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Photochemical Transformations in Bis-Methacrylic Polymers for Liquid Crystal Photoalignment: IR Spectroscopy Studies

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Fourier transform infrared spectroscopy (FTIR) is applied to study photochemical transformations in poly(p-methacryloylaminophenyl methacrylate), a material with pronounced liquid crystal photoalignment capability. The characteristic bands corresponding to photosensitive groups of this polymer are identified by comparing its FTIR spectra with the spectra of model compounds having a reduced number of photochemical transformations. The changes in FTIR spectra of this material under ultraviolet illumination give evidence of two Fries rearrangements (in arylamide and arylester groups) and a conversion of C=CH$_2$ methacrylic bonds. This allows one to refine the microscopic model of photoinduced ordering in this class of polymers.

Keywords Arylmethacrylate; crosslinking; Fries rearrangement; FTIR spectroscopy; liquid crystal photoalignment

1. Introduction

The liquid crystal (LC) photoalignment technique [1–3] is among the most promising candidates capable to replace the traditional rubbing technique in the next generations of LC displays. The industrial application of this technique is hindered by several problems such as the insufficient anchoring strength, poor thermal and photo-stabilities, and alignment aging. These problems may be overcome by the optimization of photoalignment materials and the illumination process [4].

The photoaligning materials are usually classified according to photochemical reactions leading to the orientational ordering under illumination. There are photoalignment materials with photosensitive species undergoing the trans-cis photoisomerization (azopolymers and azodyes) [5,6], photodestruction (polyimides, polysilanes) [7,8], and photo-crosslinking (polymers containing cinnamate, chalcone, coumarine, anthracenyl, and some other chromophores) [3,9–12].

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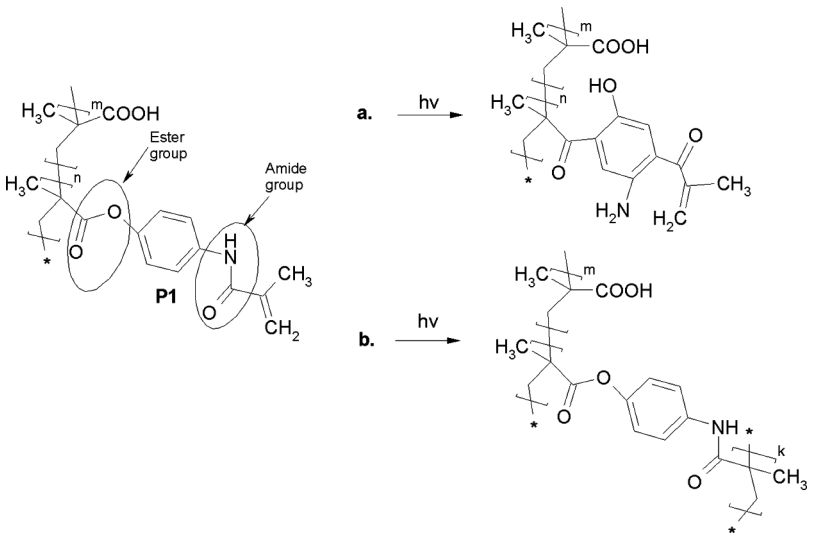

Figure 1. Structure and possible photochemical transformations in polymer **P1** representing a new class of polymers for LC photoalignment. (a) Fries rearrangements, (b) photopolymerization of free methacrylic chains.

Recently, we developed a new class of photoalignment polymers: methacryloylaminoaryl methacrylates having free methacryloyl groups [13–15]. The example of these materials is a polymer **P1** in Figure 1. The materials of this class provide the excellent LC alignment with variable pretilt angle [14], rather high anchoring energy [13], and extraordinary high thermal and photo-stabilities. The further optimization of these materials requires knowledge of their photochemistry and mechanisms of orientational ordering under illumination.

In the previous studies, spectral measurements in the UV and visible (Vis) ranges were carried out to elucidate photochemical transformations and ordering peculiarities in **P1** series [16]. It has been established that the polarized UV light illumination results in the photoinduced ordering of side polymer chains due to the photoselection mechanism. It has been also supposed that all three photochemical transformations theoretically expected in **P1**, namely two Fries rearrangements and the photopolymerization of free methacrylic groups, realize in fact and participate in the orientational ordering and the LC alignment. This assumption was based on the consideration of model compounds, in which some types of photochemical transformations allowed in **P1** were excluded. The use of model compounds was stipulated by a low potency of UV/Vis spectroscopy to distinguish different photochemical processes. In fact, the absorption bands of polymers in the UV/Vis range are very broad, so that different photochemical processes are frequently indistinguishable.

Since IR spectroscopy distinguishes vibrations of different molecular groups, it is much more efficient in photochemical studies of materials having several channels of phototransformation. Using this technique, all photochemical processes can be detected directly in the studied material in contrast to the indirect detection in case of UV/Vis spectroscopy earlier applied [16]. In view of this, the goal of the present study is to support the hypothesis concerning photochemical transformations in polymer **P1** with IR studies. It is shown that the results of IR spectroscopy

complement the results of UV/Vis spectroscopy and thus prove the photochemical concept suggested for polymer **P1** in the earlier studies.

2. Experimental Section

2.1. *Material Selection*

Polymer **P1** with a structure presented in Figure 1 was used as a representative of photoaligning bis-methacrylic polymers. The photoalignment properties of this polymer were comprehensively studied in [13,14], while UV/Vis spectra were investigated in [16]. Theoretically, under illumination with actinic light, a **P1** molecule can undergo two Fries rearrangements involving arylamide (Ar-NH-C=O) and arylester (Ar-O-C=O) groups, respectively, and the photopolymerization (photocrosslinking) of a $C=CH_2$ double bond in the methacrylic fragment (see Fig. 1).

Besides **P1**, a series of model compounds was involved because of the following reasons. (1) The modeled compounds help us to assign unambiguously vibration bands of the **P1** IR absorption spectrum. (2) They allow confirming the photoinduced changes in characteristic bands sensitive to different types of molecular transformations.

The major model compounds are polymers **Mod1-Mod4** (Fig. 2). Their structures are simplified comparing with **P1,** so that some types of photochemical transformations possible for **P1** are excluded. Compound **Mod1** does not contain free double bonds of $C=CH_2$ fragments and thus is capable to only Fries rearrangements in arylamide (Ar-NH-C=O) and arylester (Ar-O-C=O) groups. The structures of **Mod2** and **Mod3** are modified in such a way that only one Fries rearrangement (in arylamide Ar-NH-C=O and in arylester Ar-O-C=O group, respectively) can be realized. Finally, in **Mod4**, only the polymerization of $CH_2=C$ groups is possible.

2.2. *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-methacryloylamino)phenol (**2**), (4-acetylamino)phenol (**3**), 4-acetylaminobenzoic acid (**5**), 4-(methacryloyloxymethyl)benzoic acid (**6**) and phenyl methacrylate (**7**) were prepared in accordance with the standard procedure.

^{1}H NMR spectra were recorded with a Varian 400 NMR spectrometer with tetramethylsilane as the internal standard in DMSO-d_6 as a solvent. Gel permeation chromatography (GPC) measurements were performed with N,N-dimethyl formamide (DMF) as an eluent at 25°C, using a PSS apparatus with a Shodex refractive index (RI) detector under the following conditions: PSS-SDV (5 μm, 10^3 Å, $8 \times 50\,mm^2$ column) and 3 PSS-SDV (5 μm, $8 \times 300\,mm^2$ with 10^2-, 10^3-, and 10^4-Å porosities) columns and DMF eluent containing LiBr at a flow rate of $1.0\,ml \cdot min^{-1}$. The calibration curves for GPC analysis were obtained using PSS polystyrene standards (374–10^6 D). Differential scanning calorimetry (DSC) was carried out by DuPont 1090 DSC 910. For each sample, the measurements were carried out three times in a sequence heating-cooling-heating at heating rate of $16°C\,min^{-1}$. The glass transition temperatures T_g estimated from the second heating curves are presented in Table 1.

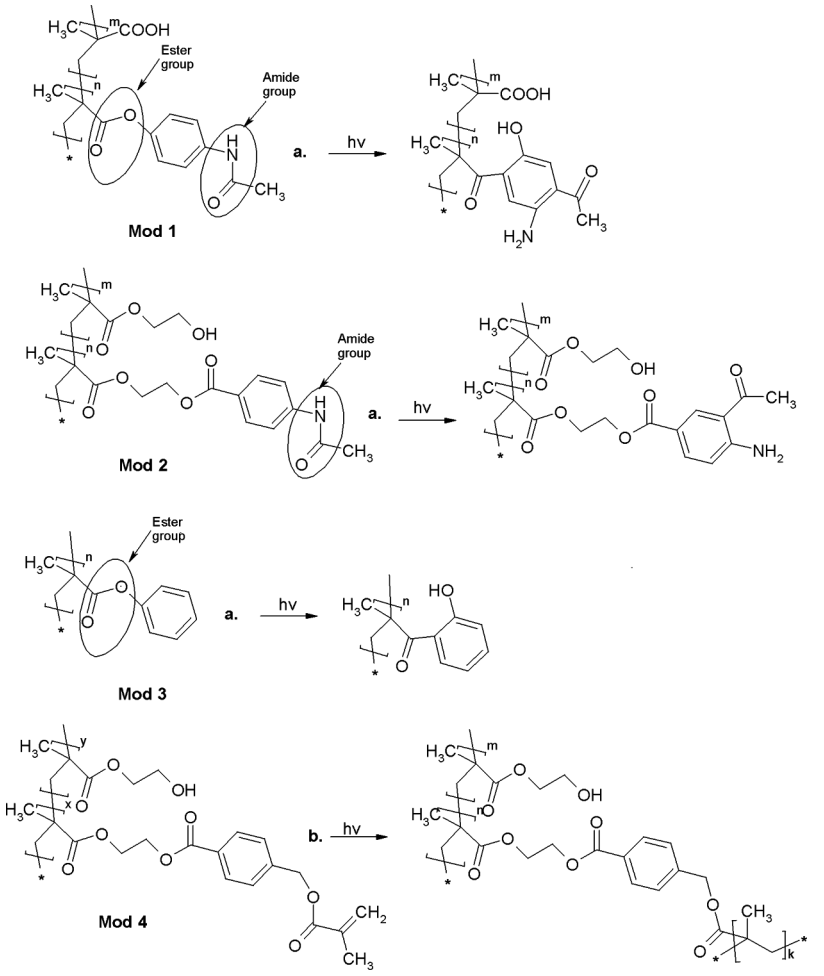

Figure 2. Structures and possible photochemical transformations in model polymers **M1-M4**. (a) Fries rearrangements, (b) photopolymerization of free methacrylic chains.

Polymer **P1** and model polymer **Mod1** were prepared by polymer analogous reactions of polymethacrylic acid (**1**) with (4-methacryloylamino)phenol (**2**) and (4-acetylamino)phenol (**3**), respectively. Model polymers **Mod2** and **Mod4** were prepared by polymer analogous reactions of poly(2-hydroxyethyl methacrylate) (**4**) with 4-acetylaminobenzoic acid (**5**) and 4-(methacryloyloxymethyl)benzoic acid (**6**), respectively, by the same method as for **P1**. Polymers **1** and **4** were obtained by radical polymerization in tetrachloromethane and toluene, respectively.

Model polymer **Mod3** was obtained by radical polymerization of phenyl methacrylate (**7**). The schemes of corresponding reactions are given in Figure 3.

*Characterization of **P1**.* GPC (RI): $M_n = 54\,000$, $M_w = 86\,300$, PD = 1.60.

H^1 NMR (400 MHz, DMSO-d_6, ppm): 9.70 (broad, NH), 7.72 (broad, Ar), 7.02 (broad, Ar), 5.81 (broad, $=CH_2$), 5.43 (broad, $=CH_2$), 1.74 (broad, CH_2), 1.24 (broad, CH_3). The relative molar ratio of n:m was evaluated by comparison of ^1H NMR integrals for the signals at 7.02 and 1.24 ppm and calculated as about 40:60.

Table 1. GPC and DSC characteristics of **P1** and model polymers

Material code	Conversion, mol.%	M_n	M_w	M_w/M_n	T_g, °C (second scan)
P1*	40	54 000	86 300	1.60	*
Mod1	30	45 300	85 300	1.88	142
Mod2	60	42 500	80 300	1.89	111
Mod3	100	20 300	40 900	2.01	100
Mod4*	60	71 100	135 000	1.90	*

*Due to the presence of free methacrylic groups capable to crosslink in a course of DSC measurements it was not possible to obtain correct T_g values.

*Characterization of **Mod1**.* H^1 NMR (400 MHz, DMSO-d_6, ppm): 9.90 (broad, NH), 7.58 (broad, Ar), 7.01 (broad, Ar), 2.04 (broad, CH_3), 1.79 (broad, CH_2), 1.25 (broad, CH_3). The relative molar ratio of n:m was evaluated by comparison of ^1H NMR integrals for the signals at 7.01 and 1.25 ppm and calculated as about 30:70.

GPC (RI): $M_n = 45\,300$, $M_w = 85\,300$, PD = 1.88. T_g (second scan): 142°C.

*Characterization of **Mod2**.* GPC (RI): $M_n = 42\,500$, $M_w = 80\,300$, PD = 1.89. T_g (second scan): 111°C.

H^1 NMR (400 MHz, DMSO-d_6, ppm): 10.13 (broad, NH), 7.86 (broad, Ar), 7.69 (broad, Ar), 4.40 (broad, -$COOCH_2$-), 4.19 (broad, -$COOCH_2$-), 3.89 (broad, -OCH_2-), 3.50 (broad, -OCH_2-), 2.08 (CH_3), 1.80 (broad, CH_2), 0.95 (broad, CH_3), 0.79 (broad, CH_3). The relative molar ratio of x:y was evaluated by comparison of ^1H NMR integrals for the signals at 7.69 and 1.84 ppm and calculated as about 60:40.

*Characterization of **Mod4**.* H^1 NMR (400 MHz, DMSO-d_6, ppm), selected: 7.94 (broad, Ar), 7.42 (broad, Ar), 6.01 (=CH_2), 5.63 (=CH_2), 5.15 (-OCH_2Ph), 4.23

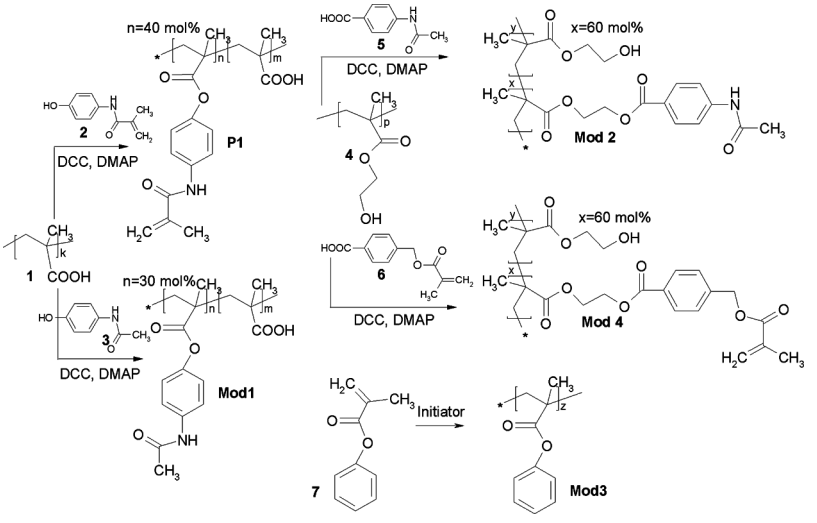

Figure 3. Scheme of synthetic procedures.

(broad, -$COOCH_2$-), 4.17 (broad, -$COOCH_2$-), 3.85 (broad, -OCH_2-), 3.52 (broad, -OCH_2-), 1.91 (broad, CH_3). The relative molar ratio of x:y was evaluated by comparison of ^{1}H NMR integrals for the signals at 7.42 and 4.23–3.52 ppm and calculated as about 60:40.

GPC (RI): $M_n = 71\ 100$, $M_w = 135\ 000$, PD = 1.90.

Characterization of ***Mod3***. GPC (RI): $M_n = 20\ 300$, $M_w = 40\ 900$, PD = 2.01. T_g (second scan): 100°C.

The starting molar ratio of polymers **1** and **4** and intermediates **2**, **3**, and **5** was 1:1. However, in the resulting polymer products **P1**, **Mod1**, and **Mod2**, only 40, 30, and 60 mol. % of free COOH or OH groups were converted. Our efforts to enhance the conversion of these groups by both a prolongation of the reaction time and an increase of the amount of precursors **2**, **3**, and **5** in the starting reaction mixture were not successful. For **P1** and **Mod4**, the enhanced amount of precursors **2** and **6** in the starting reaction mixture led to the crosslinking process in the polymers obtained. The measured characteristics of polymers **P1**, **M1**-**M4** are summarized in Table 1.

2.3. *Samples and IR Measurements*

The polymers were dissolved in dimethylformamide (DMF) at a concentration of 2 wt.% and filtered to 0.2 μm by a syringe filter. The polymer films were obtained by the spin coating of polymer solutions on the polished NaCl plates and the subsequent backing at 100°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 a Perkin Elmer Spectrum BX FTIR spectrometer. As a reference, the NaCl window was used. All spectral manipulations such as the baseline correction, smoothing, and normalization were performed using a standard software package of the spectrometer.

3. Results and Discussion

The fragments of FTIR absorption spectra of **P1** measured before and after UV irradiation are shown in Figure 4 in the "finger-print" spectral range of 950–1900 cm^{-1}. For the purpose of this paper, we limited ourselves by this spectral range only; the specific features of the high-frequency IR spectral range containing characteristic absorption bands of CH and OH stretching vibrations will be discussed elsewhere. While making the assignment of absorption bands, we mainly focused on the bands related to vibrations of the molecular groups sensitive to the photochemical transformations discussed above. We expected that Fries rearrangements do significantly change the vibration bands of arylamide (Ar-NH-C=O) and arylester (Ar-O-C=O) groups, while the photopolymerization modifies the vibration bands related to C=CH_2 fragments. Thus, the characteristic vibrations of these molecular groups were especially thoroughly identified. For this purpose, first of all, we used literature data [17,18]. However, because of a quite complicated structure of **P1**, it was difficult to make the unequivocal assignment for a number of absorption bands. To give the unambiguous assignment, a preliminary assignment based on

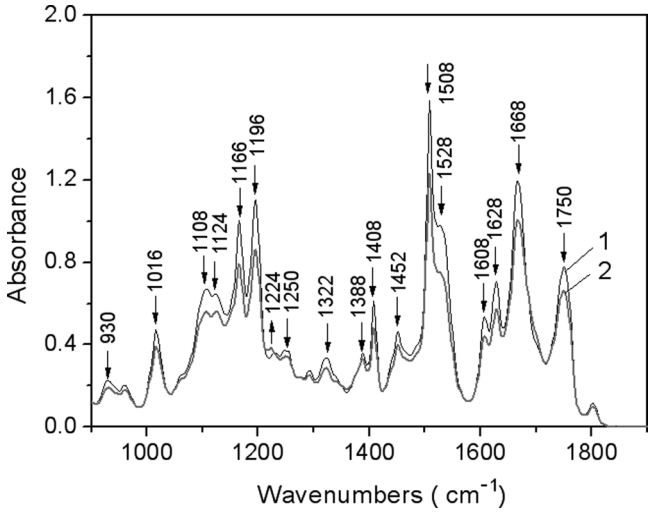

Figure 4. FTIR spectrum of a **P1** film before (1) and after (2) UV irradiation (105 mW/cm^2, 30 min).

the literature data for related compounds was performed more exactly, by comparing the FTIR spectrum of **P1** with the spectra of model polymers **Mod1**–**Mod4**, poly(methacrylic acid) (initial polymeric compound **1** in Fig. 3) and some monomer analogues such as (4-methacryloylamino)phenol (intermediate compound **2** in Fig. 3), (4-methacryloylamino)phenyl methacrylate, and itaconic acid.

3.1. *IR Spectra before Irradiation*

It is well known that the characteristic absorption bands of the amide fragment Ar-NH-CO include the bands named Amide I (ν(C=O)), Amide II (ν (C-N) + δ(C-N-H)), and Amide III (δ(NH) + δ(OCN)) [17, 18]. IR absorption spectra of **P1** and **Mod1** compounds exhibit the Amide I strong band centered at 1668 and 1666 cm^{-1}, respectively. In **Mod1**, the Amide II and Amide III vibration bands of Ar-NH-CO(CH_3) group were identified at 1555 and 1316 cm^{-1}, respectively. The Amide II band in **Mod2** was found at 1534 cm^{-1}. In the **P1** compound with α,β-unsaturated amide fragment Ar-NH-CO(C=CH_2), the peak positions of Amide II and Amide III bands are at 1528 and 1322 cm^{-1}, respectively. In **Mod3** and **Mod4** having no amide groups, Amide I-III bands are not found.

The characteristic absorption band of the arylester (Ar-O-C=O) fragment is carbonyl stretching ν(C=O). Because **P1**, **Mod1**, and **Mod3** have most similar structures of arylester (Ar-O-C=O) fragments, the peak positions of ν(C=O) vibrations of these fragments in the mentioned polymers are close, namely at 1750, 1758, and 1746 cm^{-1}. According to [17], 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 **P1**, the corresponding bands were found at 1196 and 1166 cm^{-1}. Such an assignment was proven by a comparison of the **P1** spectrum with the spectra of **Mod1** and **Mod3** having similar arylester structures and thus similar positions of characteristic bands (at 1194 and 1167 cm^{-1} in **Mod1** and at 1193 and 1160 cm^{-1} in **Mod3**).

Table 2. Assignment of the IR absorption bands in the IR spectra of **P1** and **Mod1-Mod4** compounds to vibrations of the structural elements responsible for photochemical transformations

Material code	Amide I, cm^{-1}	Amide II, cm^{-1}	Amide III, cm^{-1}	C=O in Ar-O-C=O, cm^{-1}	C=C in CH_2=C(CH_3)CO, cm^{-1}
P1	1668	1528	1322	1750	1628, 930
Mod1	1666	1555	1316	1758	*
Mod2	overlapped	1534	1311	1719	*
Mod3	*	*	*	1746	*
Mod4	*	*	*	1722	1637, 945

*Corresponding group is absent.

To identify the absorption bands corresponding to ν(C=C) vibrations of C=CH_2 fragment which are foreseen in the literature in the 1680–1620-cm^{-1} region, we have compared the IR spectra of **P1** (structural element $\underline{CH_2=C}(CH_3)$CO-NHAr) and **Mod4** (structural element $\underline{CH_2=C}(CH_3)$CO-OCH_2) with the IR absorption spectrum of itaconic acid (structural element $\underline{CH_2=C}(CH_2)$CO-OH). In the latter spectrum, the band centered at 1625 cm^{-1} can be attributed to the C=C stretching vibration. In the spectrum of **P1**, this band exhibits almost the same position (1628 cm^{-1}), whereas it is shifted by 9 cm^{-1} in the spectrum of **Mod4** toward higher wave numbers. In the model monomer (4-methacryloylamino)phenyl methacrylate, this band is centered at 1622 cm^{-1}. The other band which could be attributed to C=CH_2 fragment in the **P1** spectrum is centered at 930 cm^{-1} and appears due to the δ(C-H) vibration. Indeed, according to [18], this kind of vibrations for the CH_2=C-C=O conjugated systems has a band in the region 930–945 cm^{-1}. The corresponding band was also found in **Mod4** and in (4-methacryloylamino)phenyl methacrylate at 945 cm^{-1} and 930 cm^{-1}, respectively. No absorption bands in this region were detected in the spectra of **Mod1** and **Mod2** having no CH_2=C-C=O groups. The characteristic absorption bands related to arylamide (Ar-NH-C=O), arylester (Ar-O-C=O), and C=CH_2 groups of **P1** and **Mod1-Mod4** are summarized in Table 2.

The other set of pronounced bands of the IR spectrum of **P1** with the peaks at 1608, 1508, and 1452 cm^{-1} is related to ν(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 **M1-M4** homologues containing substituted benzene rings and are absent in poly(methacrylic acid) bearing no aromatic groups.

Such bands of the **P1** FTIR spectrum as those at 1408, 1388, 1250, 1124, and 1108 cm^{-1} could be only preliminarily assigned employing the literature data and the original IR spectrum of poly(methacrylic acid). The bands centered at 1408 and 1388 cm^{-1} could be assigned to skeleton δ(C-H) vibrations of CH_2 and C-CH_3 groups of the main polymer chain and C-CH_3 in methacrylic or acetic groups. The complex band centered at around 1250 cm^{-1} could be assigned to a combination of ν(C=O) and δ(O-H) vibrations of residual COOH groups predicted in the region 1330–1200 cm^{-1} [18]. Finally, the bands centered at 1124 and 1108 cm^{-1} could be assigned to δ(C-H) vibrations of the aromatic part of **P1** molecules.

Table 3. Peak positions of main IR absorption bands and their assignment to vibrations of selected structural elements of **P1**

Structural element	Peak position, cm^{-1}		Assignment
	Experimental	Ref [17,18].	
Ar-NH-C=O	**1668**	1680–1630	Amide I, ν (C=O)
	1528 (as a shoulder at 1508)	1570–1515	Amide II, ν (C-N) + δ(C-N-H)
	1322	1330–1200	Amide III, δ(NH) + δ(OCN)
Ar-O-C=O	**1750**	1750–1735	ν (C=O)
	1196 and **1166**	1200 and 1150–1100	ν (COC)
Aryl	**1608**	1600–1585	ν (C=C)
	1508, 1452	1500–1430	ν (C=C)
C=CH$_2$	**1628**	1680–1620	ν (C=C)
	930	930–945	δ(C-H)

Note: ν - stretching, δ - deformational vibrations.

Surprisingly, the band centered at 1016 cm^{-1} is of a significant intensity only in the spectra of **P1** and **Mod1**. In contrast, in the spectra of model polymers **Mod2-Mod4** and (4-methacryloylamino)phenyl methacrylate, this band has a minor intensity. The origin of this band is unclear at this stage of research.

Thus, the comparison of the IR absorption spectra of **P1** and those of model polymers **Mod1-Mod4** allowed us to make assignment for the majority of strong absorption bands of the **P1** polymer. These data are summarized in Table 3. 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, the FTIR spectra of **P1** and model polymers **M1-M4** before and after UV irradiation were compared. As was expected, the changes of the vibration bands attributed to Ar-O-C=O fragments were observed in the spectrum of **P1**. Namely, the intensity of the following bands is decreased: the ester ν(C=O) stretching band centered at 1750 cm^{-1} and ν(C-O) vibration bands centered at 1196 cm^{-1} and 1166 cm^{-1}(see Fig. 4). Such a behavior of the bands attributed to the ester groups was interpreted as a result of the Fries rearrangement [19], whose contribution to the photoinduced ordering in cinnamate polymers was earlier discussed [20]. In addition, a new band centered at 1224 cm^{-1} appeared after irradiation. It can be assigned to δ(C-O) stretching vibration (theoretically predicted in the region 1260–1180 cm^{-1}) of the phenol Ar-OH structure formed as a product of the Fries rearrangement. Such an assignment is supported by the fact that, in the model compound (4-methacryloylamino)phenol containing Ar-OH group (intermediate **2** in Fig. 3), the δ(C-O) vibration band has a quite similar position (peak is located at 1214 cm^{-1}).

Among the model polymers capable to the Fries rearrangement in the arylester fragment, the most pronounced changes in the absorption bands related to this fragment were observed for **Mod3**. In this polymer capable to only the Fries reaction in the ester Ar-O-C=O group (see Fig. 2), the significant weakening and broadening of the ν(C=O) stretching vibration band centered at 1746 cm^{-1} were recognized after irradiation. Additionally, a considerable decrease in the intensity of the ν(C-O) vibration bands centered at 1196 cm^{-1} and 1166 cm^{-1} was observed.

The changes were also detected for the characteristic vibration bands of the arylamide fragment Ar-NH-C=O sensitive to the second Fries rearrangement (see Fig. 1). The Amide I band of **P1** displays a decrease in the intensity and a slight broadening after UV illumination. This might be caused by the formation of new o-oxiketone and o-amino ketone structures demonstrating ((C=O) vibrations in the 1800–1650-cm^{-1} region [17]. So, the initial ester and Amide I bands start to broad and aspire to overlap under illumination due to the formation of o-oxiketone and o-aminoketone ν(C=O) stretching vibration bands with peak positions almost in the same spectral region. In the IR spectra of **P1,** the Amide II band centered at 1528 cm^{-1} and Amide III band centered at 1322 cm^{-1}, similarly to Amide I vibration band, reduce their intensity after UV illumination. Because the Amide II and Amide III bands do not overlap with other bands formed in the course of irradiation, they are more useful than the Amide I band for monitoring the Fries rearrangement in the arylamide part of a **P1** macromolecule.

Photopolymerization of $C=CH_2$ groups is also evident from the IR spectra of irradiated **P1**: photo-sensitive absorption bands centered at 1628 cm^{-1} and 930 cm^{-1} reduce their intensities. It is worth mentioning that an even more drastic decrease in the intensity of these bands was observed for the **P1** samples doped with 3 wt.% of a photoinitiator Irgacure 907 causing the efficient photopolymerization of $C=CH_2$ groups.

The photoinduced changes of the vibration bands of $C=CH_2$ groups of **Mod4** centered at 1637 cm^{-1} and 945 cm^{-1} are very similar; both of these bands practically vanish after irradiation. Since any Fries transformations are excluded in this polymer (see Fig. 2), the observed changes are fully due to the polymerization of $C=CH_2$ groups.

Finally, it is worth noting some additional facts supporting our interpretation. All photoinduced changes detected in **P1** and model compounds are well reproducible and monotonically increase with the exposure dose, which excludes any artifacts. The changes observed in **P1** compound obtained by the polymer analogous reaction (see Section 2.2) were completely reproduced in the polymer with a very similar structure obtained via the direct selective polymerization of (4-methacryloylamino)-phenyl methacrylate. The latter compound has $C=CH_2$ group in each monomer unit so that the concentration of these polymerizable groups is maximized. After UV irradiation, this polymer practically completely lost unsaturated $C=CH_2$ groups that became apparent in vanishing the 940-cm^{-1} IR absorption band.

4. Conclusions

In summary, FTIR spectroscopy is employed to study photochemical transformations in poly(p-methacryloylaminophenyl methacrylate) **P1** (Fig. 1) with a pronounced liquid crystal photoalignment capability. The IR absorption bands corresponding to vibrations of arylamide (Ar-NH-C=O) and arylester (Ar-O-C=O) groups undergoing

the Fries transformations, and those characteristic of $C{=}CH_2$ vibrations in methacrylic groups undergoing the polymerization, were identified, by using the data available from the literature and gained from the comparison of the FTIR spectra of **P1** with the spectra of model compounds having a simplified structure. The Amide II and Amide III absorption bands centered at 1528 cm^{-1} and 1322 cm^{-1}, respectively, are concluded to be the most convenient bands for monitoring the Fries rearrangement in the arylamide fragment. The absorption band centered at 1196 cm^{-1} and originated from deformation vibrations of bridging oxygen in C-O-C=O group and a new band centered at 1224 cm^{-1} are useful for monitoring the Fries reaction in the ester part of a **P1** molecule. To monitor the polymerization of $C{=}CH_2$ groups, the IR absorption bands centered at 1628 cm^{-1} and 930 cm^{-1} (δ(C-H)) could be employed. The changes observed in the FTIR spectra after UV irradiation suggest that both Fries rearrangements and the polymerization of unsaturated $C{=}CH_2$ bonds occur in the studied polymer, which confirms the hypothesis earlier formulated on the basis of results of UV/Vis spectroscopy [16]. This allows us to refine the model of LC photoalignment developed in this paper.

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