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Complex–Radical Copolymerization of Allyl Cinnamate with Styrene

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ABSTRACT: Some peculiarities in the radical copolymerization of *trans*-allyl cinnamate, a bifunctional monomer containing donor (allyl) and acceptor (cinnamic) double bonds in the molecule, with styrene in methyl ethyl ketone, at 60 °C, using 2,2′-azobis(isobutyronitile) as the initiator have been revealed. Kinetic parameters of copolymerization such as complex formation, cyclization, and copolymerization constants and ratios of chain growth rates for the participation of monomeric charge transfer complexes (CTC) and free monomers are all determined. The results show that an alternative copolymerization reaction is realized which is carried out via a "mixed" mechanism with formation of macromolecules of unsaturated cyclolinear structures. It has been established that the chain growth proceeds predominantly through the reaction of cinnamic macroradicals with CTC and free styrene monomer. It has been proved that obtained copolymer is highly sensitive to UV-irradiation, E-beams, and X-rays, providing high lithographic parameters and plasmastability for its negative resists.

Introduction

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.

Complex–radical copolymerization of mono- and bifunctional monomers of the donor (D)–acceptor (A) type may be considered as a promising example for the design of negative polymer resists with directly regulated structure and lithographical parameters. It has previously been demonstrated that complex–radical copolymerization of bifunctional monomers such as allyl esters of maleic, fumaric, acrylic, and α-(*N*-maleimido)acetic acids proceeds successfully via formation of alternating copolymers with unsaturated and cyclolinear structure.[1-5]

In this study the results of investigations on radical polymerization of the D–A monomer system with participation of bifunctional allyl cinnamate (AC) and styrene (St) in methyl ethyl ketone (MEK) at 60 °C, in the presence of 2,2′-azobis(isobutyronitrile) (AIBN), are discussed.

Unsaturated macromolecules with free cinnamyl and/or allyl groups on the side chain are extremely reactive and light-sensitive polymers which have a wide use in microelectronics as negative resists.[6-10] 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 AC were studied.[11,12] 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 chain propagation. Meanwhile, a few studies[13,14] were devoted to the investigation of radical copolymerization of unsaturated esters of cinnamic acid, where the effects of complex formation on cyclization reaction and alternating chain growth were not considered, but the mechanism of homo- and copolymerization of AC was mainly interpreted from a position of its inclination to cycloformation at the chain growth stage.

Generally, with careful selection of comonomer (D or A) for 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 D–A double bounds of AC in the complex formation, cyclization, and chain growth reactions during its radical copolymerization with St (D). 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 highly sensitive polymer resists.

Experimental Section

Materials. The initial AC is synthesized by condensation of allyl alcohol with *trans*-cinnamic acid in benzene at 80 °C. AC, after isolating from the reaction mixture by distillation in vacuum and purifying by a second distillation have the following characteristics: bp 150 °C/15 Torr, $d_4^{20} = 1.0510$, $n_D^{20} = 1.5312$.

St, a Fluka product, is purified by distillation under reduced pressure in a dry nitrogen atmosphere just before use, and it is kept over activateed silica gel; bp 25–25.5 °C/2 Torr, $d_4^{20} = 0.9058$, $n_D^{20} = 1.5462$.

A fresh 2,2′-azobis(isobutyronitrile) (AIBN) recrystallized from chloroform, mp 102 °C, is used as the initiator.

Copolymerization. Reaction kinetics is investigated dilatometrically. Copolymerization of AC with St was carried out in MEK under a nitrogen atmosphere in the presence of AIBN at 60 °C up to low conversion (≤10%). For the determination of copolymer compositions and some of their properties, the reaction glass tubes or dilatometer were cooled and opened, and the copolymers were precipitated in *n*-hexane at a predetermined time. Reaction products were purified by reprecipitation from a MEK solution with *n*-hexane, by washing with some portion of benzene and ethyl ether, and dried in vacuo to constant weight AC–St copolymer: softening temperature 155–158 °C, $[\eta]_{\text{in}}$ 0.29 dL/g in MEK at 25 °C, unsaturation 2.24%. Anal, C, 82.45; H, 7.12; O, 10.43. IR spectra (film), cm^{-1}): $\nu_{C=O}$(ester) 1730, $\nu_{C=C}$(allyl) 1650, δ_{CH}(in $-CH{=}CH_2$) 940, $\nu_{CH=}$ 3080, $\nu_{C=O}$(lactone) 1770, δ_{CH}(phenyl) 700, $\nu_{C=C}$(phenyl) 1600.

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Table 1. Alternating Copolymerization of AC with St (Reaction Conditions: Solvent, MEK, 60 °C; Initiator, AIBN (6.6×10^{-3} mol/L), [M] = 2.0 mol/L, Conversion, ≤10%)

monomer mixtures	elem anal. (%)[a]		unsaturation (%)		copolym composition (mol %)		param of Kelen–Tüdös eq[b]	
[AC]/[St]	C	H	vinyl	allyl	m_1	m_2	$\xi \times 10^2$	$\eta \times 10^2$
0.43	81.23	6.98	0.15	0.59	53.16	46.84	16.91	−4.69
0.67	81.67	7.02	0.41	0.82	51.63	48.32	31.71	−3.09
1.0	82.45	7.12	0.67	1.57	50.17	49.83	49.58	−0.33
1.5	82.64	7.06	0.97	2.32	48.75	51.25	67.54	2.31
2.33	83.02	7.21	1.37	3.38	48.02	51.98	83.08	2.94

[a] Calculated for alternating copolymer (1:1): C, 82.16; H, 7.06; allyl, 14.05%. [b] $\xi = F^2/f/(\alpha + F^2/f)$; $\eta = [F(f-1)/f]/(\alpha + F^2/f)$; $\alpha = [(F^2/f)_{\min}(F^2/f)_{\max}]^{1/2}$.

Characterization. The composition of copolymers obtained as white powders was determined by chemical and elemental analysis. The total unsaturation of copolymers was determined by the bromide–bromate method in the presence of $HgSO_4$.[15] Allyl unsaturation was found by the method of Gindin et al.[16] in the presence of CCl_4–AcOH. The difference between them yielded the content of vinyl (cinnamic) bonds on the side groups of the copolymers. Contents of cyclic fragments (m_1^c) in copolymers have been calculated from $m_1^c = m_1 - m_1^a$, where m_1 is the total content of AC in the copolymer and m_1^c is that of the AC ring with a free allyl group on the side chain; m_1 has been found from the data of elemental analysis (oxygen content).

IR spectra are recorded on an UR-20 spectrometer in the region of 400–3200 cm^{-1}. ^1H-NMR spectra recorded with a Tesla BS-487B spectrometer at 80 MHz, using hexamethyldisiloxane as an internal standard in CH_3COCH_3-d_6 at 35 °C. The spectra of pure monomers and their mixtures at different ratios and with an excess of electron-donating monomer ([St] ≫ [AC]) show an appreciable displacement of chemical shifts of cinnamic double bond protons (Δ) into the strong field. The change observed for chemical shifts with a significant excess of AC and St allow the equilibrium constant of complexing (K_{eq}) to be determined. The value of $K_{eq} = 0.095 \pm 0.01$ L/mol for the AC...St complex is found by means of the Hanna–Ashbaugh equation[17] from a graphical relationship ($1/\Delta \rightarrow 1/[St]$).

The determination of the degree of sensitivity of thin polymer coatings to E-beams is carried out by use of the high electron-beams apparatus where electrons are accelerated with a voltage of 15 kV. The beams had a diameter of 0.1 μm, while point source X-rays were used for studies with X-rays of synchrotrons of the accumulated rings (wavelength 8–44 Å).

The photosensitivities of thin polymer films are determined by a change of their optical coating densities which occurs under the effect of UV-irradiation.

The process of use of resist consists of the following consecutive stages: (a) spin-casting of polymer films at 2000 rpm, (b) drying of obtained thin films in a thermostat during 20 min at 100 °C, (c) exposure of films followed by development of the image in isopropyl alcohol at 15 °C during 30 s, (d) plasmachemical etching in the following regime: CF_3Cl plasma, power 100 W, and pressure 0.4 Torr, and (e) thermal treatment of the plates with developed pictures at 150 °C during 40 min.

Results and Discussion

In the study of radical copolymerization of AC containing two double bonds of allyl and vinyl character, it is necessary to pay attention to the evaluation of relative reactivities of C=C bonds dependent on the change of inductive effects, the character of conjugation, structural influences, and D–A properties of comonomers.

Experimental data of the copolymerization of AC with St (Table 1) show that the compositions of copolymers prepared in different monomer ratios (AC/St = 0.43–2.33) are close to equimolar and allow one to determine the copolymerization constants (r_1 and r_2) for an AC–St pair by using the Kelen–Tüdös equation[18]

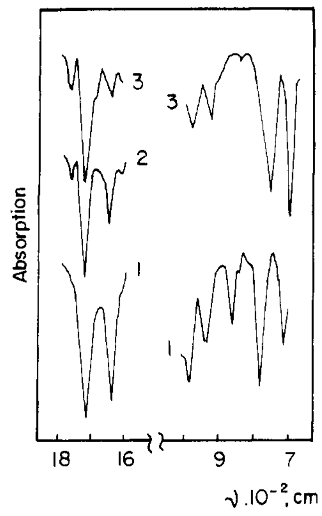


Figure 1. Fragments of IR spectra of AC (1), poly-AC (2), and AC–St copolymer (3).

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

where α is a symmetrization parameter, and η and ξ are variables determined from the copolymer composition (see Table 1). These data were used to calculate the values of $r_1 = 0.056 \pm 0.005$ and $r_2 = 0.069 \pm 0.006$ by a linear regression method. The values of $r_1r_2 \ll 0$ show clearly that AC and St monomers have a high tendency to alternating copolymerization.

According to the data of chemical and elemental analyses of copolymers in the Ac–St system, the chain growth reaction proceeds basically through the reaction of cinnamic and vinyl (St) bonds. On the other hand, an observed low value of unsaturation for copolymer synthesized in an equimolar ratio of initial monomer compared with the calculated unsaturation for an alternating copolymer allows one to assume more participation of allyl bonds in the chain growth via cyclized macroradicals. An increase in the initial concentration of AC increased the total unsaturation of copolymers. The ratio of allyl and cinnamic unsaturation in copolymers remained nearly constant (2.34–2.46) at ≥50 mol % of AC concentration in the monomer feed (Table 1). A decrease of the total unsaturation can occur either by branching, which is expected by chosen conditions of synthesis or at the expense of the intramoleclar cyclization reaction, which is confirmed by the data of the IR spectra.

The fragments of IR spectra of AC, poly(AC), and AC–St copolymer are listed in Figure 1. It is seen from comparative analysis of presented data that in the spectrum there is an intensive band at 1720 cm^{-1}, obviously being representative of the C=O ester group, and a peak at 1770 cm^{-1}, referring to C=O of the five-membered lactone. The absorption bands of six-membered cyclic lactone groups (1740 cm^{-1}) are absent in the spectrum of the copolymer. The possibility of formation of these groups in poly(AC) has been mentioned in one study.[12]

The intensity of the band at 1645 cm^{-1} ($\nu_{C=C}$) is considerably decreased from monomer to polymer, whereas the absorption bands at 940–990 cm^{-1} (δ_{CH} in –CCH=C–) of allyl fragments are almost not changed. Alkaline hydrolysis of the AC–St copolymer was carried and disappearance of the C=O lactone cycle was observed.

For the higher contents of cyclic fragments found for the AC–St copolymer (15.7–16.9%) the effect of intermolecular complex formation can be pointed out to influence the intramolecular cyclization reaction. In fact,

Table 2. Initial Copolymerization Rate (R_p) as a Function of the Total Monomer (AC:St = 1:1) and Initiator Concentrations (Conditions as in Table 1)

[AIBN] = const. (6.6 × 10^{-3} mol/L)		[M] = const. (2.0 mol/L)	
[M] (mol/L)	$R_p \times 10^5$ (mol/L·s)	[AIBN] × 10^3 (mol/L)	$R_p \times 10^5$ (mol/L·s)
1.1	0.098	1.5	0.087
1.5	0.103	3.0	0.123
2.0	0.174	6.6	0.174
2.5	0.214	8.0	0.186
3.0	0.267	9.7	0.204

in the AC–St system, this effect favors the formation of cyclic structure owing to the activation of the cinnamic bond of AC which follows intramolecular attack on the allyl bond.

The analysis of cumulative results allows one to assume that the copolymerization of AC with St proceeds with primary participation of free, complexing, and cyclized cinnamic groups during the chain growth stage, where formed macromolecules have cyclolinear structure with predominantly allyl unsaturation on the side groups.

From the kinetic data of the initial rate dependency on the concentration of monomers and initiator, the total rate of the copolymerization equation can be presented in the general form as follows:

$$R_p(60°\text{C}) = K_p[\text{M}]^m[\text{AIBN}]^n \qquad \text{(I)}$$

where $m = 1.31$ and $n = 0.5$ for the AC–St system, which were found from log(R_p) vs log([M]) and log(R_p) vs log([AIBN]) plots, respectively, by using the experimental data from Table 2; [M] is the total concentration of monomers in their equimolar ratios; [AIBN] is the concentration of initiator; K_p is the constant rate of copolymerization at 60 °C.

The values of the orders with respect to the total concentration of monomers (m) and to the initiator (n) indicate that the allyl degradative chain transfer does not take place in copolymerization under study. But the low value of m compared with the same values for the useful radical copolymerization can be explained by effects of cyclization and complex formation.

K_p and the degree of cyclization ($1/m_1^c$) are calculated by using eq I and the values determined for cyclized fragments, respectively. Constants of cyclization (K_c) under suitable conditions were determined by the following equation:

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

for various monomer ratios in conditions: [M] = 1.5 mol/L, [AIBN] = 3.0 × 10^{-3} mol/L, at 60 °C.

The curves showing the dependence of $K_p^{60°\text{C}}$ and $K_c^{60°\text{C}}$ on initial monomer ratios (Figure 2) have the same trend and show maxima of both constants at 50–55 mol %.

The observed rather sharp inclination of cyclization in the case of AC may be explained by two factors: (1) increase of probability of intermolecular reactions and (2) decrease of St concentration in the monomer feed. The inclination to cyclization is strongly expressed. These factors play an important role in the change of the chain growth mechanism, provided with various contributions of complex-connected or free monomers to radical alternating cyclocopolymerization.

On the basis of experimental data, Scheme 1 (eqs 1–5) of elementary stages of growth reactions can be proposed for participation of both complex-connected and free monomers in alternating chain growth:

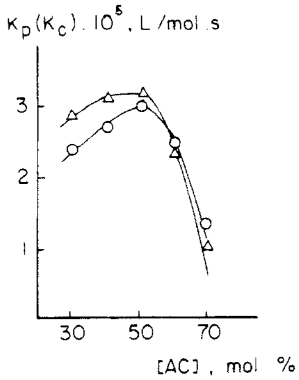
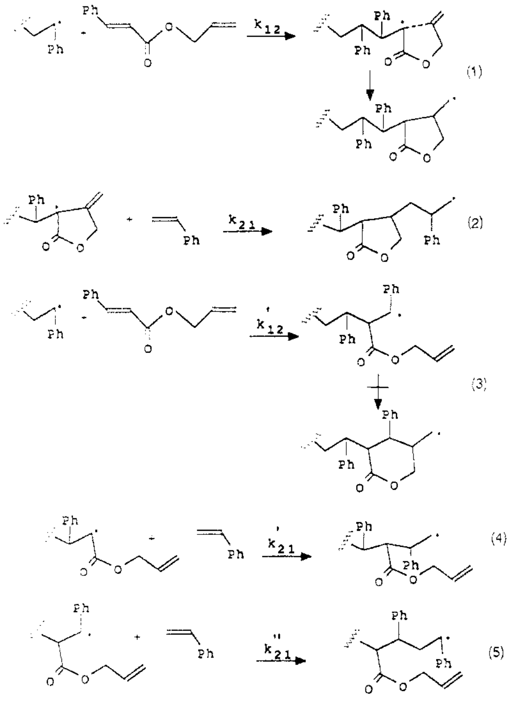


Figure 2. Plot of the product of copolymerization (K_p) and cyclization (K_c) rates against initial monomer mixture: AC–St (Δ, K_p; O, K_c).

Scheme 1

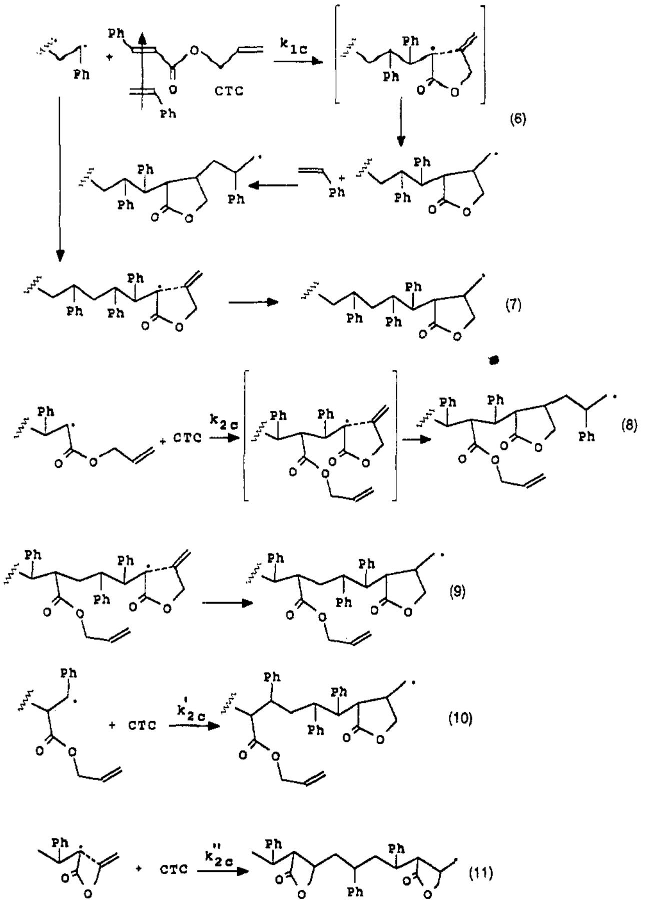


Chain growth reaction takes place mainly via the β-phenyl acrylate fragments, and allyl groups are basically consumed by formation of cyclic fragments only at the expense of intermolecular attack of the macroradical, conjugated with an carbonyl group on an allyl bond, s presented in eqs 1 and 2. The growing radical ~St• is also added to the double bond of the β-phenyl acrylate fragment on the hydrocarbon atom in the carbonyl group (eq 3), where the possibility of the reaction in eqs 4 and 5, as confirmed with the data of chemical analysis of copolymers with various monomer ratios (Table 1), is not expected.

The participation of CTC in the chain growth reactions leads finally to formation of both the cyclic fragments [Scheme 2 (eqs 6, 7, and 11)] and the side free allyl groups [Scheme 2 (eqs 8–10)]. The formation of an insignificant amount of free cinnamic fragments on the side chain is explained by the result of chain transfer reaction with growing radical ~St•. The allyl radical stabilized with π-electrons of multiple bond which is not capable for participation in the chain growth can be easily torn off from the growing radicals.

The dependence of the initial copolymerization rate on the initial monomer ratio has a unique character for the studied monomer system which is common to alternating copolymerization (Figure 3).

Scheme 2



By using the equation of Shirota et al.[19] as,

$$R_p/[\mathrm{AC}] = a[\mathrm{AC}] + b \qquad \text{(III)}$$

where

$$a = \frac{2k_{21}k_{12}(R_i)^{0.5}FK_{eq}(k_{1c}/k_{12} + (k_{2c}/k_{21})F)}{(k_{t11}k_{21}{}^2 + 2k_{t12}k_{21}k_{12}F + k_{t22}k_{12}F^2)^{0.5}}$$

$$b = \frac{2k_{21}k_{12}(R_i)^{0.5}F}{(k_{t11}k_{21}{}^2 + 2k_{t12}k_{21}k_{12}\mathrm{F} + k_{t22}k_{12}F^2)^{0.5}}$$

where R_i is the initiation rate; k_{1c}, k_{2c}, k_{12}, and k_{21} are the corresponding reactivity ratios; k_{t11} and k_{t12} are the termination rate constants; K_{eq} is the equilibrium constant of the CTC; and F is the ratio of initial monomer concentrations [St]/[AC]. Parameters a and b are calculated from a R_p/[AC] vs [AC] plot which gives straight lines for different F values as shown in Figure 4.

It is evident that the copolymerization of AC and St at different total monomer concentrations increases the participation of free monomers in the cross propagation.

Equation III reveals the fact that slopes of the straight lines in Figure 4 are related to the reactivity ratio equation by

$$K_{eq}(\beta_1 + F\beta_2) = a/b \qquad \text{(IV)}$$

where $\beta_1 = k_{1c}/k_{12}$ and $\beta_1 = k_{2c}/k_{21}$. The β_1 and β_2 values are determined from the intercept and slope of the line in Figure 5 where $K_{eq}\beta_1 = 0.2$ and $K_{eq}\beta_2 = 15.6$, respectively.

Obtained values of β_1 and β_2 indicate that the chain growth proceeds predominantly through the reactions of macroradicals ~AC• with CTC and free St monomer.

The dependence of the initial copolymerization rate on the ratio of initial monomers (Figure 3) is observed by "shifts of maximum" on the curves, which in turn proves that along with CTC the free monomers also take part in the alternating copolymerization. In this case, for determination of the cross propagation ratio k_{12}/k_{21}, the following kinetic equation[20] is used:

$$(k_{12}/k_{21})(k_{1c}/k_{12})\{2K_{eq}[\mathrm{AC}][\mathrm{St}]\} + (k_{12}/k_{21})(k_{2c}/k_{21})K_{eq}\{[\mathrm{St}]^2 - [\mathrm{AC}][\mathrm{St}]\} + (k_{12}/k_{21})[\mathrm{St}] + (k_{1c}/k_{12})\{1/[\mathrm{St}]K_{eq}[\mathrm{AC}]^2([\mathrm{St}] - [\mathrm{AC}])\} - (k_{2c}/k_{21})2K_{eq}[\mathrm{AC}]^2 = [\mathrm{AC}]^2/[\mathrm{St}] \qquad \text{(V)}$$

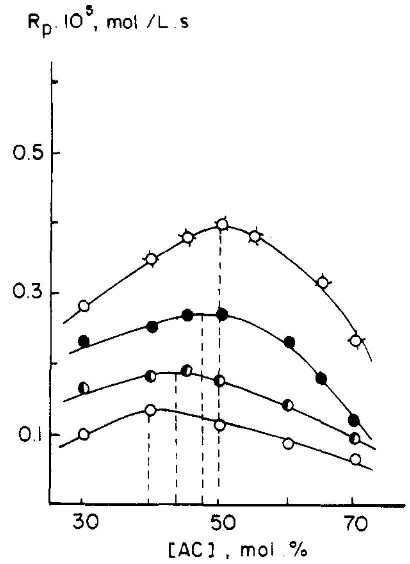


Figure 3. Plot for AC–St copolymerization rates versus monomer composition and overall concentration of monomers. Solvent, MEK, 60 ± 0.1 °C. [AIBN] = 6.6 × 10^{-3} mol/L. [M] = 1.5 (○), 2.0 (◐), 2.5 (●), and 3.0 (-ϕ-) mol/L.

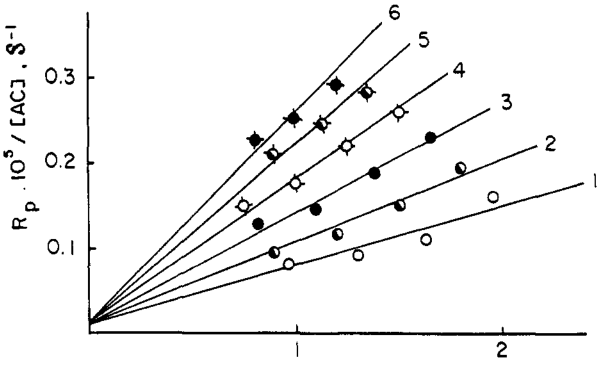


Figure 4. Plot of R_p/[AC] versus [AC] at different [St]/[AC] = F ratios in the copolymerization of St(M_1) and AC(M_2). F = 0.538 (1), 0.667 (2), 0.818 (3), 1.0 (4), 1.22 (5), and 1.5 (6).

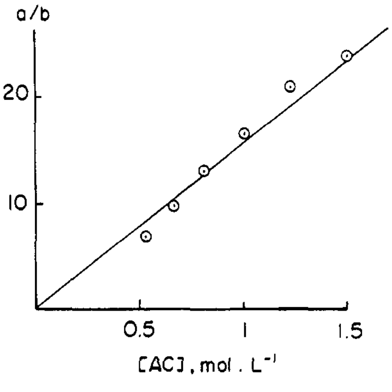


Figure 5. Plot of $K_{eq}(\beta_1 + F_{\beta 2}) = a/b$ versus F in the copolymerization of St and AC.

Transforming eq V to a more simplified view,

$$(k_{12}/k_{21})(k_{1c}/k_{12})a + (k_{12}/k_{21})(k_{2c}/k_{21})b + (k_{12}/k_{21})c + (k_{1c}/k_{12})d + (k_{2c}/k_{21})e = f \quad \text{(VI)}$$

and substituting the experimentally found values of a, b, c, d, e, and f into eq VI under the condition of maximum $dR_p/d[AC] = 0$, $[M] =$ const., and the known value of K_{eq} for the three positions of R_{max}, the following equation system was prepared:

$$(4.56\alpha + 0.51)\beta_1 - (20.58\alpha + 3.04)\beta_2 + 60\alpha = 26.27 \quad \text{(VII)}$$

$$(10.53\alpha + 0.22)\beta_1 - (48.74\alpha + 8.28)\beta_2 + 84\alpha = 51.87 \quad \text{(VIII)}$$

$$(18.95\alpha + 0.82)\beta_1 - (89.28\alpha + 17.15)\beta_2 + 105\alpha = 85.95 \quad \text{(IX)}$$

Solving eqs VII–IX by analytical method led to the following value of the cross propagation rate constant $k_{12}/k_{21} = 0.48$ which is evidence of the fact that the AC monomer is being added to the $\sim$St$^\bullet$ macroradical almost twice as easier than that of St monomer to $\sim$AC$^\bullet$ macroradical.

Synthesized reative polyfunctional copolymer shows a high sensitivity to different kinds of irradiation such as UV-irradiation, E-beams, and X-rays and is easily transferred to the insoluble form that allows one to use it as a negative resist. The lithographic characteristics of thin polymer coatings are presented in Table 3.

Data shown in Table 3 prove that the resists on the base of AC–St copolymer have sufficiently high lithographic parameters and can be used in microelectronic technology of nanolithography.

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Table 3. Lithographic Parameters of Thin Coating Formed from a MEK Solution of AC–St Alternating Copolymer

	AC–St copolymer solution	
lithographic parameters	15%	20%
layer thickness of resist (μm)	0.47	0.51
photosensitivity (J/cm^2)	64	68
E-beams sensitivity (C/cm^2)	2.1×10^{-7}	2.5×10^{-7}
permitted capacity (μm)	1.8	1.9
X-rays sensitivity (mJ/cm^2)	52	55
permitted capacity (μm)	0.9	0.9
plasma resistance [relative to poly(MMA)]	1.5	1.5

References and Notes

(1) Rzaev, Z. M.; Gurbanov, K. I.; Mamedova, S. G.; Guseynov, M. M.; Sharifov, G. S. *Vysokomol. Soedin.* **1984**, *A26* (4), 736.
(2) Rzaev, Z. M.; Mamedova, S. G.; Rasulov, N. Sh.; Agaev, U. H. *Vysokomol. Soedin.* **1987**, *A29* (2), 352.
(3) Mamedova, S. G.; Rzaev, Z. M.; Medyakova, L. V.; Rustamov, F. B.; Askerova, N. M. **1987**, *A29* (9), 1922.
(4) Mamedova, S. G.; Mamedov, A. C.; Medyakova, L. V.; Rzaev, Z. M. *Vysokomol. soedin.* **1991**, *A33* (10), 2074.
(5) Mamedova, S. G.; Rzaeva, S. A.; Medyakova, L. V.; Rzaev, Z. M. *Vysokomol. soedin.* **1991**, *A33* (10), 2088.
(6) Watanable, S.; Ichimura, K. J. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, (11), 3261.
(7) Bokov, Yu. S. *Photo-, Electron- and Rentgenorezisty* (*Rus*).; Radio i Svyaz: Moscow, 1982; *Chem. Abstr.* **1982**, *97*, 153878v.
(8) Schwabel, W.; Sotobayashi, H. *Prog. Polym. Sci.* **1993**, *9* (2), 297.
(9) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, England, 1985.
(10) Sugita, K.; Ueno, N. *Prog. Polym. Sci.* **1992**, *17* (3), 319.
(11) Novichkova, L. M.; Dmitrenko, A. V.; Ospanova, K. M.; Rostovskii, E. N. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* **1977**, *27* (1), 86; *Chem. Abstr.* **1977**, *86*, 156057k.
(12) Kratz, E. O.; Novichkova, L. M.; Bandareva, N. S.; Pokrovskii, E. I.; Rostovskii, E. N. *Vysokomol. Soedin.* **1974**, *B16* (2), 105.
(13) Roovers, J.; Smets, G. *Makromol. Chem.* **1963**, *60*, 89.
(14) Sumida, G.; Vogl, O. *Polym. J.* **1981**, *13* (6), 521.
(15) *Analytical Chemistry of Polymers*; Kline, G. M., Ed.; Interscience Publishers: New York, 1962; Part 1, p 609.
(16) Gindin, L.; Medvedev, S.; Fleshler, E. *Zhur. Obsh, Khim.* **1949**, *19* (9), 127; *Chem. Abstr.* **1950**, *44*, 1020a.
(17) Hanna, M. W.; Ashbaugh, A. L. *J. Phys. Chem.* **1964**, *68*, 811.
(18) Kelen, T.; Tüdős, F. *J. Macromol. Sci., Chem.* **1975**, *A9* (1), 1.
(19) Yoshimura, M.; Nogami, T.; Yokoyama, M.; Mikawa, H.; Shirota, Y. *Macromolecules* **1976**, *9*, 211.
(20) Georgiev, G. S.; Zubov, V. P. *Eur. Polym. J.* **1978**, *14* (2), 93.