Alternating cyclopolymerization of allyl *trans*-cinnamate and maleic anhydride

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Some features of the radical copolymerization of allyl cinnamate bifunctional monomers, containing donor (allyl)–acceptor (β-phenylacryl) double bonds in the molecule, with maleic anhydride have been revealed. The kinetic parameters of the reactions, including their complex-formation, cyclization and copolymerization constants, as well as the ratios of chain growth rates for the participation of monomeric charge-transfer complexes and free monomers, are all determined. It has been established that an alternative cyclocopolymerization reaction is realized, which is carried out via a complex mechanism with the formation of macromolecules with unsaturated cyclo-linear structures. The synthesized copolymers show high sensitivity to ultraviolet irradiation, electron beams and X-rays, but their negative resists differed, with high lithographic parameters and plasma stability.

(Keywords: cyclocopolymerization; allyl cinnamate monomers; kinetics)

INTRODUCTION

Bifunctional monomers with two polymeric double bonds of donor–acceptor type are very attractive, first, for development of complex-radical copolymerization theory, and, secondly, for preparation of polyfunctional macromolecules with given composition and structure and with special properties.

It has been shown that there are some trends in the radical copolymerization of the allyl esters of maleic, fumaric, acrylic and α-(N-maleimide)acetic acids, with the formation of alternating copolymers having unsaturated and cyclo-linear structures[1–5].

Macromolecules with cinnamyl and allyl groups on the side chain are extremely reactive and light-sensitive polymers, which have wide use in microelectronics as resists for photo- and submicrometre lithography[6–8]. One popular method for preparation of such polymers is by homo- and copolymerization of derivatives of cinnamic acid. The radical polymerization of allyl cinnamate (AC) has been well studied[9,10], and it has been established that it mostly proceeds with the participation of β-phenylacrylic (further 'vinyl') groups, and in fact only 10% of allyl multiple bonds take part in formation of macromolecules with cyclo-linear structure. A few studies[11,12] have been devoted to investigation of radical copolymerization of unsaturated esters of cinnamic acid, where the influence of complex formation on the cyclization reaction and alternating chain growth is not considered; but the mechanism of homo- and copolymerization of AC is mainly interpreted from the viewpoint of its tendency to cycloformation at the chain growth stage.

In this study some results on the radical polymerization of a donor–acceptor monomer system with the participation of a bifunctional monomer of allyl cinnamate (AC) — the allyl ester of *trans*-cinnamic acid — and maleic anhydride (MA) are discussed.

It is of interest to discover the degree of participation of the donor–acceptor double bonds of AC in complex-formation reactions, cyclization and chain growth during its radical copolymerization with MA. From the results of these investigations these bonds 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 highly sensitive polymer resists.

EXPERIMENTAL

Materials

The initial AC is synthesized by condensation of allyl alcohol with cinnamic acid in benzene at 80°C; b.p. 150°C/15 mmHg; $d_4^{20} = 1.0510$, $n_D^{20} = 1.5312$.

MA is recrystallized from benzene and sublimed twice *in vacuo*; m.p. 52.8°C.

2,2′-Azobisisobutyronitrile (AIBN) recrystallized from chloroform, m.p. 102°C, is used as the initiator.

Copolymerization kinetics is investigated dilatometrically. Reaction of AC with MA is carried out in methyl ethyl ketone (MEK) under nitrogen atmosphere in the presence of AIBN at 60°C. Copolymer is isolated from the reaction mixture by precipitation with n-hexane, purified by washing with some portions of benzene and diethyl ether, and dried *in vacuo* to constant weight.

Copolymer compositions are determined by elemental and chemical (potentiometric titration and bromide–

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bromate method of anhydride groups and C=C bonds respectively) analyses.

AC–MA copolymer

Softening point 142–145°C; $[\eta]_{in} = 0.17\ \mathrm{dl\,g^{-1}}$ in MEK at 25°C; unsaturation 7.89%; acid number (*AN*) 390 mg KOH $\mathrm{g^{-1}}$; which contains C 67.25%, H 5.01% by elemental analysis. I.r. spectra (in vaseline oil) gave the following characteristic peaks ($\mathrm{cm^{-1}}$); $\nu_{C=O}$(ester) 1720, $\nu_{C=O}$(anhydride) 1780, 1840, $\nu_{C=C}$(β-phenylacryl) 1640, ν^{as}_{C-O-C} 1180–1270, δ_{CH} (in –CH=CH-*trans*) 980 and 775.

Methods

^{1}H n.m.r. spectra (recorded with a Tesla BS-487B spectrometer at 80 MHz, using hexamethyldisiloxane as internal standard in $D_3C–CO–CD_3$) of pure monomers and their mixtures in different ratios and with an excess of electron-donating monomer (AC≫MA) show an appreciable displacement of chemical shift of anhydride protons to high field. The changes observed for the chemical shifts with a significant excess of AC allow the equilibrium constant of complexation to be determined. The value of $K_{eq} = 0.16\ \mathrm{l\,mol^{-1}}$ for the AC···MA complex is found by means of the Hanna–Ashbaugh equation[13] from the graphical relationship ($1/\Delta \rightarrow 1/\mathrm{AC}$).

The determination of degree of sensitivity of a thin polymer coating to electron beams was carried out by use of a high-energy electron beam apparatus where electrons are accelerated with a voltage of 15 kV and had a diameter of bundles of 0.1 μm. For studies with X-rays of synchrotons of the accumulated rings (wavelength 8–44 Å) point sources of X-rays are used.

The photosensitivities of thin polymer films are determined by the change in their optical coating densities.

Table 1 Complex-radical alternating copolymerization of AC with MA. Reaction conditions: solvent, MEK; 60°C; initiator, $[\mathrm{AIBN}] = 6.6 \times 10^{-3}\ \mathrm{mol\,l^{-1}}$; $[\mathrm{M}] = 1.5\ \mathrm{mol\,l^{-1}}$; conversion ≤ 10%

Monomer mixture (mol%)		*AN*	Unsaturation (%)		Copolymer composition	
[AC]	[MA]	(mg KOH $\mathrm{g^{-1}}$)	Vinyl	Allyl	m_1	m_2
30	70	393	5.44	0.41	48.91	51.09
40	60	392	5.76	0.70	49.15	50.85
50	50	390	7.21	0.89	50.28	49.72
60	40	390	8.52	3.35	51.22	48.78
70	30	390	9.32	4.20	52.51	47.49

Table 2 Formation of vinyl, allyl and cyclic-containing fragments in AC–MA copolymer depending on composition of monomer mixture

Monomer mixture (mol%)		Copolymer composition (mol%)					
[AC]	[MA]	m_1^v	m_2^v	m_1^a	m_2^a	m_1^c	m_2^c
30	70	22.54	23.54	1.06	1.11	25.31	26.54
40	60	23.90	24.73	1.85	1.91	23.40	24.21
50	50	29.99	29.65	2.33	2.31	17.96	17.76
60	40	35.47	33.78	3.07	2.92	12.68	12.08
70	30	38.90	35.18	3.86	3.49	9.75	8.82

RESULTS AND DISCUSSION

In radical copolymerization of AC (with unsymmetric unconjugated dienes of two multiple bonds with allyl and vinyl character), it is of interest to study the relative reactivities of the C=C bonds as functions of change of inductive effects, conjugation character and other structural influences.

By radical copolymerization of AC with MA in MEK, copolymers are synthesized with a constant composition with alternating high degree of monomer links, as evidenced by experimental data (*Table 1*). It is seen that when the monomer ratio is between 0.43 and 2.33 the copolymer composition changes slightly near to equimolar for the investigated systems.

According to the chemical analysis data of copolymers in the AC–MA system, the chain growth reaction is realized at the expense of allyl groups of AC and MA. Increase of AC in the initial mixture increases the content of free acryl groups (m_1^v) in the side chains and decreases the content of cyclic fragments (m_1^c) (*Table 2*). In the case of using equimolar ratio of monomers in the initial mixture, $m_1^v \sim 30$ mol% and $m_1^c \sim 18$ mol% were found.

The composition data obtained for copolymers (*Tables 2* and *3*) allow one to determine the copolymerization constant for the AC–MA pair, after use of the well known Kelen–Tüdös equation[14], which yielded the following: $r_1(\mathrm{AC}) = 0.48 \pm 0.0002$, $r_2(\mathrm{MA}) = 0.038 \pm 0.0015$.

The preferred high tendency to alternation in AC–MA copolymers may be explained by the strong intermolecular donor–acceptor interaction ($K_{eq} = 0.16\ \mathrm{l\,mol^{-1}}$) of the allyl fragment and the maleic double bond. Apparently, this effect is the main determining and responsible factor for various forms of double bonds of AC observed in the chain growth reaction during its copolymerization with the electron-acceptor monomer (MA).

The copolymers synthesized at rather low conversions of 10–15% were all soluble in the organic solvents used (acetone, dioxane, dimethylformamide, etc.) with evidence about their linear sewing structures and unsaturation as determined by the bromide–bromate method. The degree of unsaturation of the AC–MA copolymer synthesized by use of an equimolar ratio of initial monomers is found to be 7.88%, with 7.21% 'vinyl' and 0.67% 'allyl'. The content of unreacted vinyl bonds is insignificant here, and the 'allyl' bond (1.57%) makes the basic contribution to total unsaturation. An analogous change is observed for copolymers prepared by use of different ratios of monomers in the initial mixture (*Table 2*). A decrease of total unsaturation can occur either at the expense of

Table 3 Parameters of Kelen–Tüdös equation[a] for determination of copolymerization constants (r_1 and r_2). Conditions as in *Table 1*

$F = [\mathrm{AC}]/[\mathrm{MA}]$	$f = m_1/m_2$	F^2/f	$F(f-1)/f$	$\xi \times 10^2$	$\eta \times 10^2$
0.429	0.957	0.192	−0.0193	16.49	−1.66
0.667	0.966	0.460	−0.0235	33.12	−1.64
1.0	1.011	0.989	0.0109	50.43	0.55
1.5	1.050	2.143	0.0714	68.79	2.29
2.333	1.106	4.921	0.2227	83.51	3.78

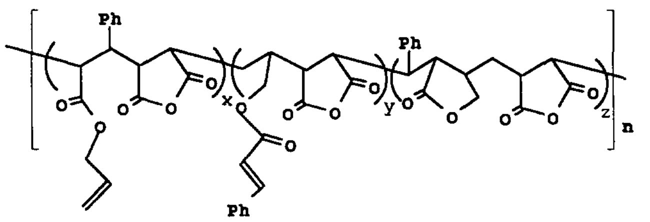
[a] $\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$ (ref. 14)

$$\text{where } \xi = \frac{F^2/f}{\alpha + F^2/f} \quad \text{and} \quad \eta = \frac{F(f-1)/f}{\alpha + F^2/f}$$

Symmetrization parameter $\alpha = [(F^2/f)_{\min} \times (F^2/f)_{\max}]^{1/2} = 0.972$

crosslinking, which is expected owing to the chosen conditions of synthesis, or at the expense of intramolecular cyclization reaction.

The analysis of accumulated results allows one to conclude that the copolymerization of AC with MA is realized with primary participation of allyl multiple bonds during the chain growth stage, and the macromolecules formed have the following structure:



where $x \ll y > z$

From the kinetic data of the initial rate dependence on the concentration of monomers and initiator, the total rate of the copolymerization equation can be represented in the general form:

$$v_{(60^\circ C)} = K_p[M]^m[AIBN]^n \tag{1}$$

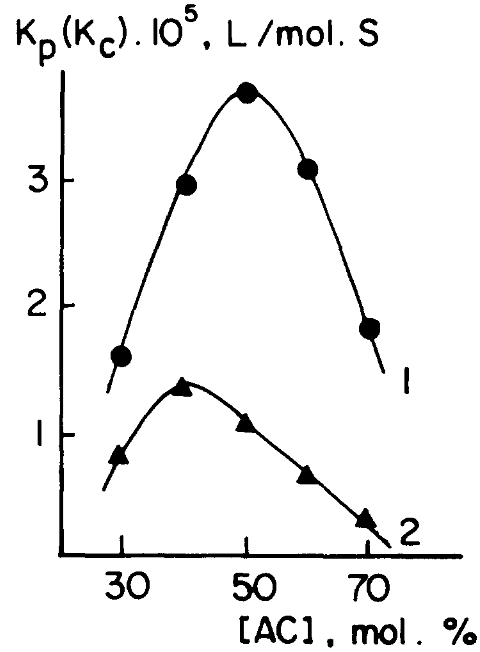
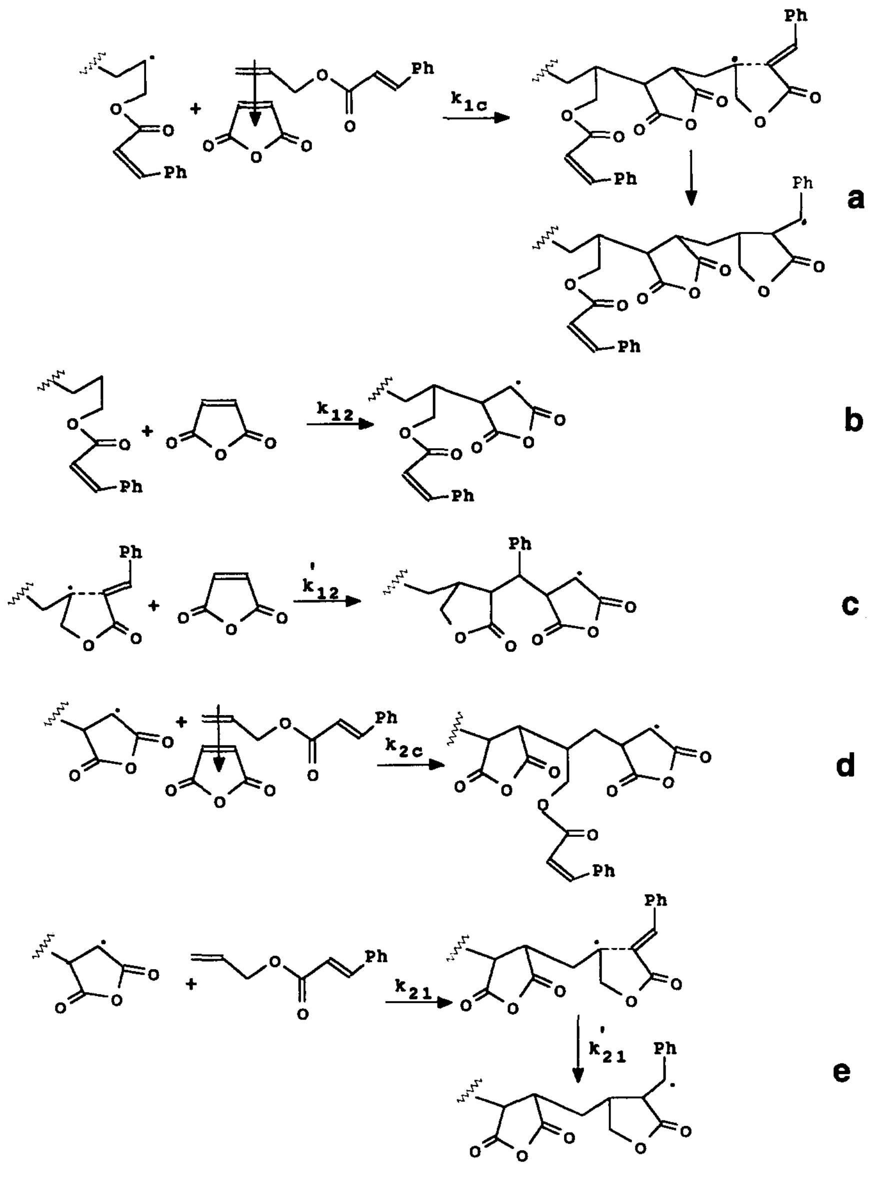
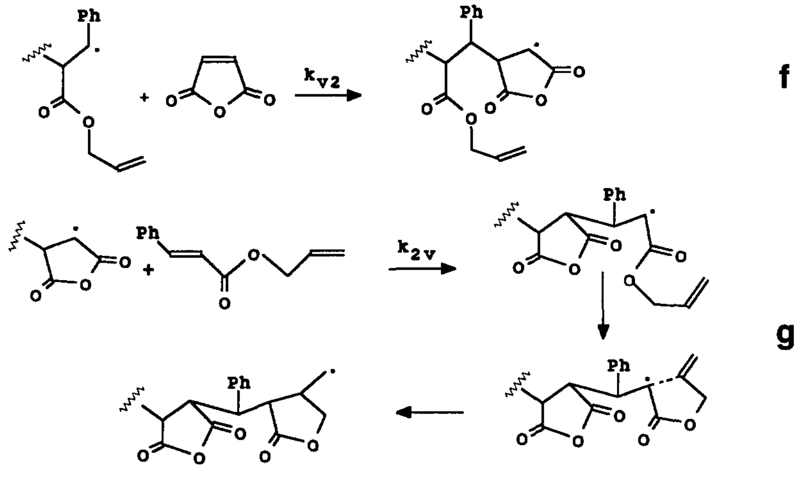


Figure 1 Plot of copolymerization rate K_p (curve 1) and cyclization rate K_c (curve 2) against [AC] in initial monomer mixture AC–MA



Scheme 1



Scheme 2

where the powers are $m = 1.47$ and $n = 0.51$, [M] is the concentration of monomers in their equimolar ratios (1–3 mol l^{-1}) and [AIBN] is the concentration of initiator ((0.15–1.0) × 10^{-4} mol l^{-1}).

The nth order of the initiator indicates that allyl degradation/chain transition does not play an essential role because of suppression of complex formation[15].

The ratio of copolymerization constants and the degree of cyclization are calculable by using the values found for cyclized fragments (m_1^c), after use of equation (2):

$$1/m_1^c = 1 + (K_p/K_c)[\mathrm{M}] \qquad (2)$$

Cyclization constants (K_c) under suitable conditions were determined by equation (2) with the use of K_p values calculated from equation (1) for various monomer ratios for $[\mathrm{M}] = 1.5$ mol l^{-1} and $[\mathrm{AIBN}] = 3.0 \times 10^{-3}$ mol l^{-1}, 60°C.

The curves showing the dependences of $K_{p,60°C}$ and $K_{c,60°C}$ on initial monomer ratios (*Figure 1*) have the same trend and showed maxima at 40–50 mol%. The most favourable condition for formation of cyclized fragments corresponds to a ratio of AC:MA = 40:60.

On the basis of experimental data, *Scheme 1* shows the elementary growth reactions that can be proposed for participation in alternating chain growth for both complex-connected (a) and (c) and free monomers (b) and (d). These also correspond to the experimental data on the composition and structure of synthesized copolymers with unsaturated cyclo-linear fragments.

The formation of five-membered lactone ($m_1^c = 12.68$–25.31 mol%) is mainly stipulated by the reaction of the growing macroradical with a charge-transfer complex (CTC) in scheme (a), and also by chain growth reactions (c) and (f) in which selective intramolecular interaction takes place during addition of the allyl radical to the β-phenylacrylate fragment on that part of the hydrocarbon atom with a double bond that is conjugated with a carbonyl group. Since formation of a six-membered cyclic structure completely eliminates the addition of an allyl radical to a double bond on a phenyl group, the result of stabilization of the macroradical as a result of the influence of the phenyl nucleus is of interest as well as the reaction between vinyl aromatic monomers with allyl monomers[16].

The formation of macromolecules with free β-phenylacrylate fragments on the side chains ($m_1^v = 22.54$–38.9 mol%) occurs mainly at the expense of the participation of complex-connected monomers during chain growth, as presented in .(a) and (d) in *Scheme 1* and also in reactions of $\sim \mathrm{m}_1{}^{\mathrm{a}}$ with MA (b) and $\sim \mathrm{MA}^{\bullet}$ with AC (e), although both are usually insignificant.

The availability of an insignificant amount of allyl fragments on the side chains ($m_1^a = 1.06$–3.86 mol%) may be provided by reactions of the growing macroradicals $\sim \mathrm{m}_1^{\bullet \mathrm{v}}$ and $\sim \mathrm{m}_2^{\bullet}$ with MA and AC monomers (with phenylacryl side chains), respectively. However, in the $\sim \mathrm{m}_2^{\bullet}$ and AC reaction, the possibility of cyclization by forming allyl macroradicals as shown in (g) in *Scheme 2* has not been accepted.

The dependence of initial copolymerization rate on the composition of the reaction mixture has a unique character for both of the monomer systems, which is common to alternating copolymerization (*Figure 2*).

The dilution of the reaction mixture in the AC–MA system does not influence the position of $v_{\max}$, which is fixed at an equimolar ratio of components, whereas in the styrene (St)–AC system such dilution leads to a certain displacement of the position of $v_{\max}$ on the x axis (from 44 to 50 mol% of AC in the monomer mixture). All of these observations are evidence for a change in the chain growth mechanism, depending on the degree of contribution of free complex-connected monomer in the alternating growth reaction. For quantitative estimation of these contributions, it is necessary to carry out a careful treatment of kinetic data for the system (*Figure 2*), using the following equations (for initial rates of alternating copolymerization, presented for AC–MA system)[17]:

$$v/[\mathrm{MA}] = a[\mathrm{MA}] + b \qquad (3)$$

where

$$a = \left(\frac{v_i}{K_t}\right)^{0.5} \frac{K_{eq}(k_{12}k_{2c}F + k_{21}k_{1c}F^2)}{k_{12} + k_{21}F}$$

$$b = \left(\frac{v_i}{K_t}\right)^{0.5} \frac{2k_{12}k_{21}F}{k_{12} + k_{21}F}$$

$$F = [\mathrm{AC}]/[\mathrm{MA}]$$

In equation (3), copolymerization of AC with MA is assumed to proceed mainly with the participation of the allyl groups of AC, entering into the chain of macromolecules in either the free or complex-connected state. The observed independence of the position of $v_{\max}$

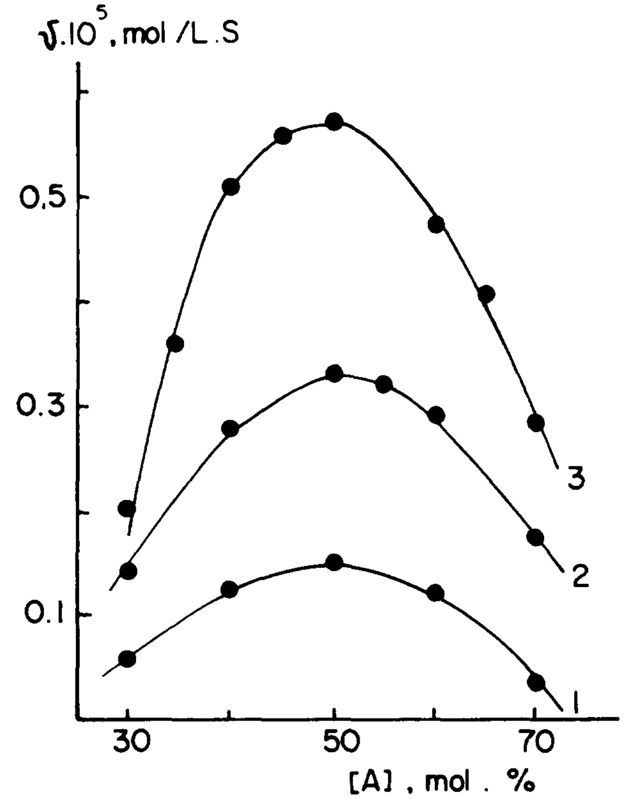


Figure 2 Plot for AC–MA copolymerization rates vs. monomer composition and overall concentration of monomers. Solvent, MEK; $60 \pm 0.1°C$; $[AIBN] = 6.6 \times 10^{-3}$ mol l^{-1}; $[M] = 1.0$ (curve 1), 1.5 (curve 2) and 2.0 mol l^{-1} (curve 3)

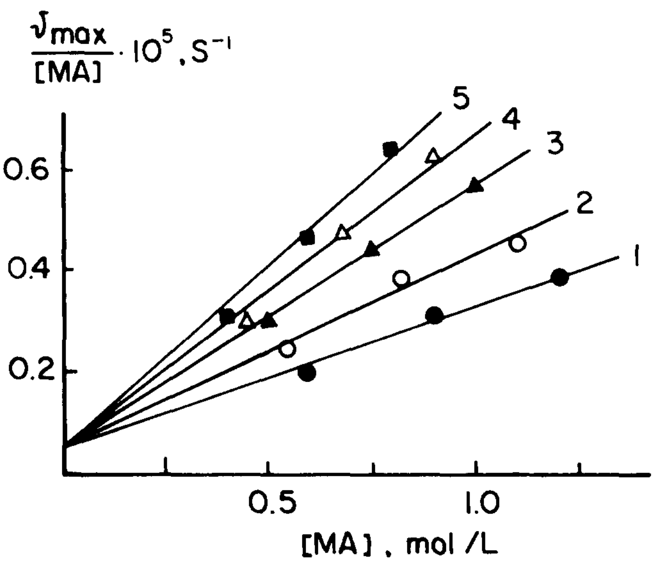


Figure 3 Plot of 1/[MA] vs. [MA] at various ratios of starting monomers $F = [AC]/[MA]$: $F = 0.67$ (curve 1), 0.82 (curve 2), 1.0 (curve 3), 1.22 (curve 4) and 1.5 (curve 5)

on the concentrations of monomers (*Figure 2*) also fits with equation (3).

On the basis of a and b found (slope and intersect in *Figure 3*, respectively), the F values calculated are plotted as $(2a/b)/K_{eq}$ vs. F (*Figure 4*) in accordance with the equation $(2a/b)/K_{eq} = (k_{1c}/k_{12})F + k_{2c}/k_{21}$, from which the following ratios of the chain growth reaction rate constants for the AC–MA system are calculated:

$$k_{1c}/k_{12} = 112.9 \quad \text{and} \quad k_{2c}/k_{21} = 4.5$$

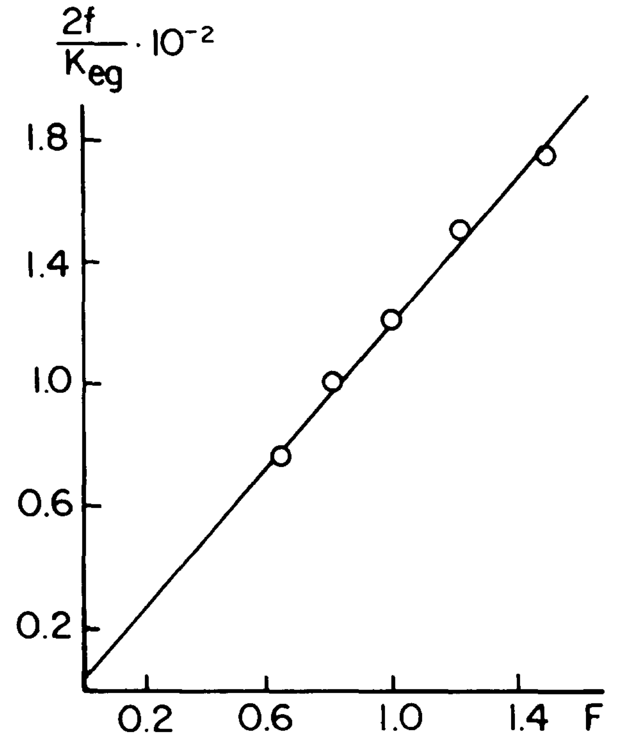


Figure 4 Plot of $2f/K_{eq}$ vs. F for the evaluation of quantitative contribution of AC···MA complex to propagation reaction ($f = a/b$)

Table 4 Lithographic parameters of thin coating formed from solution of AC–MA copolymer in MEK by ultracentrifugation

	AC–MA	
Lithographic parameters	15%	20%
Layer thickness of resist (μm)	0.51	0.53
Photosensitivity ($C J^{-1}$)	56	58
E-beam sensitivity ($C cm^{-2}$)	1.3×10^{-7}	1.5×10^{-7}
Permitted capacity (μm)	1.7	1.8
X-ray sensitivity ($mJ cm^{-2}$)	48	50
Permitted capacity (μm)	0.8	0.8
Plasma resistance (relative to PMMA)	2.5	2.5

The calculated values of $k_{1c}/k_{12} \gg 1$ and $k_{2c}/k_{21} > 1$ support the chain growth reactions with the participation of CTC with the dominating contribution of the reaction $\sim AC^{\bullet}$ with MA···AC complexomer.

It is interesting to see that the ratios of growth rate constants for the complex-connected monomers are very large and can exceed almost 25-fold that of free monomers.

Synthesized reactive polyfunctional copolymers show high sensitivity to different kinds of irradiation and are easily transferred to insoluble form, which allows them to be used as negative resists (*Table 4*).

It has been established that the synthesized copolymers are capable of crosslinking under the action of various sources of radiation, which makes it possible to use them as negative resists.

Data in *Table 4* prove that the polymer resists based on AC–MA copolymer have sufficiently high lithographic parameters and can be used in microelectronic technology or nanolithography.

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REFERENCES

1 Rzaev, Z. M., Gurbanov, K. I., Mamedova, S. G., Guseynov, M. M. and Shafirov, G. S. *Polym. Sci. USSR (A)* 1984, **26** (4), 815

2 Rzaev, Z. M., Mamedova, S. G., Rasulov, N. Sh. and Agaev, U. H. *Polym. Sci. USSR* (*A*) 1987, **29** (2), 392

3 Mamedova, S. G., Rzaev, Z. M., Medyakova, L. V., Rustamov, F. B. and Askerova, N. M. *Polym. Sci. USSR* (*A*) 1987, **29** (9), 2111

4 Mamedova, S. G., Mamedov, A. C., Medyakova, L. V. and Rzaev, Z. M. *Polym. Sci. USSR* (*A*) 1991, **33** (10), 2074

5 Mamedova, S. G., Rzaeva, S. A., Medyakova, L. V. and Rzaev, Z. M. *Polym. Sci. USSR* (*A*) 1991, **33** (10), 2088

6 Watanabe, S. and Ichimura, K. *J. Polym. Sci., Polym. Chem. Edn.* 1982, **20** (11), 3261

7 Bokov, Y. S. 'Fotoelektron i Rentgenorezisty', Radio i Svyaz, Moscow, 1982 (in Russian)

8 Guillet, J. 'Polymer Photophysics and Photochemistry', Cambridge University Press, Cambridge, 1985

9 Novichkova, L. M., Dmitrenko, A. V., Ospanova, K. M. and Rostovsky, E. N. *Izv. Akad. Nauk Kaz. SSR, Ser. Chem.* 1977, **1**, 86

10 Kratz, E. O., Novichkova, L. M., Bandareva, N. S., Pokrovsky, E. I. and Rostovsky, K. M. *Vysokomol. Soyed.* (*B*) 1974, **16** (2), 105

11 Roovers, J. and Smets, G. *Makromol. Chem.* 1963, **60** (1), 89

12 Sumida, G. and Volg, O. *Polym. J.* 1981, **13** (6), 521

13 Hanna, M. W. and Ashbaugh, A. L. *J. Phys. Chem.* 1964, **68**, 811

14 Kelen, T. and Tüdös, F. *J. Macromol. Sci., Chem.* (*A*) 1975, **9** (1), 1

15 Rzaev, Z. M., Jafarov, R. V., Ibrahimova, D. S., Masterova, M. N. and Zubov, V. P. *Vysokomol. Soyed.* (*B*) 1982, **24** (2), 728

16 Ham, E. 'Copolymerization', Wiley-Interscience, New York, 1968

17 Georgiev, G. S. and Zubov, V. P. *Eur. Polym. J.* 1978, **14** (2), 93