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L. F. Kim[a]; L. L. Stotskaya[a]; B. A. Krentsel[a]; V. P. Zubov[a]; V. B. Golubev[a]; I. L. Stoyachenko[a]
[a] A. V. Topchiev Institute of Petrochemical Synthesis Academy of Sciences of the USSR Moscow, USSR and M. V. Lomonosov Moscow State University, Moscow, USSR

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Kinetic Features and Mechanism of Alternating Copolymerization of Indene with Maleic Anhydride

L. F. KIM, L. L. STOTSKAYA, B. A. KRENTSEL, V. P. ZUBOV,
V. B. GOLUBEV, and I. L. STOYACHENKO

A. V. Topchiev Institute of Petrochemical Synthesis
Academy of Sciences of the USSR
Moscow, USSR

and

M. V. Lomonosov Moscow State University
Moscow, USSR

ABSTRACT

The radical copolymerization of indene (IN) with maleic anhydride (MA) was investigated. The charge-transfer complexes (CT complexes) between comonomers were studied by means of spectrophotometric measurements. It was found that the maximum copolymerization rate occurred at a comonomer feed ratio that did not correspond to the composition of the CT complex and the composition of copolymer. It was shown that rate maximum was displaced towards an excess of IN in the solvents with strong donicity. The Acceptor Number of solvent influences neither the initial rate nor the position of the rate maximum. Some kinetic calculations were made to assess values of the cross-propagation rate constants and to elucidate the mechanism of propagation of macromolecular chains.

On the basis of these calculations it was shown that propagation of the polymer chain for the IN-MA system occurred mainly in accordance with the mechanism of consecutive addition of monomers with unequal rate constants of cross propagation.

INTRODUCTION

The donor-acceptor (DA) interaction concept, as applied to the polymerization process, includes several aspects. One of the latter consists in possible participation of DA or charge-transfer (CT) complexes in the polymer chain propagation reaction, as manifested in a peculiar activation of monomers, with further polymerization under the action of the usual initiating agents. Specifically, the formation of π-π-type DA complexes can provide conditions for the radical polymerization of monomers not polymerizing by the free-radical mechanism, as well as for the generation of alternating copolymers having a number of valuable technical and physiological properties.

The present paper deals with the kinetic features and mechanism of alternating radical copolymerization of IN with MA. The possibility of IN and MA copolymerization was originally reported by Henglein and Stolzenbach [1], but DA interaction between comonomers and its influence on the polymer chain propagation reaction had not been studied.

EXPERIMENTAL

Complexes of the π-π type are weak, as a rule, and exist only in solution; for this reason electronic spectroscopy was selected to investigate the formation of complexes between IN and MA. Electron spectra were recorded in quartz cells 1 cm thick with a Specord spectrophotometer in the range from 250 to 500 nm, and with a Hitachi spectrophotometer in the range from 280 to 360 nm. The cells were thermostatted with a precision of 0.1°C. The composition of the CT complex was determined by using the isomolar series technique.

To study the copolymerization reaction of IN and MA, the ampoule and dilatometry techniques were employed. The solvents were purified by conventional procedures and their purity was followed by spectrophotometry. IN was dried by storage over $CaCl_2$ for 72 hr, after which it was distilled twice in a dry argon, bp 182°C. MA was recrystallized twice from chloroform; directly before the experiment it was sublimed in vacuo to exclude any traces of maleic acid, mp = 53°C. Benzoyl peroxide (BP) was used as the initiator.

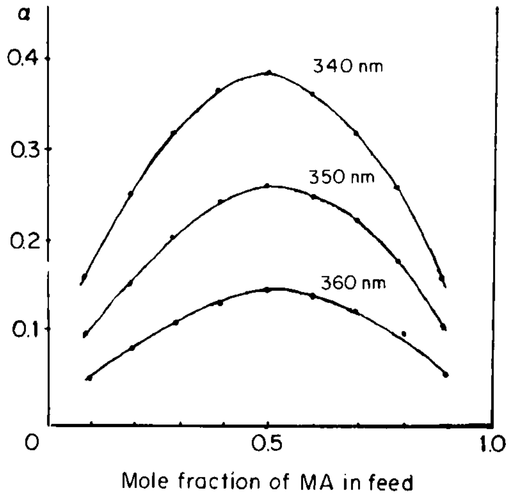

FIG. 1. Dependence of optical density of IN and MA CT-complex on the MA content in the monomer feed. [IN + MA] = 0.24 mole/liter, ethyl acetate .

RESULTS AND DISCUSSION

The CT-complex composition turned out to be equal to 1:1 in the wavelength range measured (340-360 nm) (Fig. 1). To determine the equilibrium constant of the complex formation K_e and the molar extinction coefficient ϵ, the Benesi-Hildebrand equation was used (Table 1). At 25°C, $K_e = 0.32 \pm 0.14$ liter/mole and $\epsilon = 240 \pm 80$ liter/mole-cm; at 45°C, $K_e = 0.16 \pm 0.08$ liter/mole and $\epsilon = 460 \pm 220$ liter/mole-cm.

An equimolar composition of alternating copolymer was obtained in all cases irrespective of the monomer feed ratio (Fig. 2). In a study of the dependence of the copolymerization rate on the composition of the monomer mixture, it was found that the maximum rate occurred at a comonomer ratio which is not consistent with the composition of the CT complex and that of the polymer (Fig. 2).

To explain the "anomalous" position of the rate maximum, the kinetic features of copolymerization in different solvents were studied. The initiation rate had been shown practically independent on the monomer feed composition (Table 2).

Experimental date presented in Table 3 show that, in most solvents, irrespective of the dielectric constant, the maximum of the

TABLE 1. Determination of K_e and ϵ of CT Complex between IN and MA[a]

	$\frac{1}{[D]}$	Optical density d of CT complex (λ = 330 nm)		[A] ℓ/d	
Solution		25°C	45°C	25°C	45°C
1	7.14	0.085	0.075	0.090	0.102
2	3.57	0.160	0.150	0.048	0.051
3	2.38	0.225	0.210	0.034	0.036
4	1.78	0.315	0.285	0.024	0.026

[a] [A] = MA concentration = 0.00762 mole/liter; [D] = IN concentration = 0.14-0.56 mole/liter.

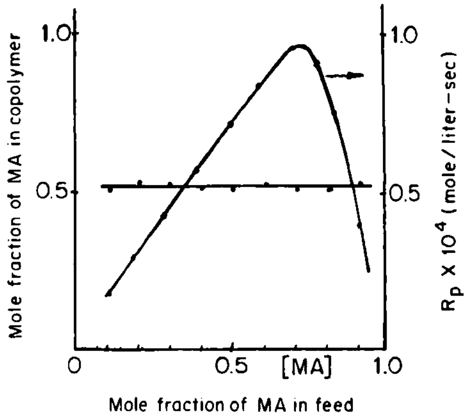

FIG. 2. Dependence of copolymer composition and copolymerization rate on the monomer feed composition; 60°C; [BP] = 0.02 mole/liter, [IN + MA] = 2 mole/liter, dioxane.

TABLE 2. Dependence of the Initiation Rate of IN and MA Copolymerization on the Monomer Feed Composition[a]

[MA] molar fraction in the monomer mixture	Inhibition time τ (sec)	$R_{init} = [R\cdot]/\tau\ .10^7$ $\times\ 10^7$ (mole/liter-sec)
0.3	2580	0.39
0.5	2280	0.44
0.9	2340	0.43

[a] Conditions: 50°C; solvent = dioxane; $[R\cdot] = 0.0001$ mole/liter (concentration of stable radical, 2,2,6,6-tetramethylpiperidine-1-oxyl); $[BP] = 0.02$ mole/liter $[IN + MA] = 2.0$ mole/liter.

rate of copolymerization rate of IN and MA is found at MA content in the monomer feed of about 0.7-0.8 molar fraction. Only in solvents having strong donor characteristics is the rate maximum shifted in the direction of an excess of IN. Thus, in dimethylformamide with donor number 26.6 [2], the rate maximum is observed at a MA content in the monomer feed of 0.3 molar fraction.

The magnitude of the initial copolymerization rate correlates with the donor capacity of the solvents. It diminishes with an increase of the donor number and is practically zero in strongly donating hexamethylphosphortriamide (DN = 38.8). The solvent acceptor capacity also has little effect on either the initial copolymerization rate or the position of the rate maximum.

The dependence of the copolymerization rate on the monomer feed ratio at different total monomer concentrations was studied in benzene (Fig. 3). The position of the rate maximum does not depend on the total concentration of comonomers.

Tables 4 and 5 show experimental data on the dependence of the copolymerization rate on the product of comonomer concentrations for different monomer feed compositions. These data indicate that the reaction rate order with respect to the product of the monomer concentrations is close to 0.5 and increases insignificantly with an increase in proportion of MA in the monomer feed.

The equilibrium constant of the complex formation diminishes with increasing temperature. Therefore, if CT complexes play an important role in the reaction, the total rate of copolymerization should decrease with temperature if the initiation rate is kept constant. The corresponding data, presented in Table 6, indicate the participation of CT complexes in the formation of an alternating copolymer of IN and MA.

TABLE 3. Influence of Different Solvents on the IN and MA Copolymerization Rate and the Position of the Rate Maximum

No.	Solvent	ϵ	μ (Debye)	J (eV)	DN[b]	AN	$R_p \times 10^4$ at [MA] = 0.5 molar fractions (mole/liter-sec)	Maximum $R_p \times 10^4$ (mole/liter-sec)	Maximum rate position, molar fraction of MA in comonomers mixture	$\frac{k_{AD}}{k_{DA}}$
1	Mesitylene	2.28		8.39			0.599	0.928	0.70	5.5
2	Benzene	2.28	0.0	9.24	0.1	8.2	0.798	1.177	0.75	9.0
3	p-Xylene	2.27		8.44			0.618	0.975	0.75	9.0
4	Acetonitrile	37.50	3.44	12.39	14.1	18.9	0.761	1.035	0.75	9.0
5	Dioxane	2.20	0.40	9.52	14.8	10.8	0.662	0.893	0.80	16.0
6	Methyl ethyl ketone	18.20		9.55	17.0		0.687	0.853	0.80	16.0
7	Ethyl acetate	6.02		10.09	17.1		0.566	0.776	0.80	16.0
8	Dimethylformamide	37.60	3.86		26.6	16.0	0.194	0.301	0.30	0.18
9	Hexamethylphosphortriamide	29.60	5.37		38.8	10.6	0.0	0.0	-	-

[a] Conditions: 60°C; [IN + MA] = 2 mole/liter; [BP] = 0.02 mole/liter.

[b] DN = donor number of the solvent [2]; AN = acceptor number of the solvent [2].

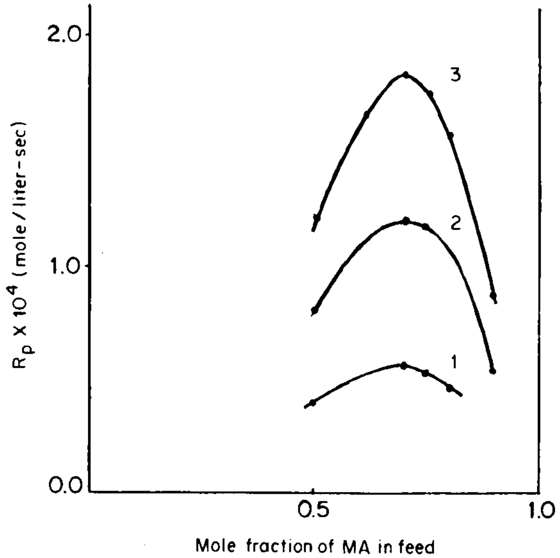

FIG. 3. Dependence of copolymerization rate on the monomer feed composition; 60°C, [BP] = 0.02 mole/liter, benzene: (1) [IN + MA] = 1 mole/liter; (2) [IN + MA] = 2 mole/liter; (3) [IN + MA] = 3 mole/liter.

Thus all the experimental data provide strong evidence for the participation of DA complexes in the alternating copolymerization process.

It should be noted that different theories exist concerning the problem of the mechanism of chain propagation in alternating copolymerization, among which two extreme standpoints can be singled out. According to one of them, this type of copolymerization is considered as the homopolymerization of CT complexes of the comonomers [3-9]. According to the other point of view, high values of the chain cross-propagation rate constants are responsible for the alternation of monomer units. In this case, a consecutive addition of monomers to the propagating chain end occurs due to formation of a CT complex between the free monomer and the growing polymer radical [10-12].

And, finally, systems may be found where both mechanisms are operative with variable contribution [13].

For the IN-MA system studied, the observed half order with respect to the product of comonomer concentrations, in accordance with general features of radical copolymerization [14], implies that the polymer chain propagation reaction proceeds primarily by the mechanism of consecutive addition of the free monomers.

TABLE 4. Dependence of the Initial Rate of IN and MA Copolymerization on the Total Concentration of Comonomers at Different Monomer Feed Ratios[a]

[IN + MA] (mole/liter)	[MA], molar fraction	$R_p \times 10^4$ (mole/liter-sec) In ethyl acetate	In benzene	In dioxane
1.0		0.293	0.400	0.114
2.0	0.5	0.566	0.798	0.267
3.0		0.836	1.210	0.359
1.0		0.350	0.494	-
2.0	0.6	0.692	1.065	-
3.0		1.010	1.660	-
1.0		0.381	0.534	-
2.0	0.7	0.740	1.081	-
3.0		1.159	1.830	-
1.0		0.319	0.460	0.197
2.0	0.8	0.776	1.126	0.465
3.0		1.150	1.610	0.619

[a]Conditions: 60°C; [BP] = 0.02 mole/liter.

TABLE 5. Influence of the IN and MA Ratio in the Monomer Feed on the Order of the Copolymerization Reaction with Respect to the Product of Comonomer Concentrations in Different Solvents[a]

[MA], molar fraction	Rate order of the copolymerization with respect to the product of comonomers concentrations: In ethyl acetate	In benzene	In dioxane
0.5	0.48	0.50	0.49
0.6	0.49	0.55	-
0.7	0.50	0.56	-
0.8	0.58	0.57	-
0.9	0.59	-	-

[a]Conditions: 60°C; [BP] = 0.02 mole/liter.

TABLE 6. Dependence of the IN and MA Copolymerization Rate on the Temperature at a Constant Rate of Initiation[a]

Temperature of reaction (°C)	[BP] (mole/liter)	$R_{init} \times 10^7$ (mole/liter-sec)	$R_p \times 10^4$ (mole/liter-sec)
50	0.02	0.44	0.264
60	0.00316	0.44	0.189

[a] Conditions: solvent, dioxane; [IN + MA] = 2 mole/liter; [IN] : [MA] = 1:1.

The fact that the position of the initial rate maximum for copolymerization is independent of the total comonomer concentration gives one grounds to believe that the reaction of the polymer chain propagation proceeds only according to either of the two above-mentioned mechanisms. The "anomalous" position of the copolymerization rate maximum is evidence for the inequality of the chain cross-propagation rate constants in terms of the "free monomers" mechanism.

Since the rate maximum in most solvents is observed in the presence of an excess of acceptor monomer, it is practically independent of the presence of acceptor solvents and moves in the direction of donor monomer excess in strongly donating solvents, it is apparent that the rate constant of the donor monomer addition to the acceptor end of the propagating chain (k_{AD}) is greater than the rate constant of the addition of the acceptor monomer to the donor end of the growing polymer radical (k_{DA}).

To make a quantitative evaluation of the cross-propagation rate constants and achieve a clearer understanding of the propagation mechanism of the polymer chain for the system under investigation, some kinetic calculations were carried out.

The kinetic scheme of the reaction can be represented by Eqs. (1)-(4):

$$\sim A\cdot + D \xrightarrow{k_{AD}} D\cdot \tag{1}$$

$$\sim A\cdot + C \xrightarrow{k_{AC}} A\cdot \tag{2}$$

$$\sim D\cdot + A \xrightarrow{k_{DA}} A\cdot \tag{3}$$

$$\sim D\cdot + C \xrightarrow{k_{DC}} D\cdot \tag{4}$$

where A is acceptor monomer (MA), D is donor monomer (IN), C is comonomer complex, and

$$\beta_1 = k_{AC}/k_{AD}$$

$$\beta_2 = k_{DC}/k_{DA}$$

$$\alpha = k_{AD}/k_{DA}$$

Proceeding from the fact that the overall copolymerization rate R_p equals to the sum of the rates of addition of free and complexed monomers and taking into account that monomer concentration is a constant value, that the chain termination takes place mainly according to the bimolecular mechanism (Fig. 4), that the value of the equilibrium constant for the formation of CT complex (K_e) is low, and that the initiation rate does not depend on the comonomer feed ratio $\varphi = [D]/[A]$, one can derive the following relationship [13]:

$$R_p/[A] = F(\varphi)K_e[(k_{AC}/k_{AD}) + (k_{DC}/k_{DA})\varphi]\,[A] + F(\varphi) \qquad (5)$$

where

$$F(\varphi) = R_{init}^{0.5}\, k_{AD}\, \varphi/(k^{\circ}_{AA} + 2k^{\circ}_{AD}\,\alpha\varphi + k^{\circ}_{DD}\,\alpha^2\varphi^2)^{0.5} \qquad (6)$$

The dependence of the "reduced" copolymerization rate $R_p/[A]$ on the acceptor monomer concentration $[A]$ is a linear equation:

$$R_p/[A] = a_i + b_i[A] \qquad (7)$$

where

$$a_i = F(\varphi) \qquad (8)$$

$$b_i = F(\varphi)\,K_e[(k_{AC}/k_{AD}) + (k_{DC}/k_{DA})\,\varphi] \qquad (9)$$

Experimental data necessary to obtain a dependence of $R_p/[A]$ on $[A]$ for different values of φ are shown in Table 7.

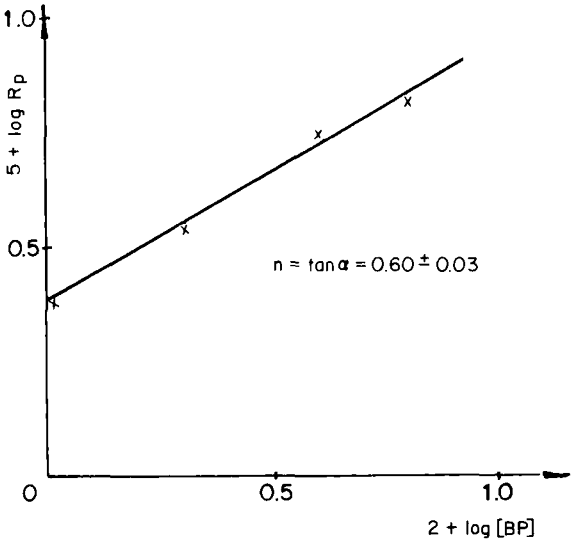

FIG. 4. Determination of the reaction order with respect to the initiator; 50°C; [IN + MA] = 2 mole/liter; [MA] = 1 mole/liter; ethyl acetate.

For copolymerization of IN and MA carried out in ethyl acetate and benzene, a set of straight lines has been obtained which are almost parallel to the abscissa (Fig. 5). In other words, $b_i \cong 0$. Then we derive:

$$(k_{AC}/k_{AD}) + (k_{DC}/k_{DA})\,\varphi \cong 0 \tag{10}$$

This may be in the case if the k_{AC} and k_{DC} values are very small, i. e., the addition of the comonomer complex to the growing polymer radical does not play a significant role in the process. So the chain propagation for the IN-MA system proceeds mainly by the mechanism of consecutive addition of monomers.

When the position of the copolymerization rate maximum is known, one can determine the ratio of rate constants of the chain cross-propagation $\alpha = k_{AD}/k_{DA}$ in different solvents by using the equation [12]:

$$[(1 - M_D)/M_D]^2 = k_{AD}/k_{DA} \tag{11}$$

TABLE 7. Dependence of the "Reduced" Copolymerization Rate of IN and MA on the Concentration of the Acceptor Monomer for a Different Total Monomer Concentration and a Different Monomer Feed Composition[a]

[MA], molar fraction	$\varphi = \frac{[D]}{[A]}$	$R_p \times 10^4/[A]$ in benzene (sec^{-1})			$R_p \times 10^4/[A]$ in ethyl acetate (sec^{-1})		
		[IN + MA] = 1 mole/liter	[IN + MA] = 2 mole/liter	[IN + MA] = 3 mole/liter	[IN + MA] = 1 mole/liter	[IN + MA] = 2 mole/liter	[IN + MA] = 3 mole/liter
0.50	1.0	0.800	0.798	0.807	0.586	0.566	0.557
0.60	0.67	0.823	0.888	0.922	0.583	0.577	0.561
0.70	0.43	0.763	0.772	0.871	0.544	0.529	0.552
0.75	0.33	0.717	0.784	0.782	-	-	-
0.80	0.25	0.575	0.704	0.671	0.397	0.485	0.479
0.90	0.11	-	0.311	0.325	0.178	0.262	0.244

[a] Conditions: 60°C; [BP] = 0.02 mole/liter.

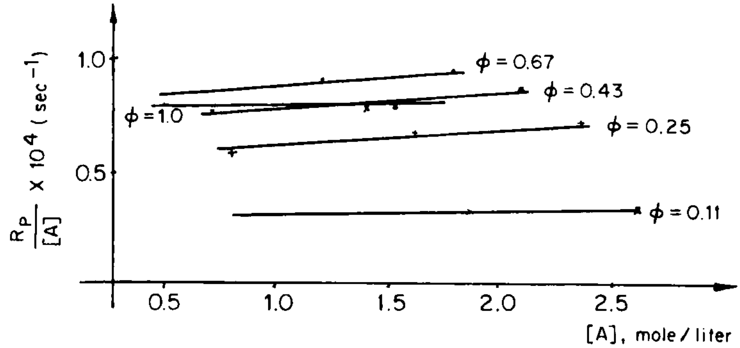

FIG. 5. Dependence of "reduced" rate of copolymerization $R_p/[A]$ on $[A]$ for different values of φ; 60°C [BP] = 0.02 mole/liter; benzene.

where M_D is the molar fraction of the donor monomer (IN) in the monomer feed at which the maximum copolymerization rate is observed and k_{AD} and k_{DA} are the rate constants for addition of donor molecule to the acceptor end of the propagating chain and for addition of acceptor molecule to the donating end, respectively. The α values found in this way are given in Table 3.

As should be expected, $k_{AD} > k_{DA}$ in most solvents, since the anhydride radical has a high reactivity due to the induction effect of the carbonyl groups in the α and β positions. Only in the strongly donating solvent (dimethylformamide) does k_{AD} become lower than k_{DA}, due to competing DA interaction of solvent with the acceptor radical.

To conclude, the experimental data obtained and their interpretation indicate that the alternating copolymerization of indene with a maleic anhydride proceeds according to the mechanism of consecutive addition of monomers having unequal cross-propagation rate constants. The participation of CT complexes in the reaction is probably realized on the level of interactions of adding monomers with the propagating radicals in the transition state of chain propagation.

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