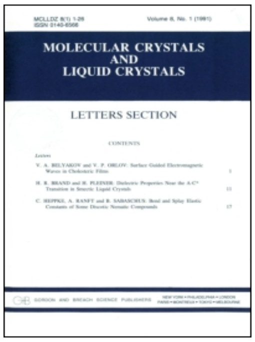

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

The photochemical behavior of polyhydroxy styrene with azofragments containing free methacrylic double bounds

Oksana Nadtoka, Lyudmyla Vretik, Tetiana Gavrylko & Volodymyr Syromyatnikov

To cite this article: Oksana Nadtoka, Lyudmyla Vretik, Tetiana Gavrylko & Volodymyr Syromyatnikov (2017) The photochemical behavior of polyhydroxy styrene with azofragments containing free methacrylic double bounds, Molecular Crystals and Liquid Crystals, 642:1, 115-123, DOI: 10.1080/15421406.2016.1257329

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1257329

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2017, VOL. 642, 115–123
http://dx.doi.org/10.1080/15421406.2016.1257329

The photochemical behavior of polyhydroxy styrene with azofragments containing free methacrylic double bounds

Oksana Nadtoka[a], Lyudmyla Vretik[a], Tetiana Gavrylko[b], and Volodymyr Syromyatnikov[a]

[a]Taras Shevchenko National University of Kyiv, Kyiv, Ukraine; [b]Institute of Physics, NASU, Kyiv, Ukraine

ABSTRACT
Polymer material which combines advantages of photoaligning azo-compounds with thermal stability of the induced anisotropy provided by free methacryloyl groups was synthesised. FTIR spectroscopy was employed for clarification its photochemical behavior. Two Fries rearrangements in arylester groups and photoinitiated cross-linking in methacryloyl functional groups were established after the action of UV-irradiation.

KEYWORDS
Azopolymer; FTIR spectroscopy; photopolymerization

1. Introduction

Azobenzene derivatives have attracted interest of a large number of researches in the field of photonic materials. A polarized light-induced anisotropy has been observed in polymer films; since the 1980, this type of anisotropy has been studied in polymers doped with azo dyes for transient polarization holography [1]. It has also been utilized as new optical switching materials in the liquid crystal systems, because the photoinduced orientation of azo dyes by irradiation with a polarized light can be a driving force for the alignment of the liquid crystals [2–3]. It has been demonstrated that photoinduced orientation of dye-containing liquid crystalline polymers can be used for reversible optical data storage [4].

Recently we developed a new class of photoaligning polymers: methacryloylaminoaryl methacrylates having free methacryloyl groups [5–8]. The materials of this class provide excellent LC alignment with variable pretilt angle, rather high anchoring energy and extraordinary high thermal and photo-stability. It was established that polarized UV light illumination results in photoinduced ordering of side polymer chains due to photoselection mechanism. It has been proven that photochemical transformations theoretically expected in such kind of materials, namely Fries rearrangements and photopolymerization of free methacrylic groups, participate in orientational ordering and LC alignment.

Our intention was to create a polymer material which would combines such advantages of azo containing photoaligning materials as a requirement of very low recording powers, large photoinduced birefringence, high resolution, and high efficiency with thermal stability of the induced anisotropy what could be provided by free methacryloyl groups.

CONTACT Oksana Nadtoka ✉ oksananadtoka@ukr.net

This paper was originally submitted to *Molecular Crystals and Liquid Crystals*, Volumes 639–640, Proceedings of the 10th International Conference on Electronic Processes in Organic and Inorganic Materials (ICEPOM-10).
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

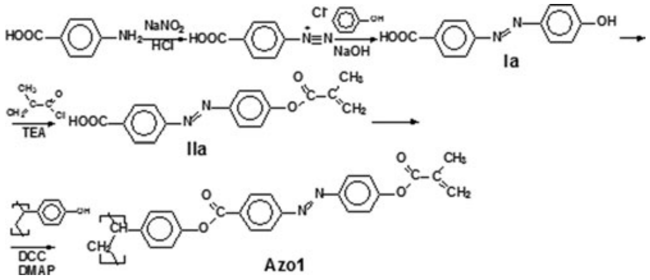

Figure 1. Scheme of synthesisof azopolymer **Azo1**.

For these reasons polymer **Azo1** containing in the same side chain azo and phenylmethacrylate groups (Fig. 1) was synthesised. It is well established that photochromic transformations in azo compounds are related to the induced *trans-cis* isomerisation of their azo-containing core. However, for more complicated molecules such as proposed **Azo1** the photochemical behaviour is not so clear. In addition to *cis-trans* isomerisation also two Fries rearrangements in arylester groups and photoinitiated cross-linking in methacryloyl functional groups are possible. Thus, FTIR spectroscopy was employed for clarification of photochemical behavior of **Azo1** and results obtained are discussed in the presented paper.

2. Experimental section

2.1. Synthesis and characterization of materials

All solvents of p.a. quality (Aldrich) were stored over molecular sieves of 3 or 4 Å. Other chemicals were purchased from Aldrich and used without further purification. Intermediate (4-methacryloyloxy)-benzoic acid was prepared in accordance with standard procedure by acylation of starting compound with methacryloyl chloride. Syntheses of intermediates 4-(4-hidroxyphenylazo)-benzoic acid (**Ia**, see Sheme 1), 4-(4-dimethylaminophenylazo)-benzoic acid (**Ib**) and 4-(4-methacryloxyphenylazo)-benzoic acid (**II**) for polymers **Azo1** and **Azo2** was done as described below.

Thin layer chromatography was performed on Merck Kieselgel plates 60-F254. ^{1}H NMR spectra were recorded with a Varian 400 NMR spectrometer with tetramethylsilane as internal standard in DMSO-d$_6$ or $CDCl_3$ as solvents.

Synthesis of 4-(4-hidroxyphenylazo)-benzoic acid (Ia). 4-aminobenzoic acid was selected for preparing diazonium salt. 0.05 mol 4-aminobenzoic acid, 2 g (0.05 mol) sodium hydroxide and 25 ml water was mixed with stirring. Keeping the temperature at 0–5°C and the solution of sodium nitrite (3.5 g, 0.05 mol) in 20 ml water was added dropwise with stirring. After stirring for further 10 min 25 ml of 8 wt.% solution of hydrochloric acid (0.05 mol) was added. Then put it into an ice-salt bath and stirred rapidly about 20 min. Then the diazonium salt as paste was obtained. Phenol (4.9 g, 0.05 mol) was dissolved in a 10 wt. % solution of NaOH (4 g, 0.05 mol). The mixture was cooled to lower than 10°C with an ice bath and 10 g ice was added. Then the diazonium salt was slowly added at the low temperature. The resultant mixture was vigorously stirred for one hour, and then the saturated solution of sodium acetate was added to the adjust pH value at 6–7. The obtained mixture was filtered and washed with a large excess of water and dried at room temperature.

Ia: orange crystals; yield 69 wt.%, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 8.09$ (d, 2H, Ar), 7.85 (d, 2H, Ar), 7.81 (d, 2H, Ar), 6.91 (d, 2H, Ar). Elem. Anal. Calcd for $C_{13}H_{10}O_3N_2$: C, 64.46%; H, 4.13%; N, 11.57%. Found: C, 64.56%; H, 4.16%; N, 11.52%.

Synthesis of 4-(4-dimethylaminophenylazo)-benzoic acid (Ib). The diazonium salt of 4-aminobenzoic acid was obtained the same way as **Ia**. Dimethyl(phenyl)amine was dissolved in a 10 wt. % solution of HCl (0.05 mol). The mixture was cooled to lower than 10°C with an ice. Then the diazonium salt was slowly added at the low temperature. The resultant mixture was vigorously stirred for further an hour, and then the saturated solution of sodium acetate was added to the adjust pH value at 6–7. The obtained mixture was filtered and washed with a large excess of water and dried at room temperature.

Ib: red crystals; yield 71%, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 8.06$ (d, 2H, Ar), 7.8 (dd, 4H, Ar), 6.79 (d, 2H, Ar), 3.12 (s, 6H, $2CH_3$). Elem. Anal. Calcd for $C_{15}H_{15}O_2N_3$: C, 71.66%; H, 4.78%; N, 13.38%. Found: C, 71.58%; H, 4.76%; N, 13.32%.

Synthesis of 4-(4-methacryloxyphenylazo)-benzoic acid (II). The azocompound **Ia** (9.7 g, 0.05 mol) and N,N,N-triethylamine (0.05 mol, 7 ml) were dissolved in THF (50 ml). The solution was kept in an ice bath for 10 min. A solution of distilled methacryloyl chloride (6.0 ml, 0.05 mol) was added slowly to the above mixture. After the addition was completed, the resulting mixture was stirred at room temperature overnight. Then the solution was poured into distilled water (1 L) and the obtained residue was filtered and air-dried. Recrystallization of **II** was carried out in ethanol.

II: yellow crystals; yield 60 wt.%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 8.17$ (d, 2H, Ar), 8.08 (d, 2H, Ar), 8.04 (d, 2H, Ar), 7.5 (d, 2H, Ar), 6.34 (s, 1H, $=CH_2$), 5.88 (s, 1H, $=CH_2$), 2.06 (s, 3H, $-CH_3$). Elem. Anal. Calcd for $C_{17}H_{16}O_4N_2$: C, 65.38%, H, 5.13%; N, 8.97%. Found: C, 65.40%, H, 5.19%; N, 9.01%.

Synthetic root for preparation of azopolymers **Azo1** and **Azo2** is shown on Scheme (Figure 1).

Synthesis and characterization of azopolymer Azo1. To the solution of 1.20 g (0.01 mol) of poly(4-hydroxystyrene) (Mw = 8000) in 10 ml of dry THF was added 10 ml dry THF solution of 3.11g (0.01 mol) of 4-(4-methacryloxyphenylazo)-benzoic acid **(II)**, 2.06 g (0.01 mol) of N,N'-dicyclohexylcarbodiimide (DCC) and 0.3 g of 4-dimethylaminopyridine (DMAP). The reaction mixture was stirred at 20°C during 4 days. A residue was formed and filtered off, the filtrate was poured into 400 ml of distilled water and 2.9 g of polymer **Azo1** was obtained. The obtained polymer was dissolved in 4 ml of DMF and precipitated into 100 ml of methanol. The mass of the formed polymer was 2.52 g (yield 58 wt.%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 8.75 (broad, Ar), 7.8 (broad, Ar), 6.9 (broad, Ar), 6.27 (broad, $= CH_2$), 5.87 (broad, $= CH_2$), 1.98, 1.62, 1.25 (broad, CH_3, CH_2, CH). The relative molar ratio of n:m was evaluated by comparison of ^{1}H NMR integrals for the signals at 7.19 and 5.84 ppm and calculated as about 25:75.

Synthesis and characterization of azopolymer Azo2. Polymer **Azo2** was prepared by the same polymer analogues reaction of poly(4-hydroxystyrene) ($M_w = 8000$) with 4-(4-dimethylaminophenylazo)-benzoic acid (**Ib**). Yield 42 wt.%. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): $\delta = 8.75$ (broad, Ar), 7.8 (broad, Ar), 7.5 (broad, Ar) 1.98, 1.62, 1.25 (broad, CH_3, CH_2, CH). The relative molar ratio of n:m was evaluated by comparison of ^{1}H NMR integrals for the signals at 6.8 and 6.3 ppm and calculated as about 24:76.

Model polymer **Mod1** was prepared by polymer analogues reaction of poly(4-hydroxystyrene) ($M_w = 8000$) with methacryloyl chloride. The relative molar ratio of n:m was evaluated by comparison of ^{1}H NMR integrals for the signals at 6.82 and 5.77 ppm and calculated as about 35:65. Model polymer **Mod2** was prepared by polymer analogues reaction of poly(4-hydroxystyrene) ($M_w = 8000$) with intermediate (4-methacryloyloxy)-benzoic acid.

Synthesis and characterization of Mod2. To the solution of 1.20 g (0.01 mol) of poly(4-hydroxystyrene) ($M_w = 8000$) in 10 ml of dry THF was added 10 ml THF solution of 2.06 g

(0.01 mol) of (4-methacryloyloxy)-benzoic acid, 2.06 g (0.01 mol) of DCC and 0.3 g of DMAP. The reaction mixture was stirred at 20°C during 4 days. A residue was formed and filtered off, the filtrate was poured into 400 ml of distilled water and 1.97 g of polymer **Mod2** was obtained. The obtained polymer was dissolved in 4 ml of ethylacetate and precipitated into 100 ml of hexane. The mass of the formed polymer was 1.37 g (yield 43%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 8.01 (broad, Ar), 6.66 (broad, Ar), 6.27 (broad, $= CH_2$), 5.87 (broad, $= CH_2$), 1.98, 1.62, 1.25 (broad, CH_3, CH_2, CH). The relative molar ratio of n:m was evaluated by comparison of ^{1}H NMR integrals for the signals at 7.19 and 5.84 ppm and calculated as about 25:75.

2.2. Samples and IR measurements

The polymers were dissolved in N,N-dimethylformamide (DMF) at concentration 2 wt. % and filtered to 0.2 μm by syringe filter. The polymer films were obtained by spin coating of the polymer solutions on the KBr plates and subsequent backing at 80°C over 30 min for the solvent evaporation. The films were subsequently exposed to a broad-band unpolarized irradiation from a high pressure mercury lamp DRS-500 (Russia) directed normally to the films. The integral intensity of irradiation was 105 mW/cm^2. The room temperature FTIR absorption spectra of the polymer films were measured in the spectral range 400–4000 cm^{-1} with a resolution of 1 cm^{-1} with Perkin Elmer Spectrum BX FTIR spectrometer. Reproducibility of peak position measurements in the FTIR spectra is ±0.5 cm^{-1}. An error in absorbance measurements is determined by systematic instrumental errors and equals 0.1%. As a reference, the KBr window was used. All spectral manipulations, such as baseline correction, smoothing and normalization, were performed using the standard "Spectra" (PE) standard spectroscopy software package.

3. Results and discussion

While making an assignment of the absorption bands of **Azo1**, we mainly focused on the bands related to vibrations of the molecular groups which are sensitive to photochemical transformations discussed above. We expected that Fries rearrangements do significantly change the vibration bands of arylester (both benzoate and methacrylate types) groups, while photopolymerization modifies the vibration bands related to $C = CH_2$ fragments. Finally, it would be necessary to identify bands useful for monitoring of *trans-cis* isomerization of azo group N = N.

Thus, characteristic vibrations of Ar–O–C=O (methacrylate), Ar(C=O)–O (benzoate) and $C = CH_2$ molecular groups were especially thoroughly identified. For this purpose, first of all, we used literature data [9–11]. However, because of quite complicated structure of **Azo1**, it was difficult to make unequivocal assignment for a number of the absorption bands. To give unambiguous assignment, a preliminary assignment based on the literature data for related compounds was defined more exactly by comparing the FTIR spectrum of **Azo1** with the spectra of model polymers **Azo2**, **Mod 1** and **Mod 2** for their structures (see Fig. 2).

3.1. IR spectra before irradiation

As an illustrative example, the infrared spectrum in the 500–1600 and 3000–3900 cm^{-1} regions of **Azo1** film is presented in Fig. 3, parts a and b.

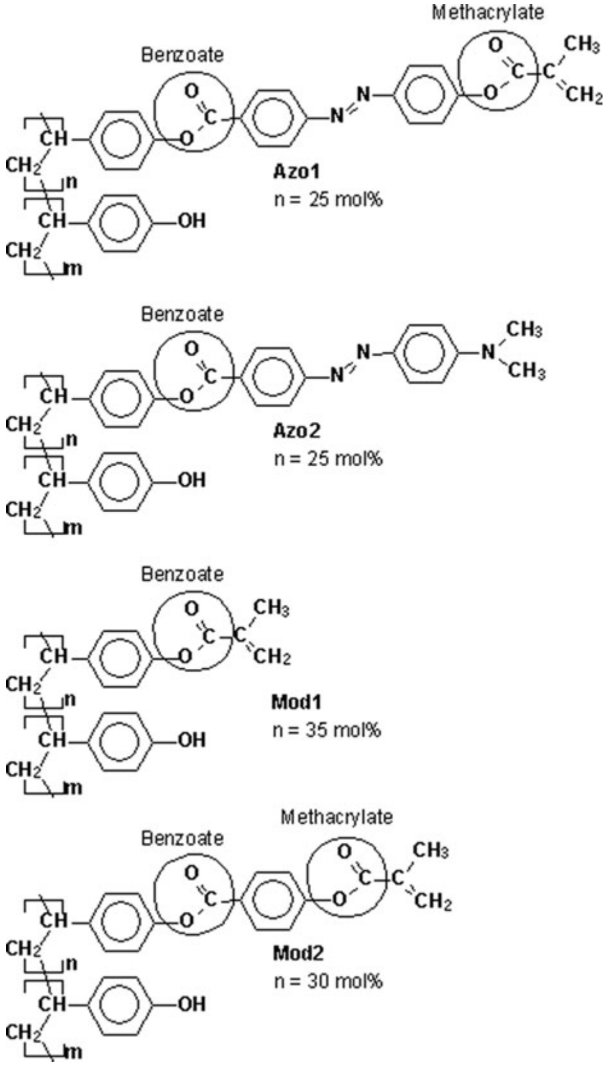

Figure 2. Structures of model polymers **Azo2, Mod 1**, **Mod 2** in comparison with structure of azopolymer **Azo1**.

Like other carbonyl compounds, esters are primarily recognized by their strong carbonyl band at around 1740 cm^{-1} [9] and corresponds to carbonyl stretching $\nu(C = O)$. Because **Azo1, Mod1** and **Mod2** have similar structures of arylester fragments, the peak positions of $\nu(C = O)$ vibrations of these fragments in the mentioned polymers are close, namely at 1734, 1734 and 1738 cm^{-1}. In addition, according to [9, 10], the other characteristic bands of the ester group are two ν(C-O) vibration bands with a peak position at around 1200 cm^{-1} and in the range 1150–1100 cm^{-1}. In the IR spectra of **Azo1**, corresponding bands were found at 1200 cm^{-1} for methacrylate fragment and 1264 cm^{-1} for benzoate. Such assignment was proven by a comparison of **Azo1** spectrum with the spectra of **Azo2**, **Mod1** and **Mod2** having similar arylester structures and thus similar positions of characteristic bands (at 1257 cm^{-1} in **Azo2** for benzoate, at 1204 cm^{-1} in **Mod1** for methacrylate and at 1202 cm^{-1} and 1266 cm^{-1} for methacrylate and benzoate in **Mod2**).

To identify the absorption bands corresponding to $\nu(C = C)$ vibrations of $C = CH_2$ fragment, foreseen in literature in 1680–1620 cm^{-1} region, we have compared the IR spectra of

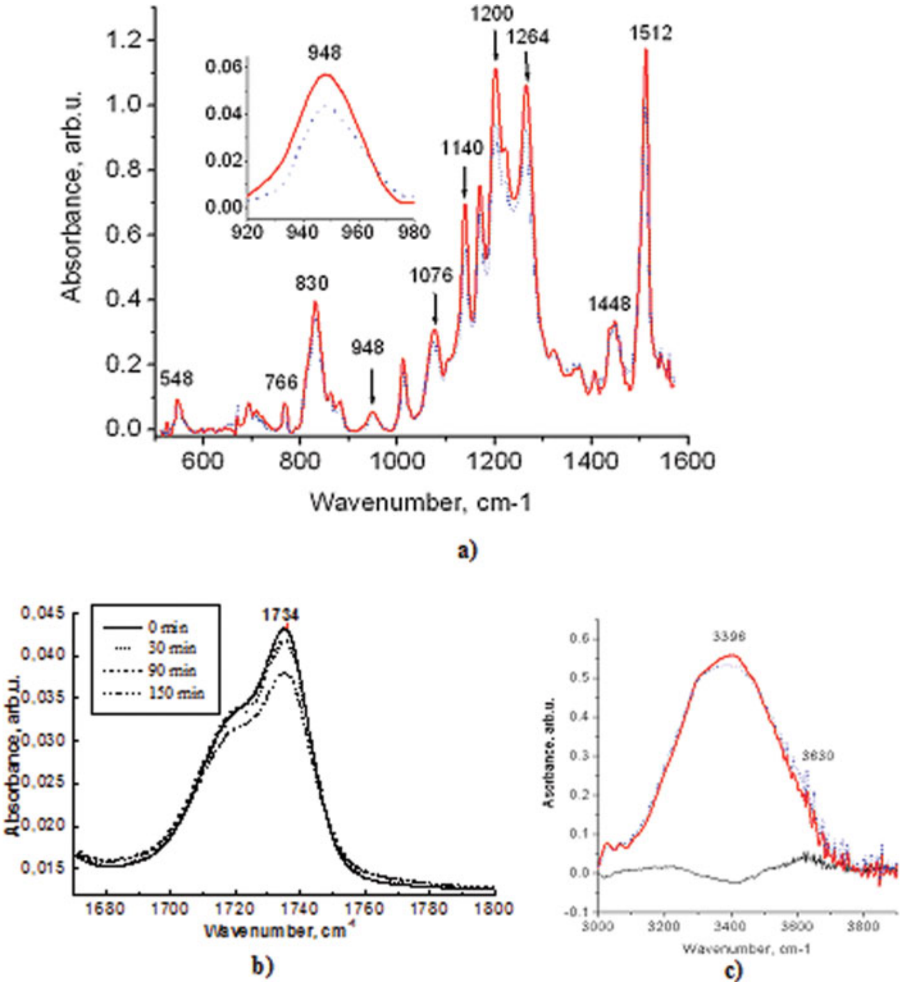

Figure 3. FTIR spectra of **Azo1** before (solid line) and after (dotted line) UV irradiation (I = 105 mW/cm^2) in the 400–1600 (a), 1660–1800 (b) and 3000–3800 cm^{-1} (c) region. The inset in the upper picture shows changes in the absorption of CH$_2$ groups. Solid line in the bottom picture represents a difference between the two depicted spectra.

Azo1 with **Mod 1, Mod 2** as well as with data presented in [9]. In accordance with [9], the band centered at 1628 cm^{-1} was attributed to the C = C stretching vibration. In the spectrum of model polymer **Mod 1** this band exhibited at 1638 cm^{-1} while in the spectrum of **Mod 2** it is shifted by 1cm^{-1} towards higher wave numbers (1639 cm-1). Finally, this band in the **Azo1** spectrum was recognized at 1636 cm^{-1} and no detected in **Azo2**.

The other band which could be attributed to C = CH$_2$ fragment in the **Azo1** spectrum is centered at 948 cm^{-1} and appears due to the δ(C-H) vibration. Indeed, according to [9] for the CH$_2$ = C-C = O conjugated systems this kind of vibration has a band position in the region 930–945 cm^{-1}. Corresponding band was also found in **Mod 1** and **Mod 2** at 948 cm^{-1} and 946 cm^{-1}, respectively. No absorption bands in this region were detected in the spectra of poly(hydroxystyrene) and poly(acetylhydroxystyrene) and **Azo2**. The characteristic absorption bands related to groups mentioned above of **Azo1** and **Mod 1, Mod2** are summarized in Table 1.

Table 1. Assignment of the IR absorption bands in the IR spectra of **Azo1** and **Mod1, Mod2** compounds to the vibrations of the structural elements responsible for photochemical transformations.

Material code	Ester, C = O	Ester, C-O-C	C-H in CH_2 = , cm^{-1}
Azo1	1734, 1718*	1200 (methacrylate), 1264 (benzoate)	948
Azo2	1718	1259 (benzoate), overlapped	Absent
Mod1	1734, 1718*	1204 (methacrylate)	948
Mod2	1738	1202 (methacrylate), 1266 (benzoate)	946

*hydrogen bonded

Band centered at 1222 cm^{-1} can be assigned to δ (C-O) stretching vibration (theoretically predicted in the region 1260–1180 cm^{-1}) of the residual phenol Ar-OH structure.

The other set of pronounced bands of the IR spectrum of **Azo1** with the peaks at 1598, 1610, 1512 and 1448 cm^{-1} relate to Q(C· · ·C) vibrations of benzene rings. The correctness of this assignment is confirmed with a fact that all these bands are present in the IR spectra of **Mod 1** and **Mod 2** homologues containing substituted benzene rings.

Such bands of **Azo1** FTIR spectrum as 1406, 1376, 1322, 1140 and 1076 and 1012 cm^{-1} could be only preliminary assigned employing literature data and original IR spectrum of poly(4-hydroxy styrene). The bands centered at 1376 and 1322 cm^{-1} could be assigned to skeleton δ(C-H) vibrations of CH_2 groups of the main polymer chain and C-CH_3 in methacrylic groups. In this region could exist also an absorption band associated with a vibrational coupling between the $\nu(N = N)$ and Q(C· · ·C) stretching vibration [14]. Finally, the bands centered at 1076 and 1012 cm^{-1} could be assigned to δ (C-H) vibrations of aromatic part of the **Azo1** molecules.

The bands observed at 2852 and 2926 cm^{-1} are assigned to the main chain methylene symmetric and antisymmetric CH stretching modes, respectively. The bands centered at 3020 and 3067 cm^{-1} refer to aromatic CH stretching vibrations.

A single broad O-H stretching bands is observed at 3396 cm^{-1}; this band is due to hydrogen bond formation [15] between the O-H group in the phenol moiety and the C = O group in the benzoate moiety (O-H· · · O = C). This result is supported by the appearance of C = O stretching band at 1718 cm^{-1} being originated by the formation of hydrogen bonds between the carbonyl and hydroxyl groups. The same signal was detected at 1718 cm^{-1} for **Mod 1**.

Theoretically, the *azo* group shows only weak bands at between 1000–1615 cm^{-1} [12], and since a lot of bands generally occur in this region, it is not possible to make definite conclusions more correctly. As reported previously by Buffeteau et al. [15], the band at 1385 cm^{-1} is assigned to a vibration coupling of between the $\nu(N = N)$ and the Ø-N stretching vibration. However, in the spectrum of the **Azo1** compound, corresponding spectral region is concealed by the absorption of other functional groups, and therefore it was not possible to identify such vibration band.

Thus, the comparison of the IR absorption spectra of **Azo1** and those of model polymers **Mod1** and **Mod2** allowed us to make an assignment for the majority of strong absorption bands of the **Azo1** polymer, Table 2. The assignment of some minor absorption bands remains unclear and needs additional investigations which are beyond the scope of this paper.

3.2. Changes in IR spectra after UV irradiation

At the next stage, FTIR spectra of **Azo1** before and after UV irradiation (I = 105 mW/cm^2) were compared. As was expected, in the spectrum of **Azo1** the changes of the vibration bands attributed to both types of ester fragments were observed, such as lowering the intensity of

Table 2. Peak position of main IR absorption bands and their assignment to vibrations of selected structural elements of **Azo1**.

	Peak position, cm^{-1}		
Structural element	Experimental	Ref. [10, 11]	Assignment
Methylene, main chain	**2924**	2926	$\nu_{as.}$ (CH)
	2852	2843–2863	$\nu_{sym.}$ (CH)
Ester	**1734**	1750–1735	$\nu(C=O)$
	1264, 1200 and **1168**	1310–1250 and 1150–1100 (benzoates), 1300–1200 (acrylates)	ν (COC)
Aryl	**3022**	3030 [11], 3100–3000 [10]	ν_{ar}(C-H)
	1598, 1610	1600–1585	Q(C···C)
	1512	1500–1430	Q(C···C)
	830	804–830	$\delta_{o.o.p.}$ (C-H), p-substituted
$C=CH_2$	**1636, partially overlapped**	1680–1620	$\nu(C=C)$
	948	930–945	δ(C-H)

Note: ν, Q - stretching, δ -deformational vibrations

the following bands: ester $\nu(C=O)$ stretching band centered at 1734 cm^{-1} and hydrogen bonded at 1718 cm^{-1}, ν(C-O) vibration bands centered at 1266 and 1202cm^{-1} (see Fig. 3, a., b.). Such a behavior of the bands attributed to the ester groups was interpreted as the result of Fries rearrangement (see Fig. 4) described in the literature for aromatic esters [16]. Small changes observed in the region of OH stretching vibrations (Fig. 3, b), such as insignificant drop in intensity and broadening at the high-frequency side of the band, can be attributed to rearrangement of intra-molecular H-bonds.

Photopolymerization of $C=CH_2$ groups is also evident from the IR spectra of irradiated **Azo1**: photo-sensitive absorption band centered at 948 cm^{-1} slightly reduce its intensity after 90 min of irradiation (see an inset in Fig. 3, a).

Insignificant growth and broadening of some absorption bands in 1400–1370 cm^{-1} regions is completely understandable taking into account a possibility of the photopolymerization reaction (Fig. 4, b.) in UV-irradiated film which leads to the formation of new $-C(CH_3)-CH_2-$ fragments having $\delta(C-CH_3)$ bands at 1380–1450 cm^{-1} [10].

In spite of the reported in [13, 15, 17] and references therein, possible band formation at ~-1515 cm^{-1} attributed to the $N=N$ stretching vibration of the *cis* species, was not detected in **Azo1** spectrum after UV irradiation may be due to its small intensity and overlapping with strong Q(C···C) band at 1512 cm^{-1}.

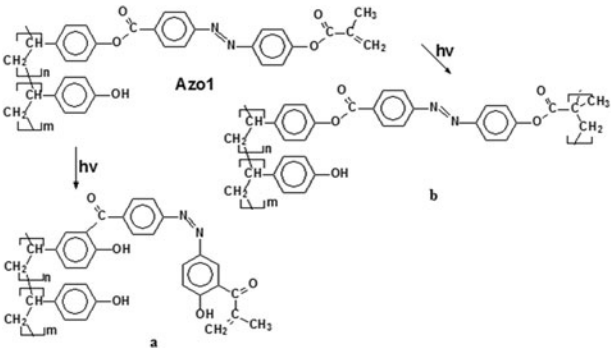

Figure 4. Possible photoshemical transformations of azopolymer**Azo1**: **a** - Fries rearrangements and *trans-cis* isomerization, **b** -photopolymerization of free methacrylic groups.

Conclusions

As was expected, Fries rearrangements do significantly changes in the vibration bands of arylester (both benzoate and methacrylate types) groups at 1734 cm^{-1}, 1718 cm^{-1}, 1264 cm^{-1} and 1200 cm^{-1}. A photopolymerization related to $C = CH_2$ fragments evident due to decrease of absorption band centered at 948 cm^{-1}. Thus, both types of photochemical reactions (Fries rearrangement and photopolymerization) could be recognized in FTIR spectra of the UV-irradiated **Azo1** films.

References

[1] Todorov, T.; Nikolova, L.; Tomova, N. et al. (1981). *Opt. Quantum Elektron 13*, 209.
[2] Wu, Y., Zhang, Q., Kanazawa, A., Shiono, T., Ikeda T., & Nagase Y. (1999). *Macromolecules*, *32*(12), 3951.
[3] Ichimura K. (2000). *Chem. Rev.*, *100*(5), 1847.
[4] Kawata, S., & Kawata, Y. (2000). *Chem. Rev.*, *100*(5), 1777.
[5] Vretik, L. O., Syromyatnikov, V. G., Zagniy, V. V., Paskal, L. P., Yaroshchuk, O. V., Dolgov, L. O., Kyrychenko, V. I, & Lee, C. D. (2007). *Mol.Cryst.Liq.Cryst.*, *479*, 121.
[6] Vretik, L. O., Paskal, L. P., Syromyatnikov, V. G., Zagniy, V. V., Savchuk, O. A., Dolgov, L. O., Yaroshchuk, O. V., & Lee, C. D. (2007). *Mol.Cryst.Liq.Cryst.*, *468*, 173.
[7] Vretik, L. O., Syromyatnikov, V. G., Zagniy, V. V., Savchuk, E. A., & Yaroshchuk, O. V. (2008). *Mol.Cryst.Liq.Cryst.*, *486*, 7.
[8] Kyrychenko, V., Smolyakov, G., Zagniy, V., Vretik, L., Paskal, L., Syromyatnikov, V., & Yaroshchuk, O. (2008). *Mol.Cryst.Liq.Cryst.*, *496*, 278.
[9] Gunzler H, & Gremlich, H. U. (2002). *IR Spectroscopy. An introduction*. Wiley-VCH Verlag Gmbh, Weinheim.
[10] Bellamy, L. J. (1963). *The infra-red spectra of complex molecules*. John Wiley& Sons, New York.
[11] Kim, S. H., Jang, J., Jeon, H. et al. (2008). *Applied Physics letters*, *92*, 183306.
[12] Vretik, L., Kyrychenko, V., Smolyakov, et al. Photochemical transformations in bis-Methacrylic polymers for liquid crystal photoalignment: IR spectroscopy studies (2011). *Mol.Cryst.Liq.Cryst.*, *536*, 224.
[13] Biswas, N., & Umapathy, S. (1997). *J. Phys. Chem. A*, *101*(30), 5555.
[14] Zemskov, A. V., Rodionova, G. N., Tuchin, Yu. G. et al. (1987). *Zhurnal Prikladnoi Spektroskopii A*, *101 49*(4), 581.
[15] Buffeteau, T., Labarthet, F. L., Pezole M. et al. (1998). *Macromolecules*, *31*, 7312.
[16] Bellus, D. (1971). *Adv. Photochem.*, *8*, 109.
[17] Buffeteau, T., Labarthet, F. L., Pezole M. et al. (2001). *Macromolecules*, *34*, 7514.