

Complex-Radical Terpolymerization of Maleic Anhydride (Styrene), Allyl Propionate and Methyl Methacrylate

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Abstract

The radical terpolymerization reactions of the acceptor-donor-acceptor and donor-acceptor-donor systems, maleic anhydride (MA)-allyl propionate (AP)-methyl methacrylate (MMA) and styrene (St)-MMA-AP, had been studied. The terpolymerizations were carried out in methyl ethyl ketone at 60-75°C in the presence of 2,2'-azoisobutyronitrile (ABIN) used as the initiator. Some kinetic parameters and copolymerization constants - for both, system were determined by dilatometric and Kelen-Tudos or Seiner-Lift methods. The obtained results are discussed in terms of the free monomer and complex chain growth models. It is shown that terpolymerization was carried out at a stage close to binary copolymerization of MA...AP complex with free MMA and St...MMA complex with AP in the both studied system, respectively. These systems are also used as model for interpretation of cyclocopolymerization mechanism in allyl methactylate-MA (or St) system. DTA and TGA analyses indicated the relatively high thermal stability of St-MMA-AP terpolymer. It is shown that this terpolymer decomposes through a one-step reaction at 310°C, however MA-AP-MMA terpolymer decomposes through a multi-step reactions at 150, 260 and 310°C.

Introduction

Ternary monomer systems in terms of the conjugation type in monomer molecule and the mechanism of chain growth can be classified by following groups: (a) donor (D_1)-donor (D_2)-donor (D_3), (b) acceptor (A_1)-acceptor (A_2)-acceptor (A_3), (c) donor (D_1)-acceptor (A)-donor (D_2) and (d) acceptor (A_1)-donor (D)-acceptor (A_2). Complex-formation not take placed in the (a) and (b) systems monomers of which have similar type of double bound conjugation. Therefore reaction submitted to usual equations of random copolymerization and differed by complexity in term of the «controlling» by radical reactions of chain growth. However, (c) and (d) monomer systems comprised donor-acceptor monomers which can be presented by two $D...A_1$ and $D...A_2$ complexes for (c) system and $A...D_1$ and $A...D_2$ complexes for (d) system in propagation reactions. Number of elementary chain growth reactions in these ternary systems depended on complex formation and homopolymerization properties of comonomers in given terpolymerization conditions.

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 [1-8].

In several publications some attention has been focused on the study of monomer charge transfer complexes (CTC) effect in radical terpolymerization by using following donor-acceptor ternary systems: maleic anhydride(MA)-styrene(St)-methacrylates [9], MA-St (or trans-stilbene)-N-phenylmaleimide [10,11], MA-St-citraconic anhydride [12], MA-St-vinylacetate [13], MA-trans-stilbene-phenanthrene [11,14], MA-allyl-glycigyl ether-methyl methacrylate [15] and other systems containing MA [5,11]. Similar effects were observed in radical copolymerization of bifunctional monomers (allylcinnamate, monoallylmaleate, N-allylmaleimides, allylmethacrylate and etc.) with MA or St which can by also considered as ternary systems containing three donor-acceptor type double bounds [16-20]. The results of these studies were allowed to discover new aspects of the complex-radical copolymerization mechanism and to synthesize the

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functional terpolymers with given composition, structure and properties.

The objective of present work is to elucidate some regularities of radical terpolymerization of two new A_1 -D- A_2 and D_1 -A- D_2 systems, MA-allyl propionate (AP)-methyl methacrylate (MMA) and St-MMA-AP, and binary copolymerization of MA with AP as well as to use the results obtained for interpretation of mechanism of radical copolymerization of bifunctional monomer such as allyl methacrylate (AMA) with MA and St.

Experimental

Materials

MMA, St and AMA, supplied by Fluka Chem. AG, are distilled before use and have following characteristics: MMA - bp 101°C, d_4^{20} 0.9441, n_D^{20} 1.4143; St - bp 25.5°C/ 5 torr, d_4^{20} 0.9058, n_D^{20} 1.5462; AMA - bp 67°C/6.7 kPa, d_4^{20} 0.9335, n_D^{20} 1.4358. MA (Fluka) is purified by recrystallization twice from benzene followed by sublimation *in vacuo*, mp 52.8°C.

AP is synthesized by esterification of propionic acid with allyl alcohol in benzene in the presence of *p*-toluene sulfonic acid as a catalyst. After distillation in vacuum under N_2 , AP prepared had bp 44.5°C/ 15 torr, d_4^{20} 0.9017, n_D^{20} 1.4158.

2,2-Azobisisobutyronitrile (AIBN) as a initiator was recrystallized from methanol.

Copolymerization

Reactions were carried out in degassed glass tubes or dilatometers at 60-75°C in methylethylketone (MEK) under nitrogen atmosphere in the presence of AIBN as a initiator. After the reaction for a given time, the reaction mixtures prepared were poured into a large amount of *n*-hexane to precipitate the copolymer and the powder-like product obtained was purified by multiple washing in *n*-hexane and in diethyl ether, and was dried under vacuum at 40°C to constant weight. Terpolymers were characterized by nonaqueous potentiometric titration of the free anhydride group in side chain (for MA-AP-MMA terpolymer), by elemental analysis and by FTIR spectroscopy. Composition of terpolymers was also determined by chromatographic analysis of reaction mixture before and after copolymerization for a given time.

The copolymers synthesized by use of an equimolar ratio of initial monomers had following characteristics:

MA-AP-MMA terpolymer - softening point 112-115°C, $[\eta]$ in MEK at 20°C 0.22 dL/g, acid number 352 mg KOH/g. FTIR spectra (film), cm^{-1} : 2865-2940 (ν_{CH} in CH_2 and CH_3 groups), 1860 and 1785 ($\nu_{C=O}$ in anhydride group), 1730 ($\nu_{C=O}$ in ester group), 1465-1385 (δ_{CH} in CH_2 and CH_3), 1160-940 (ν_{C-O-C} in anhydride and ester groups).

St-MMA-AP terpolymer - softening point 118-122°C, $[\eta]$ in MEK at 20°C 0.26 dL/g. FTIR spectra (film), cm^{-1} : 2865-2935 (ν_{CH} in CH_2 and CH_3 groups), 1735 ($\nu_{C=O}$ in ester group), 1605-1590 (ν_{C-C} in aromatic ring), 1470-1385 (δ_{CH} in CH_2 and CH_3), 1150-935 (ν_{C-O-C} in ester groups), 765 (δ_{CH} in monosubstituted benzene), 700 (phenyl group).

Measurements

Fourier transformation IR spectra were recorded with FTIR Nicolet 510 spectrometer in the 4000-400 cm^{-1} range where 30 scans are taken at 4 cm^{-1} resolution.

1H -NMR. spectra were taken with a AC-80 Bruker spectrometer with tetramethylsilane as internal standard and deuterated acetone as solvent at $35 \pm 0.1^\circ C$. For the determination of charge transfer complex (CTC) formation constant (K_c), the 1H -NMR method [21] was used.

Terpolymerization kinetics is studied by dilatometry at the following values of K volumers:

$$K = (1/\rho_m - 1/\rho_c)/l/\rho_m$$

where ρ_m and c are the densities of the initial monomer mixture and copolymers- respectively; $\rho_m = 0.937$ -0.945 g/ cm^3 , $\rho_c = 0.965$ -0.983 g/ cm^3 and $K = 0.029$ -0.038 for monomer mixtures and copolymers, respectively.

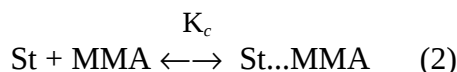
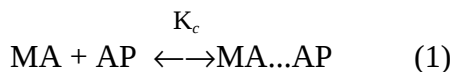
Copolymerization constants (r_1 , r_2 , r_{1c} , r_{1c1} and r_{1c2}) are determined by Kelen-Tüdös [22] and Seiner-Litt [23] methods. Contents of AP and MMA monomers were found by chromatographic analysis (CHROM-5) of monomer mixture before and after reaction at low conversion of $\leq 15\%$; conditions of analysis: column temperature 200°C, evaporator temperature 300°C, absorbent - 10 % Apiezon on Celite-545, internal standard - chlorobenzene, carrier gas - highly purified helium. The yield and composition of the copolymer were found from the quantities of unreacted AP and MMA.

Differential thermal (DTA) and thermogravimetric (TGA) analyses were carried out with a Paulik-Erdy derivatograph in air at a heating rate of 5°C /min.

Results and discussion

Charge Transfer Complex Formation

From the donor-acceptor properties of monomers for ternary systems studied, one can predict that the formation of equimolecular (1 : 1) CTC's as follows:



Equilibrium constants of 1:1 mixtures (K_c) between MA as acceptor monomers and AP as donor monomer were determined using $^1\text{H-NMR}$ spectral data and the well known Hanna-Ashbaugh equation [21]:

$$[\text{MA}] / \Delta_{\text{exp}} = 1 / \Delta_c + 1 / (\Delta_c \cdot K_c) [\text{D}] \quad (3)$$

where Δ_{exp} is the difference between the chemical shifts (free and complexed) of MA protons, Δ_c is the chemical shift of MA protons in the MA/AP mixtures, K_c is the equilibrium constant of a 1:1 complex, $[\text{D}]$ is the concentration of AP monomer. The concentration of the acceptor monomer (MA) was kept constant at 0.1 mol/L while that of the donor was varied. The change chemical shift for anhydride protons ($\delta^f = 6.95$ ppm) with excess of donor monomers ($\Delta_{\text{exp}} = \delta^f - \delta^c$) allows determination of K_c from the relationship of $1/\Delta_{\text{exp}} \rightarrow [\text{D}]$ (Fig. 1). The K_c obtained for MA...AP complex is 0.14 ± 0.01 L/mol. For identification of St...MMA complex known K_c value for St...AMA (allyl methacrylate) [25] complex was used ($K_c = 0.22 \pm 0.02$ L/mol).

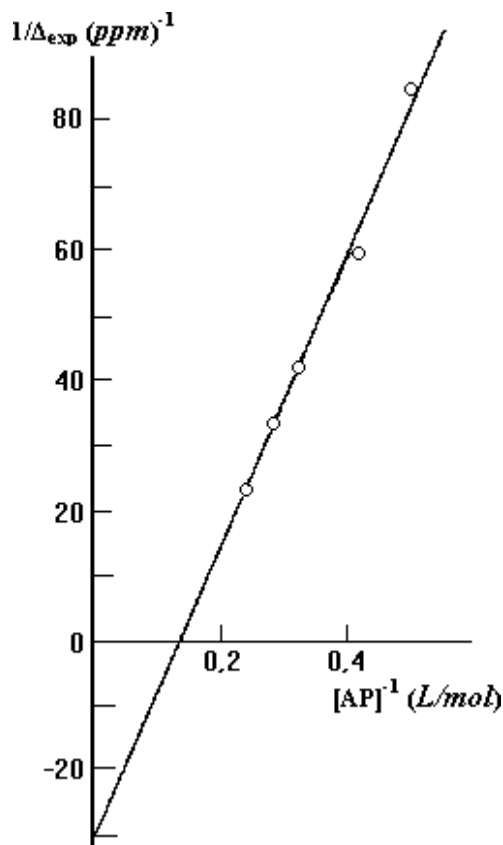


Fig. 1. Graphic determination of K_c constant for MA...AP charge transfer complex. $1/\Delta_c$ is y-axis, $\text{tg}\alpha = 1/\Delta_c K_c$; $1/\Delta_{\text{exp}}$ is the difference between chemical shift of MA protons in $^1\text{H-NMR}$ spectra and those in the mixtures of $[\text{AP}] \gg [\text{MA}]$.

Terpolymerization

Free monomer propagation mechanism

In generally, there are nine types of possible growth reactions that determine the composition of a ternary copolymer product [25]. Consumption rates of monomers are expressed by the following equations:

$$-\frac{d[M_1]}{dt} = k_{11}[m^{\bullet}_1][M_1] + k_{21}[m^{\bullet}_2][M_1] + k_{31}[m^{\bullet}_3][M_1] \quad (4)$$

$$-\frac{d[M_2]}{dt} = k_{22}[m^{\bullet}_2][M_2] + k_{12}[m^{\bullet}_1][M_2] + k_{32}[m^{\bullet}_3][M_2] \quad (5)$$

$$-\frac{d[M_3]}{dt} = k_{33}[m^{\bullet}_3][M_3] + k_{13}[m^{\bullet}_1][M_3] + k_{23}[m^{\bullet}_2][M_3] \quad (6)$$

where $[m^{\bullet}_1]$, $[m^{\bullet}_2]$ and $[m^{\bullet}_3]$ are the concentrations of growing macroradicals derived from M_1 (MA or St), M_2 (AP) and M_3 (MMA) respectively; M 's are the monomer concentrations and k 's are the propagation rate constants.

Since MA (M_1) and AP (M_2) in the MA-AP-MMA

system can not add to their own radicals, and MMA (M_3) is easily added to it own as compared with reaction of $\sim\text{MMA}^{\bullet}$ macroradical which also can not proceed in terpolymerization conditions, the following equations for consumption of monomers can be considered:

$$-\frac{d[M_1]}{dt} = k_{21}[m^{\bullet}_2][M_1] + k_{31}[m^{\bullet}_3][M_1] \quad (7)$$

$$-\frac{d[M_2]}{dt} = k_{12}[m^{\bullet}_1][M_2] + k_{32}[m^{\bullet}_3][M_2] \quad (8)$$

$$-\frac{d[M_3]}{dt} = k_{13}[m^{\bullet}_1][M_3] + k_{23}[m^{\bullet}_2][M_3] \quad (9)$$

The relative terpolymer composition can be derived

from the ratio of Eq. (7) to Eq. (8):

$$-\frac{d[M_1]}{d[M_2]} = \frac{m_1}{m_2} = \frac{k_{21}[m^{\bullet}_2][M_1] + k_{31}[m^{\bullet}_3][M_1]}{k_{12}[m^{\bullet}_1][M_2] + k_{32}[m^{\bullet}_3][M_2]} \quad (10)$$

For the stationary state, we have:

$$k_{21}[m^{\bullet}_2][M_1] = k_{12}[m^{\bullet}_1][M_2] \quad (11)$$

$$k_{23}[m^{\bullet}_2][M_3] = k_{32}[m^{\bullet}_3][M_2] \quad (12)$$

If numerator and denominator in Eq. (10) are divided by $k_{21}[m^{\bullet}_2][M_1]$, one obtains:

$$m_1 / m_2 = 1 / \{1 + (k_{23} / k_{21}) \cdot [M_3] / [M_1]\} \quad (13)$$

Analogously, for the other ratios, the following equations can be derived:

$$m_2 / m_3 = 1 + (k_{21} / k_{23}) \cdot [M_1] / [M_3] \quad (14)$$

$$m_1 / m_3 = (k_{21} / k_{23}) \cdot [M_1] / [M_3] \quad (15)$$

where m_1 , m_2 and m_3 are the instantaneous representation of structural units of monomers in the MA-AP-MMA and St-MMA-AP terpolymers, respectively.

The experimental data on the terpolymerization of both systems are presented in Table 1. It follows from these results that a change made in the content of monomers within a wide range in the initial monomer mixture, low affects the m_1/m_2 ratio in both terpolymers.

From the data of Table 1 and according to equa-

tions (13)-(15), average value of ratio k_{21}/k_{23} for both systems are calculated from the plot of M_1/M_3 vs. m_1/m_3 (Fig. 2) by linear square analysis. The value of k_{21}/k_{23} is calculated as 3.25 for MA-AP-MMA and as 0.28 for St-MMA-AP systems, which indicate that the MA is more reactive than MMA toward the $\sim\text{AP}^{\bullet}$ macroradical and the AP is more 4 times more reactive than St toward the $\sim\text{MMA}^{\bullet}$ macroradical in both systems studied, respectively.

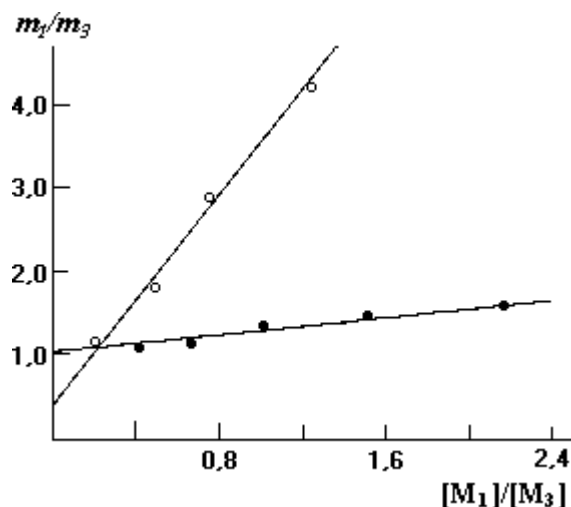


Fig. 2. Plot of m_1 / m_3 (in terpolymer) vs. $[M_1] / [M_3]$ (in monomer feed); $\text{tg}\alpha = k_{21} / k_{23}$.

Table 1

Radical terpolymerization of MA-AP-MMA and St-MMA-AP ternary systems. Reaction conditions:
solvent, MEK; 70°C; initiator, [AIBN] = 0.012 mol/L; [M]_{total} = 2.45 mol/L; conversion ≤ 15 %

Monomer mixture (mol %)			Acid Number (mg KOH/g)	Analysis (%)		Copolymer composition* (mol %)		
[M ₁]	[M ₂]	[M ₃]		C	H	m ₁	m ₂	m ₃
MA - AP - MMA								
15	15	70	361.0	58.87	6.74	35.24	35.75	29.10
25	25	50	398.4	58.73	6.60	39.25	39.62	21.13
30	30	40	329.0	58.63	6.48	42.78	42.94	14.28
40	40	20	442.2	58.67	6.45	44.22	44.73	11.05
50	25	25	416.1	58.72	6.55	41.28	42.34	16.38
15	50	35	346.3	59.68	6.98	44.85	47.36	7.79
25	50	25	352.1	59.64	6.96	45.46	47.85	6.69
35	50	15	362.9	59.46	6.85	47.59	48.24	4.17
St - MMA - AP								
20	30	50	-	72.05	8.46	33.08	34.72	32.20
50	30	20	-	72.08	8.42	33.48	36.87	29.65
15	50	35	-	71.73	8.44	32.17	37.16	30.67
20	50	30	-	72.05	8.41	33.51	37.92	28.57
25	50	25	-	72.64	8.36	35.75	38.34	25.91
30	50	20	-	72.67	8.35	35.95	38.86	25.19
35	50	15	-	72.72	8.33	36.22	39.53	24.25
15	60	25	-	71.67	8.34	32.78	43.21	24.01
25	60	15	-	72.70	8.26	36.66	43.68	19.66

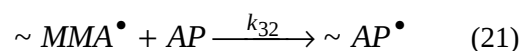
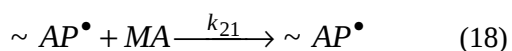
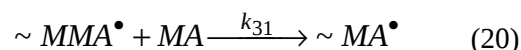
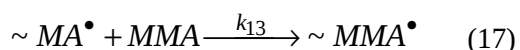
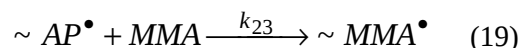
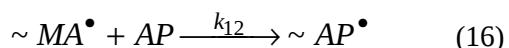
*Calculated for terpolymers with composition of m₁ : m₂ : m₃ = 1 : 1 : 1, AN 414.5 mg KOH/g, C 58.89 % and H 6.79% for MA-AP-MMA terpolymer and C 72.26 % and H 8.49 % for St-MMA-AP terpolymer.

Complex Mechanism

Based on the fact that in the terpolymerization of MA-AP-MMA and St-MMA-AP systems no MA and

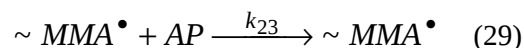
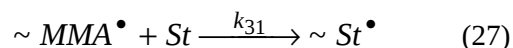
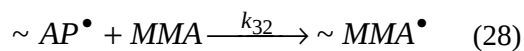
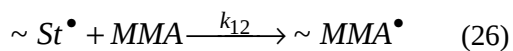
AP homopolymers are produced, St and AP are no copolymerizable pair, MA and AP as well as St and MMA are complexing pairs, the following chain growth reactions can be derived:

For the MA-AP-MMA system





For the St-MMA -AP system



The copolymerization constants for the monomer pair systems studied were calculated using the modified terminal model equation of Kelen-Tüdös (KT) [22], equation (33) and the terminal complex model equation of Seiner-Litt (SL) [23] equation (34):

$$\eta = (r_1 K_c + r_2 / \alpha) \xi - r_2 / \alpha \cdot K_c \quad (33)$$

$$(y - 1) = r_{1c} / r_{1c1} + (r_{1c} / K_c) \chi \quad (34)$$

where $F = M_1 / M_2$, $f = m_1 / m_2$, $\eta = (F^2 / f) / (\alpha + F^2 / f)$, $\xi = [F(f-1) / f] / (\alpha + F^2 / f)$, $y = (1 + r_{12} F) / (1 + r_{21} F^{-1})$, $\alpha = \sqrt{(F^2 / f)_{\min} \cdot (F^2 / f)_{\max}}$,

$\chi = 1/[M_2] \times [1 - (y-1)/r_{12}F]$, $r_{1c} = (r_{1c1} + r_{1c2}) / (r_{1c1} \times r_{1c2})$ for the condition of $k_{1c} = k_{1c1} + k_{1c2}$, K_c is CTC formation constant.

The reactivity ratios of monomers and complexomers of both systems studied were calculated by using of data of Table 2 and 3 and by means of the known equations (33) and (34). In Table 4 are summarized the values of the apparent reactivity ratios for the monomer systems studied. From the values of copolymerization constants it follows that alternating copolymerization reactions occur mainly in the MA-AP, MA-AMA [20] and St-AMA [22] systems.

Table 2

Experimental data used for determination of copolymerization constants for MA...AP(M₁)-MMA(M₂) and St...MMA(M₁)-AP(M₂) pairs.
Reaction conditions as in Table 1.

Monomer mixture (mol %)		Copolymer composition (mol %)		Parameters of KT-equation			
[M ₁]	[M ₂]	m ₁	m ₂	f	F ² /f+α*	η	ξ
MA...AP - MMA							
30	70	70.90	29.10	2.44	0.461	0.546	0.163
50	50	78.87	21.13	3.73	0.694	1.055	0.386
60	40	85.72	14.28	6.00	0.889	1.310	0.566
80	20	92.21	11.45	8.05	2.374	1.475	0.837

Table 2
Continued

St...MMA - AP							
30	70	66.05	33.95	1.95	0.665	0.284	0.153
40	60	67.80	32.20	2.11	0.774	0.452	0.273
50	50	69.33	30.67	2.26	0.986	0.585	0.429
60	40	71.43	28.57	2.50	1.339	0.734	0.579
80	20	74.81	25.19	2.97	3.670	0.878	0.847

Table 3

Experimental data used for determination of copolymerization constants for MA(M₁)-AP(M₂) and MMA(M₁)-AP(M₂) monomer pairs. Reaction conditions as in Table 1.

Monomer mixture (mol %)		AN* (mgKOH/g)	Copolymer composition** (mol %)		Parameters of KT-equation			
[M ₁]	[M ₂]		m ₁	m ₂	F ² / f	F(f-1) / f	η	ξ
MA-AP								
20	80	496.3	50.06	49.94	0.062	0.0006	0.0007	0.071
30	70	497.2	50.96	49.04	0.177	0.016	0.016	0.180
40	60	498.4	51.81	48.19	0.413	0.046	0.041	0.338
50	50	499.8	52.88	47.12	0.891	0.109	0.064	0.524
60	40	501.7	54.34	45.66	1.891	0.239	0.088	0.701
70	30	504.7	56.52	43.48	4.187	0.538	0.108	0.838
80	20	516.0	60.32	39.68	10.526	1.368	0.121	0.929
MMA-AP								
20	80	-	36.33	63.67	0.109	-0.188	-0.263	0.164
30	70	-	49.52	50.48	0.187	-0.008	-0.011	0.252
40	60	-	60.41	39.59	0.291	0.230	0.272	0.344
50	50	-	69.62	30.38	0.436	0.564	0.570	0.440
60	40	-	77.48	22.52	0.654	1.064	0.881	0.541
70	30	-	84.27	15.73	1.016	1.897	1.034	0.554
80	20	-	85.02	14.98	2.819	3.295	1.388	1.188

* Calculated for alternating copolymer with 1 : 1 composition: AN 495.9 mg KOH/g.

** Compositions of MMA-AP copolymer are calculated by using of chromatographical analysis data of monomer mixtures before and after reaction.

The reactivity ratios of MA and AP pair also were calculated by means of the Seiner-Litt equation (34). From the plot of $(\gamma-1)$ vs. χ (Fig 3) were determined following values of the apparent reactivity ratios: $r_{1c}=0.025$, $r_{1cl}=0.49$ and $r_{1c2}=0.51$. These values obtained by taking into consideration the K_c on the

relative activity of the monomers, confirm the fact that chain growth proceeds primary by addition of MA...AP complex to growing macroradicals.

In the MA-AP-MMA and St-MMA-AP ternary systems studied, binary copolymerization reactions realize in result of which terpolymers formed primary

contain m_1 and m_2 units with ratios near to 1 : 1. This fact observed also is confirmed the effect of complex-formation in ternary copolymerization reactions. In Table 4 are summarized the values of copolymerization constants for MA...AP-MMA and St...MMA-AP pairs. It follows from these values in the St-MMA-AP system as compared with MA-AP-MMA system that near to an alternating terpolymerization reaction occurs.

Table 4

The copolymerization constants for free and complexed monomer pairs of MA-AP-MMA and St-MMA-AP systems

Monomer Pairs	r_1 ($r_1 \times K_c$)*	r_2 (r_2 / K_c)*	$r_1 \times r_2$
MA-AP	0.14 ± 0.01	0.007 ± 0.001	9.8×10^{-4}
MMA-AP	2.4 ± 0.15	0.38 ± 0.025	0.912
MA...AP-M- MA	0.92 ± 0.05 (0.13)	0.17 ± 0.01 (1.21)	0.156
St...MMA-- AP	0.64 ± 0.02 (0.14)	0.11 ± 0.01 (0.50)	0.070
St-MMA [24]	0.50 ± 0.05	0.44 ± 0.05	0.220
MA-AMA [20]	0.028 ± 0.001	0.063 ± 0.005	1.76×10^{-3}
St - AMA [26]	0.105 ± 0.01	0.011 ± 0.001	1.1×10^{-3}

*The following known values of K_c are used: 0.11 L/mol for MA...AMA²⁰ and 0.22 L/mol for St...MMA or St...AMA²⁵ complexes.

FTIR spectra of AP monomer, MA-AP-MMA and St-MMA-AP terpolymers synthesized are illustrated in Fig. 4. A comparative analysis of monomer and terpolymers spectra revealed that the characteristic bands for C=C ($1680-1630\text{ cm}^{-1}$) and allyl group ($3100-3030, 990\text{ cm}^{-1}$) of AP are disappeared by the transfer from monomer form to terpolymer molecule. The changes observed as well as the presence of characteristic bands for anhydride, phenyl and ester groups allow qualitatively to identify of terpolymer compositions.

As evidence from the kinetic data (Fig. 5a) the copolymerization rate of MA-AP-MMA at 0.8-2.45 mol/L total monomer concentration is more than the rate of St-MMA-AP system: R_p are $0.43-1.07 \cdot 10^{-6}\text{ mol/L}\cdot\text{s}$ and $0.2-0.71 \cdot 10^{-6}\text{ mol/L}\cdot\text{s}$ for two ternary systems, respectively. On the other hand, the copolymerization rate of model systems, reaction of

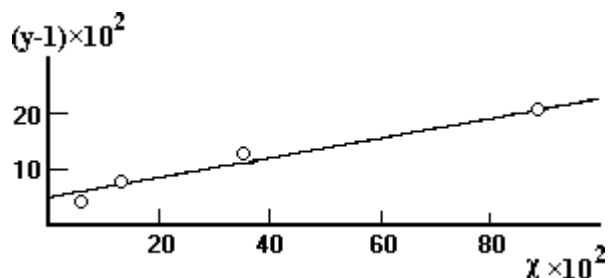


Fig. 3. Seiner-Lift plot for the copolymerization of MA with AP; $\text{tg}\alpha = r_{1c} / K_c$ and intercept $-r_{1c} / r_{1cl}$.

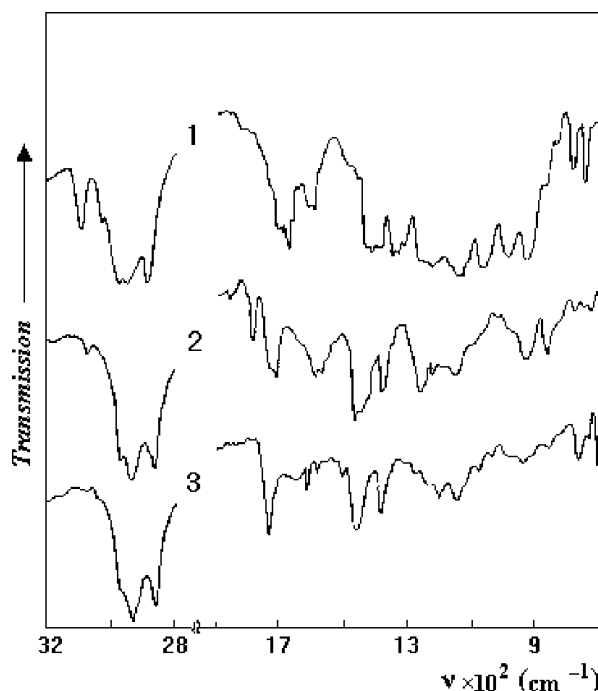


Fig. 4. FTIR spectra of AP monomer (1), MA-AP-MMA (2) and St-MMA-AP (3) terpolymers.

bifunctional monomer AMA with MA ($R_p = 0.18 \cdot 10^{-5}\text{ mol/L}\cdot\text{s}$) and with St ($R_p = 0.11 \cdot 10^{-5}\text{ mol/L}\cdot\text{s}$), is more than copolymerization rate of ternary systems studied (Fig. 5b). This fact observed allows one to conclude that the allyl and methacryl double bounds show high reactivity when they are belonged to the same monomer (AMA) as compared with ternary systems in which these double bounds belongs to different monomers (AP and MMA).

Using the kinetic data of terpolymerization of both ternary systems studied (Fig. 6a) with constant concentrations of monomers and initiator at different temperatures ($60-75^\circ\text{C}$) as well as data of Arrhenius plots for copolymerizations of AMA with MA and St (Fig. 6b), the overall activation energy (E_a) determined as: 86.2 and 92.1 kJ/mol for MA-AP-MMA and St-

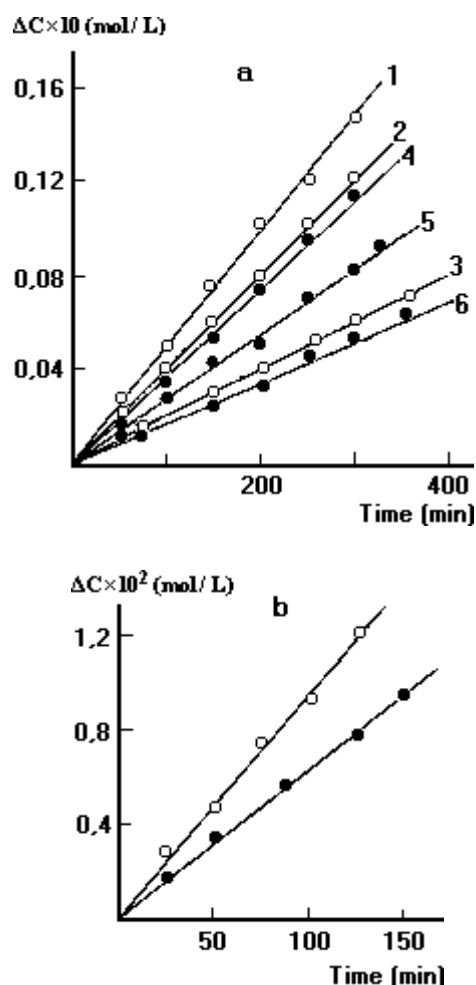


Fig. 5. Kinetic curves of copolymerization for (a) MA-AP-MMA ($\circ$ -, 1-3) and St-MMA-AP ($\bullet$ -, 4-6) ternary and for (V) AMA-MA ($\circ$ -) and AMA-St ($\bullet$ -) binary systems. Reaction conditions: $[M]_{\text{total}} = 0.8$ (3 and 6), 1.5 (2 and b, $\circ$ - and $\bullet$ -), 2.45 mol/L (1 and 4); monomer ratio of $[M_1] : [M_2] : [M_3] - 1 : 1 : 1$ (a), $[M_1] : [M_2] = 1 : 1$ (b); 65°C.

MMA-AP ternary systems, respectively; 68.7 and 62.4 kJ/mol for AMA-MA and AMA-St monomer pairs, respectively. The comparative low values of E_a for binary systems can be explained by changes of mechanism of chain growth and initiation reactions with participation of CTC's in the cyclic and linear chain growth reactions leading to energetically advantageous position. These values also indicate that allyl degradative chain transfer does not take part in binary and ternary systems studied because of complex formation.

Thermal Stability of Terpolymers

Thermostability of terpolymers synthesized is studied by thermogravimetric (TGA) and differential ther-

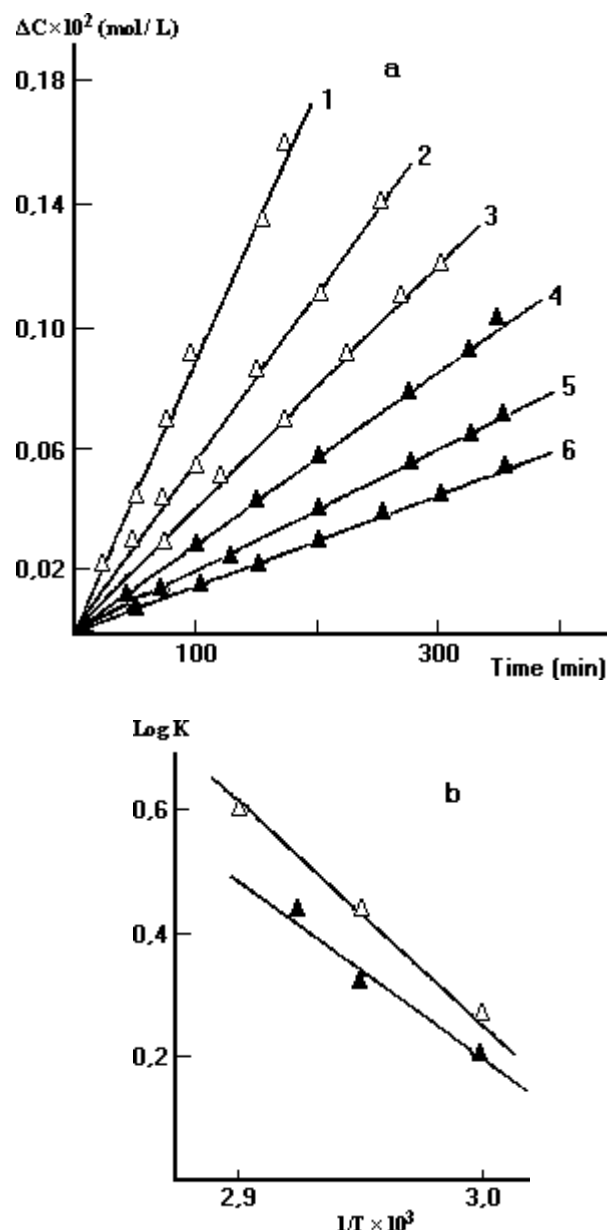


Fig. 6. Kinetic curves of terpolymerization for (a) MA-AP-MMA (Δ -, 1-3) and St-MMA-AP (Δ -, 4-6) systems at different temperature of 75 (1), 70 (2 and 4), 65 (3 and 5) and 60°C (6) and $[M]_{\text{total}} = 1.5$ mol/L; (b) - Arrhenius plot of Log K vs. $1/T$ for copolymerization of AMA-MA (Δ -) and AMA-St (Δ -) binary systems.

mal (DTA) analysis methods. These analyses were carried out in air from ambient temperature up to 500°C. The results obtained are illustrated in Fig. 7. These data show that St-MMA-AP terpolymer with composition of $m_1 : m_2 : m_3 = 35.8 : 38.3 : 25.9$ preparing at initial monomer ratio of 1 : 2 : 1 have higher thermal stability (curve 1) than the MA-AP-MMA terpolymer preparing in the analogous conditions. The weight loss till 200°C is 5.2 %, but at 300°C it is

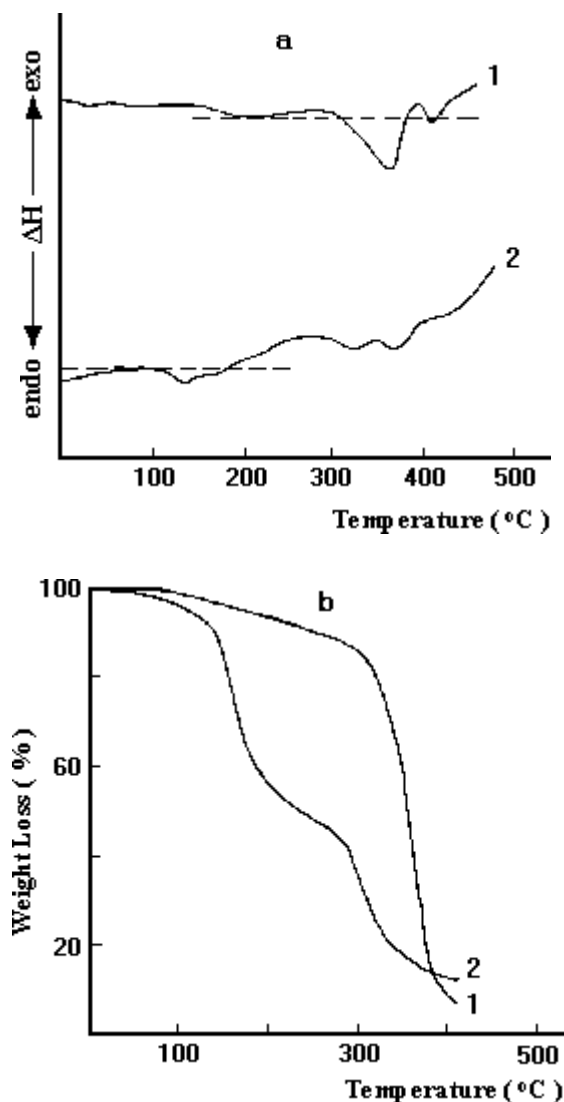


Fig. 7. DTA (a) and TGA (b) curves of St-MMA-AP (1) and MA-AP-MMA (2) terpolymers at heating rate of 5°C/min in air atmosphere.

equal to 10.5 %. The degradation point (beginning of degradation) of St-MMA-AP terpolymer is 295°C, and it loses almost 50 % of its weight at 350°C. From character of TGA curve of St-MMA-AP terpolymer it is evident that terpolymer decomposes through a one-step reaction at 310°C.

MA-AP-MMA terpolymer with composition of 45.5 : 47.8 : 6.7 shows relatively low thermal stability. The weight loss begin from 140°C and at 250°C it is equal to more 50 %. Unlike St-containing terpolymer this terpolymer decomposes through a multi-step reactions at 150, 260 and 310°C, respectively (curve 2) which can be explained by degradation processes of macromolecules associated with decarboxylation, breaking of methacrylic fragments and side-chain groups as well as chain cleavage.

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