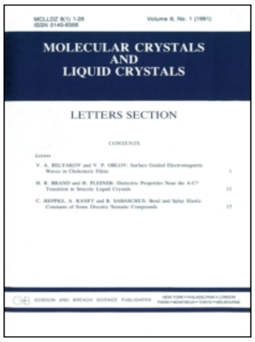
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Design, synthesis, and photochemistry of styrylquinoline - containing polymers

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ABSTRACT

Novel polymers with styrylquinoline moiety and different substituents units are presented. Styrylquinoline polymers were obtained by a three-step synthetic approach. This includes the condensation, preparation of a methacrylic monomers and their polymerization. Their photophysical and photochemical properties have been investigated. Polymers were characterized by ^{1}HNMR, UV spectroscopy and GPC, DSC techniques. The synthesized polymers exhibited glass transition temperatures in the range of 153–184°C.

KEYWORDS

aryl(meth)acrylates; radical polymerization; optical property; styrylquinoline polymers

1. Introduction

Electro-optic polymers [1] have emerged as a new class of photonic materials for different kinds of application in second order nonlinear optical devices and particularly in optically active waveguides. In the last few years nonlinear optical polymers (NLO) are widely investigated [2–4] because they can be of great importance for a variety of applications. The chromophores can be either doped into the polymer matrices or covalently attached to the polymer.

Some of the advantages of polymer-based molecular systems are their low cost, the high laser damage threshold and the fact that they can be easily tailored to match specific experimental needs [5]. Moreover, in the case of side-chain polymers stability is higher than in other types of polymer systems (i.e. guest-host systems), while the spatial organization of the active side chain residues along the polymeric backbone is of critical importance regarding mechanical and structural properties of the material. The latter case usually results to more stable systems, with increased density of chromophores and enhanced nonlinear optical response [5]. The strong nonlinearity emanates from the strong charge transfer taking place within these units [6]. These compounds are charge-transfer molecules with electron-donating and electon-accepting moiety are connected by an extended π-electron system. On the other hand, photochromism is one of photochemistry phenomena which involves light induced reversible transformation of a molecule between two states. In this respect styrylquinoline polymers are interesting due to their photochemical and photophysical properties [7, 8]. The photochromic transformations are always accompanied by changes in physical properties. There are changes in dipole moment and in the geometrical structure at the molecular level, etc. [9, 10].

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Light- induced transformations from one structure to another have been studied for styrylquinoline compounds and haven't any information about synthesis and investigation of styrylquinoline polymers and copolymers with styrylquinolines fragments in side chain. In this work we report preliminary results obtained for methacrylic polymers incorporating styrylquinolines side-group as optically active molecule.

2. Experimental

Apparatus

^{1}H NMR (400 MHz) spectra were recorded on a Mercury (Varian) 400 spectrometer with tetramethylsilane as internal standard. *UV-VIS* measurements were performed at room temperature in solution in a quartz liquid cell with a Perkin-Elmer UV/VIS/NIR Lambda 19 spectrometer. *Differential Scanning Calorimetry*: Q20 DSC model was used to determine the glass (Tg) and phase transition temperatures of all polymers. The sample was initially stabilized and after the first scan was made at a heating rate of 10°C/min up to 200°C then cooled to 20°C. Finally, a second scan was performed at a heating rate of 10°C/min up to 200°C giving the values of Tg. The glass transition temperatures by the midpoint of the heat capacity jump are given. *Size exclusion Chromatography*: The molecular weights and molecular weight distribution of all polymers were taken with a system equipped with a Spectra SYSTEM AS1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 μm Guard, 50 × 7.5 mm) followed by 2 columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 2 × 300 × 7.5 mm), with a Spectra SYSTEM RI-150 and a Spectra SYSTEM UV2000 detectors. The eluent used is THF at a flow rate of 1 ml/min at 35°C. Polystyrene standards ($580–4.83 \times 10^3$ g/mol) were used for calibration.

Materials

Standard distillation procedures were performed for triethylamine and tetrahydrofuran (THF) just prior to use. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from absolute methanol. Methacrylic chloride was vacuum-distilled, immediately before use. Methylmethacrylate (MMA) was washed with aq NaOH to remove inhibitors, dried with $CaCl_2$ under nitrogen at reduced pressure. All other reagents and solvents were commercially available and used as received.

2-(2-phenylethenyl)quinolin-8-yl propionate (1b)

A flask was charged with a mixture of 8-hydroxy-2-methylquinoline (2.8 g, 17,6 mmol), benzaldehyde (3.8 g, 35.8 mmol) and propionic anhydride (PA) (20 ml). It was refluxed and heated at 150°C 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 113–114°C.

^{1}H NMR (400 Hz, DMSO-d_6), δ, ppm: 1.42 (s, 3H, $-CH_3$), 2.88 (d, 2H, $-CH_2-$), 7.34 (d, 1H, Het), 7.40 (m, 1H, Het), 7.41 (m, 2H, Ar–H), 7.42 (m, 1H,=CH–), 7.49 (t, 1H, Ar–H), 7.64 (m, 1H, Het), 7.65 (m, 1H,=CH–), 7.73 (m, 2H, Ar–H), 7.77 (m, 1H, Het), 8.24 (d, 1H, Het).

2-[2-(4-nitrophenyl)ethenyl]quinolin-8-yl propionate (1c)

The same procedure as for **1b** was used with 4-nitrobenzaldehyde. The solid residue was recrystallized from ethanol to give **1c** yield 92%. Mp 220°C.

^{1}H NMR (400 Hz, DMSO-d_6), δ, ppm: 1.43 (s, 3H, $-CH_3$), 2.88 (d, 2H, $-CH_2-$), 7.37 (d, 1H, Het), 7.44 (m, 1H, Het), 7.48 (m, 1H,$=$CH$-$), 7.66 (m, 1H,$=$CH$-$), 7.72 (m, 1H, Het), 7.76 (m, 2H, Ar$-$H), 8.17 (m, 2H, Ar$-$H), 8.19 (m, 1H, Het), 8.21 (m, 1H, Het).

2-(2-phenylethenyl)quinolin-8-ol (2b)

The solution of **1b** (3.1 g, 10.23 mmol) in ethanol (79 ml) and concentrated hydrochloric acid (20 ml) was refluxed for 2 h. The precipitate was filtered and washed thoroughly with water. It was subsequently dissolved in ethanol (20 ml) and triethylamine (120 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 **2b** as a bright yellow powder. It was purified by recrystallization from ethanol, yield 94%. Mp 105°C.

^{1}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,$=$CH$-$), 7.42 (m, 1H, Het), 7.67–7.70 (m, 2H, Ar$-$H), 7.72 (m, 1H, Het), 8.07 (d, 1H,$=$CH$-$), 8.20 (d, 1H, Het), 9.17 (s, 1H, $-$OH).

2-[2-(4-nitrophenyl)ethenyl]quinolin-8-ol (2c)

The same procedure as for **2b** was used. Yellow-orange crystals, yield 87%. Mp 200°C.

^{1}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,$=$CH$-$), 7.73 (d, 1H, Het), 7.92 (d, 2H, Ar$-$H), 8.21 (m, 2H, Ar$-$H), 8.25 (m, 1H,$=$CH$-$), 8.28 (m, 1H, Het), 9.25 (s, 1H, $-$OH).

2-(2-phenylethenyl)quinolin-8-yl 2-methylpropil-2-enoate (3b)

A solution of **2b** (1.7 g, 6.91 mmol) and triethylamine (2 ml) was dissolved in THF (5 ml). The solution was kept in an ice bath for 10 min. A solution of distilled methacryloyl chloride (2 ml, 19.13 mmol) in THF (5 ml) was added slowly to the reaction mixture. After the addition of methacryloyl chloride, solution was stirred for 4 h an ice bath and then poured into water. The light brown powder were collected by filtration, washed with water and dried. The product was recrystallized from toluene, yield 46%, Mp 90°C.

^{1}H NMR (400 Hz, DMSO-d_6), δ, ppm: 2.30 (s, 3H, $-CH_3$), 5.94 (s, 1H,$=CH_2$), 6.50 (s, 1H,$=CH_2$), 7.30 (d, 1H Het), 7.34 (d, 1H, Het), 7.39 (t, 1H, Het), 7.46 (d, 1H,$=CH_2-$), 7.52 (t, 1H, Ar-H), 7.59 (d, 2H, Ar$-$H), 7.71 (m, 1H,$=CH_2-$), 7.75 (m, 2H, Ar$-$H), 7.79 (m, 1H, Het), 8.30 (d, 1H, Het). IR spectrum, υ, cm^{-1}: 1735, 1599, 1559, 1318, 972.

2-[2-(4-nitrophenyl)ethenyl]quinolin-8-yl 2-methylpropil-2-enoate (3c)

The yellow solid, yeld 70%, Mp 159°C.

^{1}H NMR (400 Hz, DMSO-d_6), δ, ppm: 2.30 (s, 3H, $-CH_3$), 5.94 (s, 1H,$=CH_2$), 6.47 (s, 1H,$=CH_2$), 7.48 (d, 1H Het), 7.55 (m, 2H, 7$-$H, Het), 7.59 (m, 1H,$=CH_2-$), 7.80–7.84 (m, 4H, Ar$-$H), 7.88 (m, 1H, Het), 8.22 (d, 1H,$=CH_2-$), 8.39 (d, 1H, Het). IR spectrum, υ, cm^{-1}: 1735, 1592, 1508, 1318, 978.

Polymerization

The synthesis of homopolymers **hStQ1**, **hStQ2** and copolymers **copStQ1**, **copStQ2** based on methacrylic monomers (**3c** or **3b** respectively) and methylmethacrylate (MMA) was conducted in 10% DMF solution with AIBN as radical initiator at 80°C (argon atmosphere). The mixture was degassed with repeated freeze and thaw cycles and then heated for 11 h.

Table 1. Characteristics of styrylquinoline polymers.

Sample	Mole ratio in the copolymer n/m[a]	Mn [b]	Mw [b]	Mz [b]	Mw/Mn [b]	Tg [c]
hStQ1	—	5200	9000	14600	1.73	182
copStQ1	1:2.8	5300	8700	12300	1.63	153
hStQ2	—	6400	9000	11700	1.39	184
copStQ2	1:2.6	4500	8860	14100	1.97	155

[a] Determined by ^{1}H NMR integration;
[b] Measured by GPC;
[c] Measured by DSC.

The resulting viscous solution was added into methanol to precipitate polymeric materials. The precipitation was repeated from DMF into methanol to give purified polymers. Their structures were confirmed by ^{1}H NMR spectra, as well as the respective composition in both monomers (n/m ratio). This ratio is in reasonable accordance with the initial amounts of monomers which have been introduced. Nevertheless, the styrylquinoline motifs are found in slight excess in the final composition of the polymers.

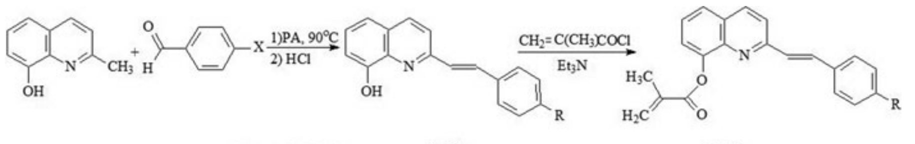
3. Results and discussion

The derivatives of 8-hydroxy-2-methylquinoline and consequently benzaldehydes were prepared by condensation with propionic anhydride, according to the procedure published previously [11]. The methacrylate monomers were synthesized by reaction the styrylquinolines alcohols with methacryloyl chloride in the presence of triethylamine as nucleophilic catalyst. The polymers were synthesized by radical polymerization using AIBN as radical initiator.

The structures of obtained polymers were confirmed by 1H NMR spectra. The compositions of the copolymers were well controlled as the initial ratio of the styrylquinoline monomers and MMA (Table 1.). However practically for all copolymers was observed styrylquinoline monomers saturation due to high-active polymerization ability of methacrylic monomers based on styrylquinolines. Glass transition temperatures (Tg) are collected in Table 1. As expected, a copolymers result in a lower Tg when conformationnally flexible methacrylate comonomer MMA is used (**copStQ1**, **copStQ2** *vs* **hStQ1**, **hStQ2**). The synthesized styrylquinoline polymers exhibited glass transition temperatures in the range of 153–184°C.

The polymers molecular weights are in the limit 8700–9000 and polydispersity indices between 1.39 and 1.97 as evaluated by GPC analisis (Table 1).

Photochemical and spectral properties of styrylquinoline derivatives in solution and in thin films have been detailed studied. These compounds undergo photoisomerization with high quantum yields in neutral and protonated forms and show bathochromic shifts of absorption bands in acidic media [7, 12]. An illustrative example is provided with polymer **copStQ1**, **copStQ2** as presented in figure 2, 3. The absorption spectra **copStQ1**, **copStQ2** during UV irradiation in THF are represented. In the spectra of absorption the THF solutions



Where R= H, NO2

2a, 2b

3a, 3b

Figure 1. Synthetic route and chemical structures of the styrylquinoline derivatives.

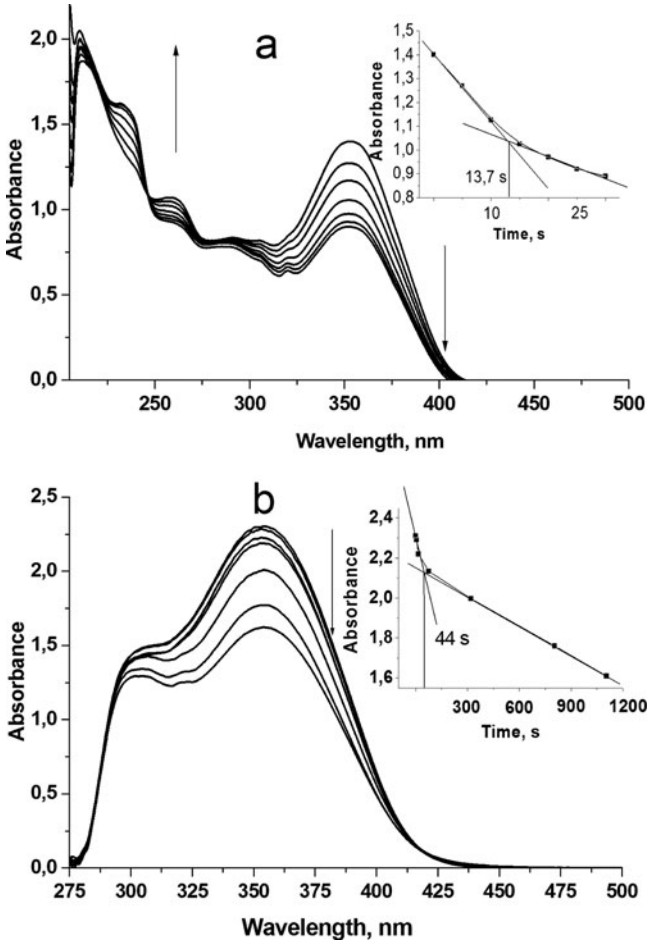


Figure 2. Changes in the absorption spectra of **copStQ1 a** - in THF before (1) and after 5 s period (2–7) **b** - in thin film: before (1) and after 5 s period (2) after 10 s (3), after 20 s (4) after 5 min (5), after 7 min (6) after 5 min (7) upon irradiation at $\lambda = 366$ nm revealing the trans-cis transformation. Insets: kinetics of the absorbance changes at $\lambda = 352$ nm.

of **copStQ1**, **copStQ2** have intensive long-wave band with approximate maximum of 352 nm and 325 nm respectively. During irradiation a decrease of absorption intensity at 352 nm for **copStQ1** and 325 for **copStQ2** assigned to π–π^* transition of the styrylquinolines unit and increase of absorption intensity at 225–245 nm with isosbestic point at 245 nm for **copStQ1**, 210–255 nm with isosbestic point at 255 nm for **copStQ2** were observed. A decreasing of the optical density at $\lambda_{\max}$ was observed for **hStQ1**, **hStQ2**, **copStQ1**, **copStQ2** polymers during light induced photochemical reaction. The isosbestic points and new maximum appearing during irradiation process can be confirmation of the total invariability of the running processes.

The spectral changes observed by the irradiation at 20°C with a UV lamp of polymers with styrylquinoline fragments with a wavelength 365 nm in THF and in solid state are shown in Fig 2, 3. In both cases, a 5 cm distance was kept between the lamp and the surface of sample during the irradiation. The initial spectra belong to the *trans*-isomers, and the final spectra belong to the photostationary states PS_{365} for **copStQ1** and **copStQ2** consisting of a mixture of *trans*- and *cis*-isomers. The half-reaction periods for **copStQ1** in THF and thin film equal

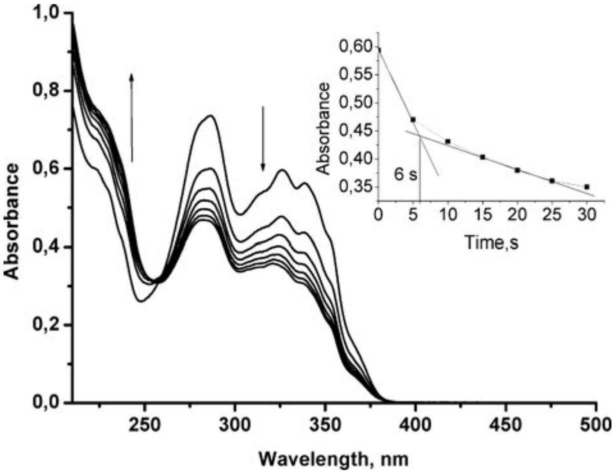


Figure 3. Changes in the absorption spectra of **copStQ2** in THF before (1) and after 5 s period (2–6) upon irradiation at $\lambda = 366$ nm revealing the trans-cis transformation. Insets: kinetics of the absorbance changes at $\lambda = 325$ nm.

13,7 s and 44 s, for **copStQ2** in THF 6 s respectively. The photostationary states were stable upon further irradiation for all compounds under study.

We can see that the *trans-cis* photoisomerization process of polymer with nitro group in side chain practically in two times higher then in polymers without substituent in benzene ring.

Photoisomerization of diarylethylenes is known to occur by one-bond-flip mechanism in fluid solutions and by hula-twist mechanism in confined media [13–15]. It is well know that as most of diarylethylenes, 2-styrylquinoline isomerizes reversibly by a diabatic mechanism, so it is impossible to convert completely one isomer into another photochemically. Under irradiation, the photostationary state can be reached, and concentrations *trans*- and *cis*-isomers in the mixture depend of the irradiation wavelength [7].

The common photochemical properties of styrylquinoline compounds are their possibility for photoisomerization through rotation about C-C bond and via the inversion of one or both of the carbon through a linear sp-hybridized transition state in which the double bond was retained. It should be noted that the transformations presented in figure 2 are always accompanied by changes in physical properties of compounds. Notably the photoinduced conformational changes in polymeric systems may result in an enormous application effect the absorption of a single photon affects not only one moiety but several neighbouring ones or even the whole macromolecule.

4. Conclusions

The present study is a first reported notice of the synthesis and investigation of photochemical properties of methacrylic polymers with styrylquinoline fragment in side chain. We have confirmed that these materials exhibit trans-cis izomerisation process. Moreover we have determined the half-reaction periods upon irradiation at $\lambda = 366$ nm. The results show that this property can be potentially useful for switching process and suggests styrylquinoline polymers might prove an interesting alternative for photonics applications.

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