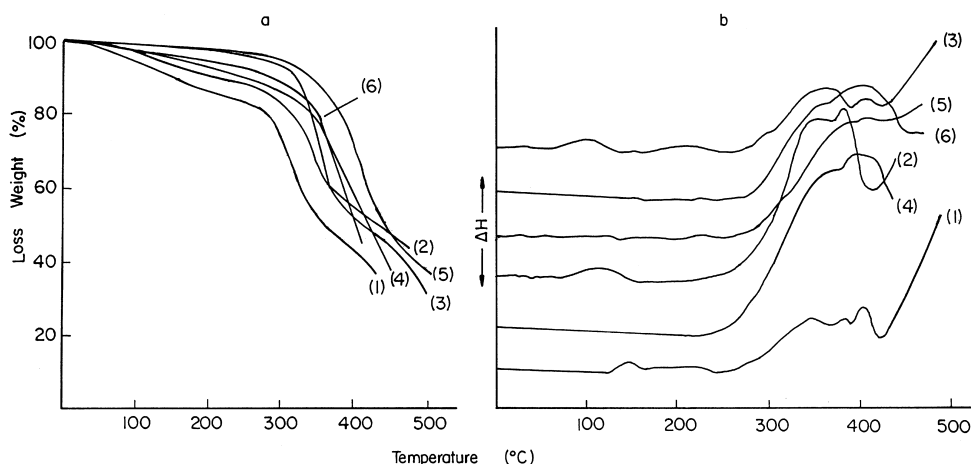


Fig. 6. TGA (a) and DTA (b) analyses of poly-AMI (1), AMI-A (2) and D-AMI (3) copolymers with unsaturation of 5.0, 36.0 and 13.0 mol%, respectively, and after thermotreatment (105°C, 30 min) (4 and 5) and UV-irradiation (25°C, 15 min) (6) of AMI-A (4 and 6) and D-AMI (5) copolymers.



Equilibrium constants of 1:1 complexes ( $K_c$ ) between AMI and D and/or A were determined by using of  $^1\text{H-NMR}$  spectral data (Table 5).

The comparatively high value of  $K_c$  for AMI $\cdots$ D complex may be explained by the high electron-donor property of D monomer toward imide double bond and because the charge transfer is realized early in the AMI–D system than in the monomer system with participation of allyl (donor) and anhydride (acceptor) double bonds. The allyl fragment of AMI does not participate in the complexing with D monomer. This is confirmed by the value of  $K_c = 0.21$  l/mol in deuterated acetic acid at 35°C obtained previously for the model [ $\alpha$ -((-maleimido)acetic acid $\cdots$ styrene)] complex [195].

As is evident from data of Fig. 5 the dependence of the copolymerization rate on the composition of the reaction mixture and the total concentration of monomers is of an extremal character which is, in general, peculiar to alternating copolymerization and the absence of the dilution effect—change of the position of the dependent of  $[M]$  indicates “mixed” mechanism predominantly the participation of CTCs in the chain growth ensuring alternation of the monomer units.

Kinetic parameters of copolymerization such as complex-formation, cyclization, and copolymerization

Table 6

Kinetic parameters of complex-radical copolymerization of AC ( $M_1$ ) with D and A

Parameters	AC–D	AC–A
Constant of complex-formation $K_c$ (l/mol) in $\text{CH}_3\text{OCH}_3\text{-d}_6$ at $35 \pm 0.1^\circ\text{C}$	$0.095 \pm 0.01$	$0.161 \pm 0.015$
Constant of cyclization $k_{\text{cyc}} \cdot 10^5$ (L/mol.s) in $[\text{M}_1]/[\text{M}_2] = 1$ at $60^\circ\text{C}$	$3.05 \pm 0.15$	$1.15 \pm 0.05$
Constant of copolymerization rate $k_p \cdot (\times 10^5 \text{ l/mol s})$ in $[\text{M}_1]/[\text{M}_2] = 1$ at $60^\circ\text{C}$	$3.32 \pm 0.15$	$3.83 \pm 0.18$
Orders to initiator ( $n$ )	0.50	0.51
and to $[\text{M}_1]_{\text{total}}$ ( $m$ )	1.31	1.47
Constant of copolymerization by KT-method:		
$r_1$	$0.056 \pm 0.005$	$0.48 \pm 0.02$
$r_2$	$0.069 \pm 0.006$	$0.038 \pm 0.002$
Ratios of constants of chain growth rate:		
$k_{1c}/k_{12}$	0.48	–
$k_{1c}/k_{12}$	0.20	112.9
$k_{2c}/k_{21}$	15.6	4.5

constants and ratios of chain growth rates for the participation of monomer CTCs and free monomers for both systems studied are all determined and summarized in Table 5. The values these parameters obtained given in Table 2 indicate the relation of crossing growth ( $\alpha$ ) points to a prevalent role of chain growth reaction through additions of free D to  $\sim\text{AMI} \cdot$  macroradical ( $\alpha > 1$ ) and free AMI to  $\sim\text{A} \cdot$  macroradical ( $\alpha < 1$ ) in the AMI–D and AMI–A systems, respectively. The values  $\beta_1 < 1$  and  $\beta_2 > 1$  show that alternating copolymerization is realized via a “mixed” mechanism in the D–AMI system and the chain growth proceeds predominantly through the reactions of macroradicals  $\sim\text{AMI} \cdot$  with CTC and free D monomer. The values of  $\beta_1 \gg 1$  and  $\beta_2 \gg 1$  show that it is very probable that the complexes add to  $\sim\text{AMI} \cdot$  and  $\sim\text{A} \cdot$  macroradicals and the chain growth proceeds predominantly via “complex” mechanism. The found ratios of rate constants of elementary steps suggest that the reactivity of the monomers to a marked degree increases when they are bound in complexes.

The character of the DTA and TGA curves (Fig. 6) of homo- and copolymers of AMI is different because before beginning of the thermodestruction processes exo-peaks at 100, 120 and  $145^\circ\text{C}$ , respectively appear, which can belong to the cross-linking reaction of macromolecules in the isothermic condition due to availability the unsaturated side fragments of allyl (for AMI–D copolymer) and/or vinylene (for AMI–A copolymer) groups in the macromolecular chain [248].

### 6.6. Allyl-trans-cinnamate

Unsaturated macromolecules with free cinnamyl and/or allyl(epoxy) groups on the side chain are extremely reactive and light-sensitive polymers which has a wide use in microelectronics as negative resists [249–253]. One of the known methods for synthesis of such polymers is the homo- and copolymerization of vinyl (allyl) esters of cinnamic acid. Relative activities of allyl and cinnamic bonds during the radical cyclopolymerization of allyl cinnamate (AC) were studied [225,254,255]. The results obtained were interpreted in terms of the contribution of chain growth via intermolecular cyclization and the higher activity of cinnamic bonds as compared to that of allyl bonds in bimolecular



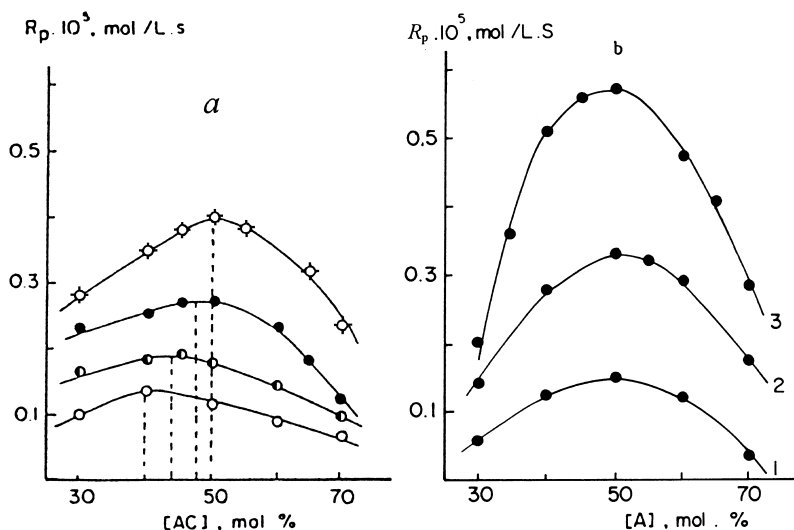


Fig. 7. Plots for AC–D (a) and AC–A (b) copolymerization rates vs. monomer composition and overall concentration of monomers. Solvent MEK;  $60 \pm 0.1^\circ\text{C}$ ;  $[\text{AIBN}] = 6.6 \times 10^{-3} \text{ mol/l}$ ; (a)  $[\text{M}] = 1.5$  ( $-\circ-$ ),  $2.0$  ( $-\bullet-$ ),  $2.5$  ( $-\bullet-$ ) and  $3.0 \text{ mol/l}$  ( $-\diamond-$ ) for AC–D system and (b)  $[\text{M}] = 1.0$  (1),  $1.5$  (2), and  $2.0 \text{ mol/l}$  (3) for AC–A system.

chain propagation. The few interesting studies [256,257] were devoted to the investigation of radical copolymerization of unsaturated esters of cinnamic acid, where the mechanism of homo- and copolymerization of AC was interpreted from a position of its inclination to cycloformation at the chain growth stage.

Generally, with careful selection of comonomer (donor or acceptor type) for reaction of copolymerization with AC, the activity of allyl and cinnamic bonds of AC may be directly changed and unsaturated copolymers can be prepared with either the “allyl” or “cinnamic” character, in principle.

It is of interest to learn the degree of participation of donor–acceptor double bonds of AC in the complex-formation, cyclization, and chain growth reactions during its radical copolymerization with styrene (D) and maleic anhydride (A). Results of these investigations are believed to play an important role in the synthesis of polyfunctional macromolecules with predetermined regulated compositions and structures and also in the preparation of special polymer materials.

Some peculiarities in the radical copolymerization of AC with D and A comonomers in methyl ethyl ketone, at  $60^\circ\text{C}$ , using AIBN as the initiator have been revealed [222,223]. Kinetic parameters of copolymerization such as complex-formation, cyclization, and copolymerization constants and ratios of chain growth rates for the participation of monomer CTCs and free monomers are all determined (Table 6).

The results obtained show that alternative copolymerization reaction is realized which is carried out via a “mixed” mechanism (displacement of the position of  $v_{\text{max}}$ , Fig. 7a) in the AC–D system and a “complex” mechanism (constant position of  $v_{\text{max}}$ , Fig. 7b) in the AC–A system with formation of macromolecules of unsaturated cycloliner structures containing predominantly allyl and/or cinnamyl groups in the side chain, respectively.

The analysis of results obtained allows one to assume that the copolymerization of AC with D proceeds with primary participation of free, complexing and cyclized cinnamic groups during the

chain growth stage, where formed macromolecules have cycloliner structure with predominantly allyl unsaturation on the side groups.

In the AC–A system the copolymerization is realized with primary participation of allyl multiple bonds during the chain growth stage, and the macromolecules formed have cycloliner structure with predominantly cinnamic unsaturation on the side groups.

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