

COMPOSITION AND STRUCTURE OF COPOLYMERS OF ALLYL(METH)ACRYLATES WITH N-PHENYLMALEIMIDE

L.V. Medyakova, E.A. Ibadov

Institute of Polymer Materials of Azerbaijan National Academy of Sciences, AZ5004,

Sumgayit, S.Vurgun Str., 124

e-mail: ipoma@science.az

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The copolymers of allyl(meth)acrylates with N-phenylmaleimide have been synthesized by a method of radical copolymerization in solution from reaction mixtures of various composition in small yields ($\leq 10-15\%$). It has been established by the chemical and IR-spectroscopic methods of analyses that the synthesized copolymers are the products of alternating structure, the macromolecules of which consist of links of cyclic and linear structure containing unreacted C = C bond of allyl and acryl type. The copolymerization constants, cyclization constants and activation energy of the cyclization reaction in formation of copolymer of allylmethacrylate-N-phenylmaleimide have been determined

Key words: *radical copolymerization, allyl(meth)acrylates, N-phenylmaleimide, unsaturation, cyclization, alternation, microstructure*

It was known that the multifunctional monomers of acryl series due to high activity in the formation reactions of polymers found a wide industrial application in various branches of technique. However, the bifunctional monomers containing two polymerizable groups of the same of various nature have been comparatively little studied, except the known Batler works [1, 3], and, undoubtedly, are of interest as the objects of fundamental investigations and also as the monomers for preparation of perspective polyfunctional reactive homo- and copolymers with valuable practical properties [4-6].

Continuing own investigations in the field of the radical copolymerization of bifunctional derivatives of unsaturated mono- and dicarboxylic acids [7-9], in this work the allyl ethers of (meth)acrylic acid and N-phenylmaleimide were used as the objects of investigations.

Purpose – synthesis of new polyfunctional, unsaturated alternating copolymers, study of their composition, structure and microstructure, determination of copolymerization, cyclization constants and activation energy of the cyclization reaction.

EXPERIMENTAL

Allyl(meth)acrylates (A(M)A) were synthesized by etherification reaction of acryl(meth)acrylic acid by allyl alcohol in the presence of p-toluenesulfoacid and purified by twofold distillation in vacuum in nitrogen atmosphere: B.p. 47°C/0.533 kPa, n_D^{20} 1.4320, d_4^{20} 0.9441 (AA); B.p. 67°C/6.66 kPa, n_D^{20} 1.4358, d_4^{20} 0.9335 (AMA).

N-phenylmaleimide (PMI) was purified by recrystallization from unsaturated solution in chloroform and subsequent sublimation in weak vacuum: m.p. 89°C.

Trans-stilbene (Stb) was purified by recrystallization from unsaturated solution in ethanol: m.p. 124°C.

The compositions of copolymers have been determined by elemental analysis, according to the data of IR-spectra, chromatography and determination of unsaturation.

The total unsaturation, including C = C bond of alkyl and allyl character has been determined by Knopp method [10], allyl – on method [11], vinyl(acryl) – on difference between total and allyl unsaturation.

RESULTS AND DISCUSSION

The copolymerization conditions of AA and AMA with PMI and the prepared results are presented in Table 1,2 it is seen from data that a change of composition of the initial reaction mixture in the ranges of $[M_1]_0 / [M_2]_0 = 0.43-2.33$ is weakly reflected on the compositions of copolymers, which are close to equimolar ratio of comonomers links in macromolecules. The experimental data have been treated on known Kelen-Tudosh equation [12], from graphical dependence of parameters of which (fig. 1, 2) the copolymerization constant values have been determined: $r_1 = 0.090$, $r_2 = 0.032$ (AA–PMI) and $r_1 = 0.040$, $r_2 = 0.074$ (AMA–PMI).

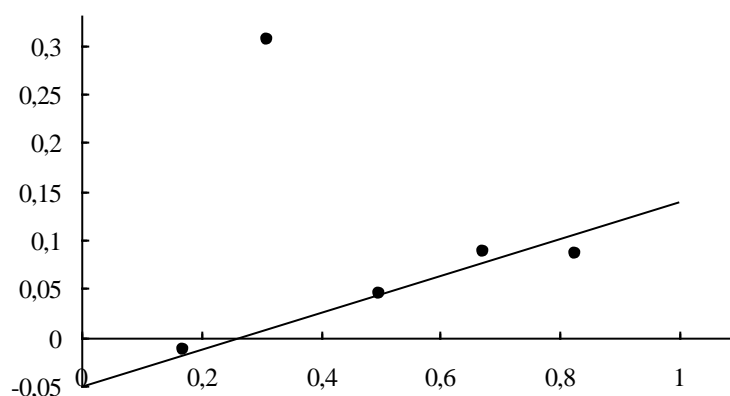


Fig. 1. Dependence of parameters of Kelen-Tudosh equation ($\eta - \xi$) for determination of copolymerization constants of AA with PMI

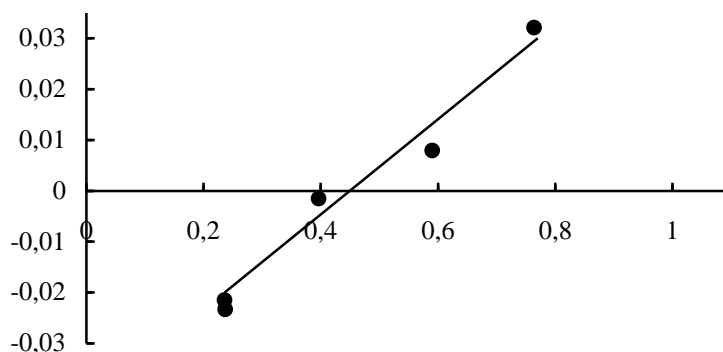


Fig. 2. Dependence of parameters of Kelen-Tudosh equation for determination of copolymerization constants of AMA with PMI

Table 1. Data of copolymerization of AA and AMA with PMI: copolymerization conditions: solvent – MEK, initiator – AIBN ($3.1 \cdot 10^{-3}$ mol/l), $[M]_{\text{sum.}} = 1.7$ mol/l, 60°C , yield $\leq 10\text{-}15\%$

Composition of initial reaction mixture, mol.%		N, %	Copolymer composition, mol.%		Parameters of Kelen-Tudosh equation*	
$[M_1]_0$	$[M_2]_0$		$[m_1]$	$[m_2]$	η	ξ
AA-PMI						
70	30	4.38	55.4	44.6	0.086	0.826
60	40	4.47	54.5	45.5	0.088	0.671
50	50	4.70	52.1	47.9	0.044	0.499
40	60	4.75	51.6	48.4	0.0306	0.311
30	70	4.95	49.2	50.8	-0.013	0.170
AMA-PMI						
70	30	4.47	52.5	47.8	0.032	0.764
60	40	4.63	50.5	49.5	0.008	0.590
50	50	4.69	49.9	50.1	-0.0015	0.396
40	60	4.84	48.3	51.7	-0.023	0.237
30	70	4.90	47.6	52.4	-0.0215	0.235

$$* \eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha; \xi = \frac{F^2/f}{\alpha + F^2/f}; \eta = \frac{F(f-1)/f}{\alpha + F^2/f}; \alpha = \sqrt{(F^2/f)_{\min} \cdot (F^2/f)_{\max}}; \alpha = 0.911 \text{ (AA-PMI),}$$

0.529 (AMA-PMI)

In the IR-spectra of poly-AMA and copolymers AMA-PMI along with absorption band at 1725 cm^{-1} ($\nu_{\text{C=O}}$ in ester group), it is appeared a peak at 1755 cm^{-1} , characterizing $\nu_{\text{C=O}}$ in γ - and δ -lactones.

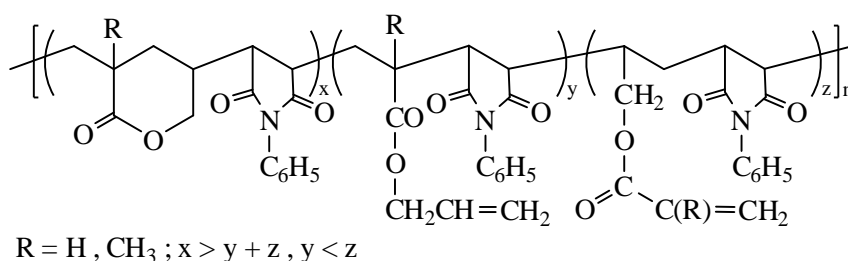
The absorption bands of deformation vibrations at 815 cm^{-1} ($\delta_{\text{=CH}}^{\text{BIII}}$ in $\text{CH}_2 = \text{CH} -$) and at 980 cm^{-1} ($\delta_{\text{=CH}}^{\text{BIII}}$ in $-\text{CH}_2\text{CH} = \text{CH}_2$) observing in the IR-spectra of copolymers AMA with PMI in considerably larger intensity of peak at 815 cm^{-1} indicate to advantageous participation of allyl C = C bond in the chain growth reactions.

It follows from experimental data presented in Table 2 that the unsaturation of the synthesized copolymers has been stipulated by two types of multiple bonds, from which a larger contribution belongs to acryl C = C bonds. For quantitative determination of allyl and acryl multiple bonds it has been used their various capacity to the addition reaction of bromine [10].

Table 2. Content of structural links in copolymers of A(M)A-PMI prepared from reaction mixtures of various composition

Composition of initial reaction mixture, mol. %		Molar fractions of structural links in copolymers (f)			
[M ₁] ₀	[M ₂] ₀	f _A	F _V	F _L	F _C
AA-PMI					
70	30	0.062	0.084	0.146	0.854
50	50	0.057	0.100	0.154	0.843
30	70	0.052	0.119	0.179	0.829
AMA-PMI					
70	30	0.059	0.092	0.151	0.849
50	50	0.051	0.113	0.164	0.836
30	70	0.043	0.124	0.167	0.833

A considerable decrease of the unsaturation of copolymers A(M)A with PMI (Table 2), in comparison with theoretical for hypothetical uncyclized alternating copolymer, in combination with data of IR-spectra indicate to formation of cyclic structural links (γ - and δ -lactones) at the stage of chain growth of macromolecules of the cycloliner structure:



The synthesized copolymers A(M)A with PMI have sufficiently close microstructures about which the found values f_A , f_B and f_C evidence.

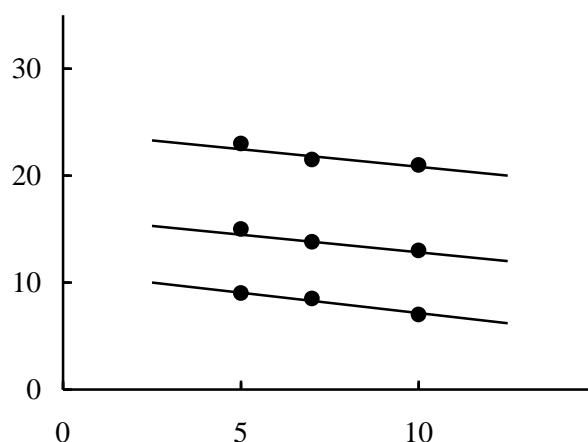


Fig. 3. Dependence of content of uncyclized links (f_L) in copolymer of AMA-PMI on yield and temperature: 1 – 50°, 2 – 60°, 3 – 70°C

In fig.3 the dependence of content of the linear links in copolymer AMA-PMI on temperature and yield is presented. It is seen that at low yields (5-10%) the values f_L and f_C are insignificantly changed but to the side of increasing of f_C , and at temperature rise from 50 to 70°C a content growth of the cyclic structural links in macromolecules of copolymer is observed.

The cyclization constants being relation of rate constants of the monomolecular cyclization reaction to the bimolecular reaction of chain growth ($K_C = K_M/K_B$) were determined according to the known equation $K_C = [M]f_C/(1-f_C)$ in the range of temperatures of 50-70°C at constant total concentration of comonomers equal to 1.5 mol/l, in the compositions of the reaction mixtures [AMA]/[PMI] = 50:50 (mol %) and yields $\leq 10\%$.

Table 3. Cyclization constant values at temperatures 50, 60 and 70°C

Temperature, °C	F_C , mol.f.	F_L , mol.f.	K_C , mol.f
50	0.805	0.195	6.19
60	0.836	0.164	7.65
70	0.842	0.157	8.05

From Arrhenius dependence $\lg K_C$ from $1/T$ (fig. 4) the value of activation energy of the cyclization reaction at copolymerization of AMA with PMI equal to 28.67 kJ/mol has been determined. For system AA-PMI this value was 28.89 kJ/mol.

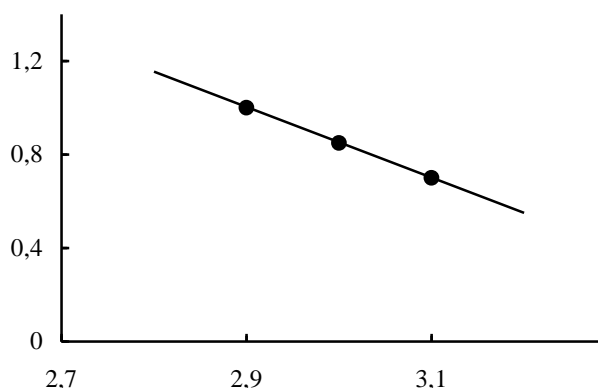


Fig. 4. Dependence of uncyclized constant (K_C) on inverse temperature ($1/T$) for determination of activation energy of cyclization at copolymerization of AMA with PMI

The close values of activation energies of the cyclization reaction in the investigated polymerization systems allows to assume the same mechanism of cycloformation by intramolecular attack of uncyclized acryl(meth)acryl radical for allyl multiple bond.

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