

REACTIVITY AND POLYMERIZATION ABILITY
OF STYRYLQUINOLINE CONTAINING METHACRYLIC MONOMERS*Oksana Kharchenko^{1, *}, Vitaliy Smokal¹, Oksana Krupka¹, Aleksey Kolendo¹*<https://doi.org/10.23939/chcht12.01.047>

Abstract. Novel styrylquinoline methacrylic monomers and their copolymers with methylmethacrylate (MMA) are presented. The polymerization was carried out in DMF with AIBN as initiator. The products of polymerization were characterized by ¹H NMR. The monomer reactivity ratios for the homogeneous free-radical copolymerization of styrylquinoline monomers and MMA were determined from ¹H NMR spectroscopy data and estimated with the Fineman-Ross (FR) and calculation methods.

Keywords: 8-methacryloyloxy styrylquinoline, Fineman-Ross method, monomer reactivity ratio, free radical polymerization.

1. Introduction

In the recent years, the development of modern technologies enables one to create polymer materials with a number of properties which would be impossible to realize in a single polymer. The side chain methacrylic polymers with different active functional group have been well studied and widely applied in many fields, such as: optoelectronics, nonlinear optics, optical storage materials, biochemicals and medicine. Thus, creation of these polymers is one of topical problems of modern polymer chemistry. Photopolymers are studied for their macromolecular properties and for the properties of the photosensitive group. Among them, polymers having photochromic dyes, such as azo, cinnamoyls, chalcones, coumarins, spirooxazines, diarylethenes, *etc.*, represent an active field of research in polymer science because of their technological applications in the fields of photolithography, nonlinear optical materials, liquid crystalline materials, and holographic elements [1-5].

The styryl dyes with quinoline nucleus were applied to various sensitive materials such as sensitizers or desensitizers formerly. With the development of new technologies, the researchers have found a new application of styrylquinoline dyes to electroluminescence

[6] and photochromism [7, 8] as well as in the field of medication [9-13].

The copolymer composition and comonomers units distribution depend on monomer reactivity ratios. The most common mathematical model of copolymerization is based on finding the relationship between the composition of copolymers and the composition of the monomer feed, in which the monomer-reactivity ratios are the parameters to be determined [14]. The calculation of the monomer-reactivity ratios requires the mathematical treatment of experimental data on the composition of copolymers and monomer in feed mixtures. The most fundamental value characterizing a copolymer is its composition on a molar basis, which is eventually used for the determination of the relevant monomer reactivity ratios. Spectroscopic methods, preferably ¹H NMR spectroscopy, and elemental analysis are probably the most widely used methods for the analysis of copolymers and the determination of reactivity ratios.

The objective of this work is to investigate the polymerization ability and reactivity ratios of 8-methacryloyloxy styrylquinoline. This paper describes synthesis of polymers by free radical homo- and copolymerization of 8-methacryloyloxy styrylquinoline with MMA initiated by AIBN.

2. Experimental

2.1. Materials

MMA, ethanol, methanol, *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), were distilled before use [15], methacryloyl chloride, azobisisobutyronitrile (AIBN) and 2-methylquinolin-8-ol were used without further purification.

2.2. Measurements

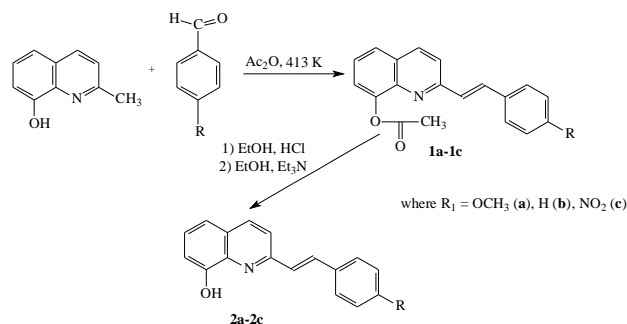
¹H NMR spectra were obtained on a “Mercury” 400MHz Bruker, using CDCl₃, DMSO-d₆ as the solvents and tetramethylsilane as an internal standard. Infrared spectra were recorded on Perkin Elmer BX with KBr.

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2.3. Synthesis of 2-Styrylquinoline-8-ol Derivatives



Scheme 1. Synthesis of 2-styrylquinoline-8-ol derivatives

2-[2-(4-methoxyphenyl)quinolin-8-yl acetate (1a). A flask was charged with a mixture of 8-hydroxy-2-methylquinoline (3.02 g, 18.99 mmol), 4-methoxybenzaldehyde (5.2 g, 38.29 mmol) and acetic anhydride (20 ml). It was refluxed and heated at 413 K for 14 h (TCL monitoring). To the cooled reaction mixture ice-cold water was added. The precipitated product, which appeared upon dilution with ice/water mixture, was filtered off, washed several times with water, dried and crystallized from ethanol, yield 58 %. Mp 397–398 K. $^1\text{H NMR}$ (400 Hz, DMSO- d_6), δ , ppm: 2.53 (s, 3H, $-\text{CH}_3$), 3.81 (s, 3H, $-\text{OCH}_3$), 6.85 (d, 2H, Ar-H), 7.52 (m, 2H, Ar-H), 7.15 (d, 1H, $-\text{CH}=\text{}$), 7.56 (m, 1H, $-\text{CH}=\text{}$), 7.15 (d, 1H, Het), 7.38 (t, 1H, Het), 7.47 (m, 1H, Het), 7.54 (m, 1H, Het), 7.96 (d, 1H, Het).

2-(2-(4-phenylethenyl)quinolin-8-yl acetate (1b) The same procedure as for **1a** was used for benzaldehyde. The solid residue was recrystallized from ethanol to give **1b** yield 76 %. Mp 386–387 K. $^1\text{H NMR}$ (400 Hz, DMSO- d_6), δ , ppm: 2.51 (s, 3H, $-\text{CH}_3$), 7.32 (m, 1H, Het), 7.36 (m, 1H, Het), 7.40 (m, 2H, Ar-H), 7.42 (m, 1H, $-\text{CH}=\text{}$), 7.50 (m, 1H, Ar-H), 7.68 (m, 2H, Ar-H), 7.74 (m, 1H, $-\text{CH}=\text{}$), 7.78 (m, 1H, Het), 7.83 (d, 1H, Het), 8.31 (d, 1H, Het).

2-[2-(4-nitrophenyl)ethenyl]quinolin-8-yl acetate (1c). The same procedure as for **1a** was used for 4-nitrobenzaldehyde. The solid residue was recrystallized from ethanol to give **1c** yield 92 %. Mp 444–445 K. $^1\text{H NMR}$ (400 Hz, DMSO- d_6), δ , ppm: 2.14 (s, 3H, $-\text{CH}_3$), 7.43 (d, 1H, Het), 7.54 (t, 1H, Het), 7.63 (d, 1H, $-\text{CH}=\text{}$), 7.79 (d, 1H, Het), 7.85 (m, 1H, $-\text{CH}=\text{}$), 7.89 (m, 1H, Het), 7.95 (m, 2H, Ar-H), 8.25 (m, 2H, Ar-H), 8.36 (m, 1H, Het).

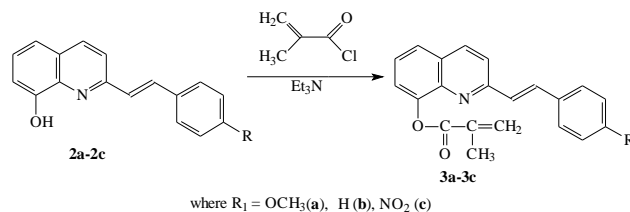
2-[2-(4-methoxyphenyl)ethenyl]quinolin-8-ol (2a). The solution of **1a** (3.5 g, 11.07 mmol) in ethanol (100 ml) and concentrated hydrochloric acid (20 ml) was refluxed for 2 h. The orange precipitate was filtered and washed thoroughly with water. It was subsequently dissolved in ethanol (50 ml) and triethylamine (17 ml)

was added and stirred at room temperature for 1 h. The ice-cool water was added and the precipitate was filtered, washed with water and dried to afford **2a** as a bright yellow powder. It was purified by recrystallization from ethanol. Yellow crystals, yield 86 %. Mp 388 K. $^1\text{H NMR}$ (400 Hz, DMSO- d_6), δ , ppm: 3.83 (s, 3H, $-\text{OCH}_3$), 6.95 (d, 2H, Ar-H), 7.62 (d, 2H, Ar-H); 7.26 (d, 1H, $-\text{CH}=\text{}$), 8.00 (d, 1H, $-\text{CH}=\text{}$), 7.03 (d, 1H, Het), 7.22 (m, 1H, Het), 7.34 (t, 1H, Het), 7.67 (d, 1H, Het), 8.16 (d, 1H, Het). 9.11 (s, 1H, $-\text{OH}$);

2-(2-(4-phenylethenyl)quinolin-8-ol (2b). The same procedure as for **2a** was used. Yellow crystals, yield 94 %. Mp 378 K. $^1\text{H NMR}$ (400 Hz, DMSO- d_6), δ , ppm: 7.03 (d, 1H, Het), 7.27 (m, 1H, Het), 7.30–7.34 (m, 2H, Ar-H), 7.38 (m, 1H, Ar-H), 7.41 (m, 1H, $-\text{CH}=\text{}$), 7.42 (m, 1H, Het), 7.67–7.70 (m, 2H, Ar-H), 7.72 (m, 1H, Het), 8.07 (d, 1H, $-\text{CH}=\text{}$), 8.20 (d, 1H, Het), 9.17 (s, 1H, $-\text{OH}$).

2-[2-(4-nitrophenyl)ethenyl]quinolin-8-ol (2c). The same procedure as for **2a** was used. Yellow-orange crystals, yield 87 %. Mp 473 K. $^1\text{H NMR}$ (400 Hz, DMSO- d_6), δ , ppm: 7.05 (d, 1H, Het), 7.29 (d, 1H, Het), 7.36 (t, 1H, Het), 7.65 (d, 1H, $-\text{CH}=\text{}$), 7.73 (d, 1H, Het), 7.92 (d, 2H, Ar-H), 8.21 (m, 2H, Ar-H), 8.25 (m, 1H, $-\text{CH}=\text{}$), 8.28 (m, 1H, Het), 9.25 (s, 1H, $-\text{OH}$).

2.4. Synthesis of 8-Methacryloyloxy Styrylquinolines (MASTQ)



Scheme 2. Synthesis of 8-methacryloyloxy styrylquinolines

2-[2-(4-methoxyphenyl)ethenyl]quinolin-8-yl 2-methylpropyl-2-enoate (3a). A substance of **2a** (2.6 g, 9.3 mmol) was dissolved in THF (10 ml) and triethylamine (1.48 ml) was added. The solution was kept in an ice bath. The methacryloyl chloride (1 ml, 9.3 mmol) was added slowly to the reaction mixture. After the addition of methacryloyl chloride, solution was stirred for 4 h in an ice bath and then poured into ice-cool water. The light-yellow powder was collected by filtration, washed with water and dried. The product was recrystallized from toluene, yield 51 %, Mp 366 K. $^1\text{H NMR}$ (400 Hz, DMSO- d_6), δ , ppm: 2.21 (s, 3H, $-\text{CH}_3$), 3.82 (s, 3H, $-\text{OCH}_3$), 6.50 (s, 1H, $\text{CH}_2=\text{}$), 5.95 (s, 1H, $\text{CH}_2=\text{}$), 6.91 (d, 2H, Ar-H), 7.54 (m, 2H, Ar-H), 7.49 (m, 1H, $-\text{CH}=\text{}$), 7.69 (m, 1H, $-\text{CH}=\text{}$), 7.15 (d, 1H, Het), 7.45 (m, 1H, Het), 7.66 (m, 1H, Het), 7.76 (d, 1H, Het), 8.25 (d, 1H, Het). IR (cm^{-1} , the most characteristic bands): 1727, 1590, 1557, 1312, 976.

Table 1

The F-R parameters of the free radical copolymerization of **3a** and MMA

Sample number	$f = M_1/M_2$	$F = m_1/m_2$	$f^2/(1-f)^2 \cdot (1-F)/F$	$f(1-2F)/(1-f)F$
1	0.25	0.33	0.2256	0.3434
2	0.33	0.39	0.3794	0.2778
3	0.50	0.49	1.0408	0.0408
4	0.67	0.58	2.7287	-0.5355
5	0.75	0.64	5.0625	-1.3125

Notes: M_1 is mole fraction of **3a** in reaction mixture; M_2 is mole fraction of MMA in reaction mixture; m_1 is mole fraction of **3a** in copolymer; m_2 is mole fraction of MMA in copolymer.

Table 2

The F-R parameters of the free radical copolymerization of **3b** and MMA

Sample number	$f = M_1/M_2$	$F = m_1/m_2$	$f^2/(1-f)^2 \cdot (1-F)/F$	$f(1-2F)/(1-f)F$
1	0.25	0.29	0.2720	0.4828
2	0.33	0.35	0.4505	0.4222
3	0.5	0.45	1.2222	0.2222
4	0.67	0.54	3.2099	-0.2876
5	0.75	0.60	6.0000	-1.0000

Notes: M_1 is mole fraction of **3b** in reaction mixture; M_2 is mole fraction of MMA in reaction mixture; m_1 is mole fraction of **3b** in copolymer; m_2 is mole fraction of MMA in copolymer.

Table 3

The F-R parameters of the free radical copolymerization of **3c** and MMA

Sample number	$f = M_1/M_2$	$F = m_1/m_2$	$f^2/(1-f)^2 \cdot (1-F)/F$	$f(1-2F)/(1-f)F$
1	0.25	0.32	0.2361	0.3750
2	0.33	0.38	0.3958	0.3111
3	0.50	0.48	1.0833	0.0833
4	0.67	0.57	2.7852	-0.5064

Notes: M_1 is mole fraction of **3c** in reaction mixture; M_2 is mole fraction of MMA in reaction mixture; m_1 is mole fraction of **3c** in copolymer; m_2 is mole fraction of MMA in copolymer.

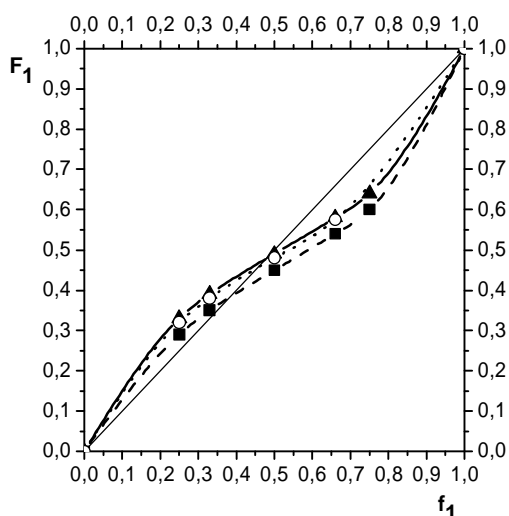


Fig. 1. Composition diagrams of the free radical copolymerization of **3a** (\blacktriangle); **3b** (\blacktriangledown) and **3c** (\bullet) with MMA

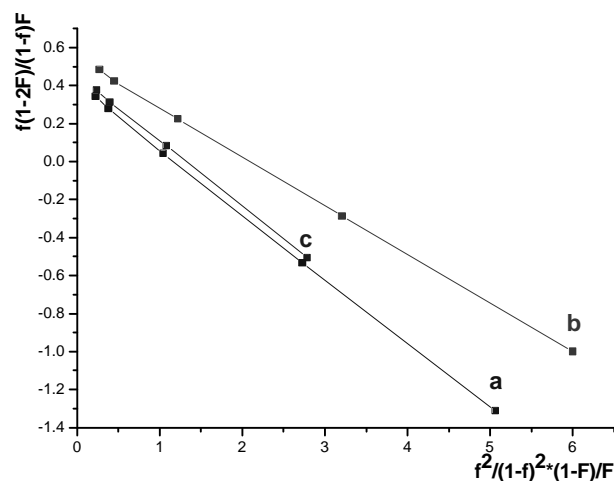


Fig. 2. Fineman-Ross plots for the free-radical copolymerization of **3a** (a), **3b** (b), **3c** (c) with MMA

Table 4

Monomer reactivity ratios and copolymerization parameters for MASTQ (M₁) with MMA (M₂)

MASTQ	Fineman-Ross method		Calculation method		$r_1 \cdot r_2$	$1/r_2$	Q	e
	r_1	r_2	r_1	r_2				
3b	0.26	0.55	0.255±0.004	0.547±0.014	0.14	1.82	2.37	1.80
3c	0.33	0.44	0.327±0.004	0.444±0.006	0.15	2.27	2.91	1.79
3a	0.34	0.41	0.339±0.004	0.411±0.011	0.14	2.44	3.16	1.80

The FR parameters were calculated for free radical copolymerization of MASTQ (**3a**, **3b**, **3c**) and MMA, and the results were summarized in Tables 1–3. It is well known that monomer reactivity ratios can be indicative of relative reactivity of comonomers. In order to estimate the relative reactivity ratio of MASTQ and MMA in free radical copolymerization FR [14, 16] the next equation have been used:

$$y = r_2 - r_1 \cdot x \quad (2)$$

where $x = (f^2/(1-f)^2) \cdot (1-F)/F$ and $y = f(1-2F)/(1-f)F$, respectively.

From the slope and intercept of the straight line, the monomer reactivity ratios of MASTQ and MMA were determined and found to be $r_1 = 0.34$, $r_2 = 0.41$ for **3a** monomer; $r_1 = 0.26$, $r_2 = 0.55$ for **3b** monomer; $r_1 = 0.33$, $r_2 = 0.44$ for **3c** monomer (Fig. 2).

The copolymer composition equation has the form $y = r_1 \cdot x + r_2$: in the calculations method for the determination of r_1 and r_2 .

$$\frac{[M_1]}{[M_2]} \cdot \left(\frac{[m_2]}{[m_1]} - 1 \right) = -r_1 \left(\frac{[M_1]}{[M_2]} \right)^2 \cdot \frac{[m_1]}{[m_2]} + r_2 \quad (3)$$

where $y = [M_1]/[M_2] \cdot ([m_2]/[m_1] - 1)$ and $x = ([M_1]/[M_2])^2 \cdot [m_2]/[m_1]$

The copolymerization parameters of monomers r_1 and r_2 determined using the calculations method are presented in Table 4. However, the monomer reactivity ratios determined by calculation methods almost completely coincide with the ratios previously determined by the FR method.

It is well known that Price and Alfrey developed a simple scheme (Q - e) to predict reactivity ratios of monomers participating in a free radical copolymerization [14]. From the Q - e scheme the resonance stabilization parameter Q and electronegativity parameter e were calculated. The Q - e scheme postulates that the reactivity ratio r_1 and r_2 can be expressed by Eqs. (4) and (5):

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)] \quad (4)$$

$$r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)] \quad (5)$$

The Q - e values of MMA have been found in the literature [17] to be the following $Q = 0.74$, $e = 0.4$. The Q - e values of **3a**, **3b**, **3c** have been found to be $Q = 3.16$,

$e = 1.8$ for **3a**; $Q = 2.37$, $e = 1.8$ for **3b**; $Q = 2.91$, $e = 1.79$ for **3c**. The monomer reactivity ratios and copolymerization parameters are presented in Table 4.

The values of parameter r_1 illustrate similar values obtained with using two different methods. These values can be explained by insufficient influence of substitute effect.

The values of reverse constants $1/r_2$ were calculated, all three new monomers can join the radical of MMA actively, moreover, the most active is monomer with methoxy group. The similar and low values of $r_1 \cdot r_2$ illustrate the common tendency of MASTQ to interchange with links of MMA. The values of Q parameters have correlated with the values of $1/r_2$, and the values of the polar factor e have been almost identical for all monomers.

4. Conclusions

Copolymers of MASTQ with MMA were prepared by free radical polymerization. The monomer reactivity ratios for MASTQ–MMA system were calculated from the feed composition and copolymer composition determined by ¹H NMR spectroscopy. The monomer reactivity ratios of MASTQ and MMA were computed using Fineman-Ross (F-R) and calculation methods (in the brackets) and were found to be $r_1 = 0.34$ (0.339±0.004), $r_2 = 0.41$ (0.411±0.011), $Q = 3.16$, $e = 1.8$ for monomer with CH₃O– group; $r_1 = 0.26$ (0.255±0.004), $r_2 = 0.55$ (0.547±0.014), $Q = 2.37$, $e = 1.8$ for 2-styrylquinolin-8-ol methacrylate; $r_1 = 0.33$ (0.327±0.004), $r_2 = 0.44$ (0.444±0.006), $Q = 2.91$, $e = 1.79$ for monomer with NO₂– group.

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РЕАКЦІЙНА ТА ПОЛІМЕРИЗАЦІЙНА ЗДАТНІСТЬ СТИРИЛХІНОЛІНВІСНИХ МЕТАКРИЛОВИХ МОНОМЕРІВ

Анотація. Синтезовано нові стирилхінолінвісні метакрилові мономери та їх кополімери з метилметакрилатом (ММА). Полімеризацію проводили в ДМФ, як ініціатор використовували АІБН. Продукти полімеризації охарактеризовано за допомогою ^1H ЯМР. Реакційну здатність нових метакрилових мономерів на основі стирилхіноліну для гомогенної вільно-радикальної кополімеризації з ММА визначено за даними ^1H ЯМР спектроскопії та проведено її оцінювання за методом Файнмана-Росса і розрахунковим методом.

Ключові слова: 8-метакрилокси стирилхінолін, метод Файнмана-Росса, реакційна здатність мономеру, вільно-радикальна полімеризація.