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Fast synthesis employing a microwave assisted neat protocol of new monomers potentially useful for the preparation of PDLC films

Invited Paper

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Abstract: It has been reported that the length of the molecular chain and the rigidity of molecules influence the structure of the polymer network in PDLC films and hence the electro-optical properties of the composites. Herein, a series of new aromatic monomeric monomethacrylates, bismethacrylates and monovinylbenzene derivatives with a mesogenic core were successfully synthesized under microwave irradiation. The microwave assisted synthesis resulted in decreased reaction times, reduced solvent requirement, increased operational simplicity, and in most cases, improved yields and selectivity.

Keywords: *Monomers synthesis • Microwave irradiation • Solventless reactions • Liquid crystals • PDLC films*

1. Introduction

In the advanced materials field, liquid crystal - polymer composites have been widely studied in the last two decades for potential applications such as switchable windows, displays, color projectors, and other electro–optical systems [1-3] which are useful in the design of integrated optical structures and devices. Polymer dispersed liquid crystal (PDLC) films consist of micron-sized nematic liquid-crystal (LC) droplets dispersed in a polymeric matrix [4]. Polymers used for PDLC preparation should exibit [5]: transparency greater than 95% for layers with thickness of about 10 μm, high adhesion ability to the designed substrates (glass or polymer), chemical stability and inertion to the liquid crystal material, and surface properties enforcing nucleation of LC droplets close to a spherical shape. Thus, the microstructure of the polymer network seriously affects their electro-optical properties [6-8].

The literature on this topic contains a limited variety of monomers for applications in PDLC films. We found that the synthetic work in the field were mainly dedicated to the preparation of mesogenic compounds to be incorporated into the polymer matrix, but the polymer chemistry side of the common PDLC films remained unexplored.

One of the key-points in designing a new polymeric material for PDLC preparation is the stabilization of the liquid crystal domains. In fact the electro-optical properties and hence the possible marketing of such devices is deeply influenced by the integrity of the films over a long period of time. One possible approach toward this stabilization uses a comonomer with the same mesogenic unit as the liquid crystal mixture used for the preparation of PDLC films [9]. Therefore, the focus of this article is on the design and synthesis of a number of photo- and thermo-polymerisable monomers, mimicking some structural elements of the LC, a multicomponent nematic mixture E7 for better miscibility and compatibility. For this purpose a number of aromatic mono-and bi-methacrylates, as well as mono-vinylbenzenes, have been synthesized. We have developed mild and solvent-free procedures, with reaction times as short as 1 to 5 min, using microwave (MW) irradiation [10] and which, in many cases, appears to be a more selective affording higher yields compared to classical thermal heating [11]. Microwave-enhanced chemistry is based on the efficient heating of materials by “microwave dielectric heating” effects. This phenomenon is dependent on the ability of dipolar materials (solvent or reagent) to absorb microwave energy and convert it into heat (tan δ). A reaction medium with a high tan δ factor is required for efficient absorption and, consequently, for rapid heating [12].

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To the best of our knowledge, the MW-assisted formation of aromatic methacrylic mono- and diesters, and aromatic vinylbenzyl ethers by the protocols described in this article, has not yet been reported.

Aromatic methacrylates are highly reactive monomers due to the presence of aromatic ring and thus form an interesting class of polymers. Poly(phenyl methacrylates) possess high tensile strength, high thermal stability and high glass transition temperatures. Therefore, they find wide applications in the preparation of materials such as photo luminescent [13], photo resist [14], adhesives for leather [15], photosensitive [16], biomaterials [17], optical telecommunication materials [18] and polymer supported catalyst [19], *etc*. Based on this information we have developed the synthesis of a library of compounds with distinct structural features: monomethacrylated monomers (Fig. 2); bis-methacrylated monomers (Fig. 3); methacryl esters and amides with spacer arms (Fig. 5); and vinylbenzenoyl derivatives (Fig. 6).

A number of photo- and thermo-polymerisable monomers, **1-27** (Figs. 2-6), have been designed to mimic some structural elements of the LC (E7, Fig. 1) [20]. In order to achieve better miscibility during preparation of PDLC-films, as well a possible control on the LC microdroplets size, and hence on their electro-optical properties, several monomers containing aromatic systems and nitrile groups were synthesized.

Esterification is one of the most general and widely used reactions in organic chemistry. A well-known conventional procedure for synthesis of aromatic methacryl esters and amides is from the corresponding phenol or amine and methacryl chloride in the presence of a base, usually triethylamine (Schemes 1,2; Tables 1,2) [21].

The syntheses have been achieved using a Microwave Synthetic Reactor under mild and solventless procedures, in short reaction times. The monomode reactor is preferentially used in chemistry due to wave focusing (reliable homogeneity in the electric field) and thus accurate control of the temperature throughout the reaction with the possibility of operating with similar temperature profiles in different experiments.

The protocol employed consisted in placing equivalent amounts of the corresponding reagents in a quartz tube, which was then subjected to microwave irradiation at 200 W and reaction times indicated in Tables 1-5. The reaction time was optimized by following the reactions by TLC every 1 min and stopped when no starting material remained.

After completion, the reaction was allowed to cool down to room temperature and after work up, the product was purified by flash column chromatography.

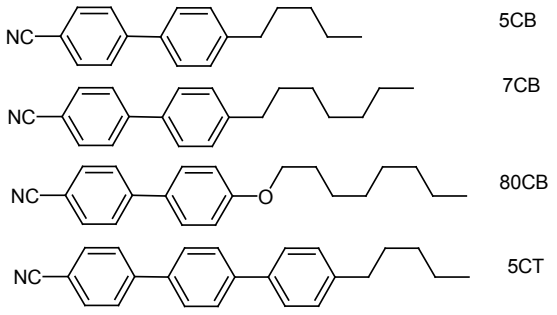


Figure 1. Structures of the components of the nematic liquid crystal mixture E7.

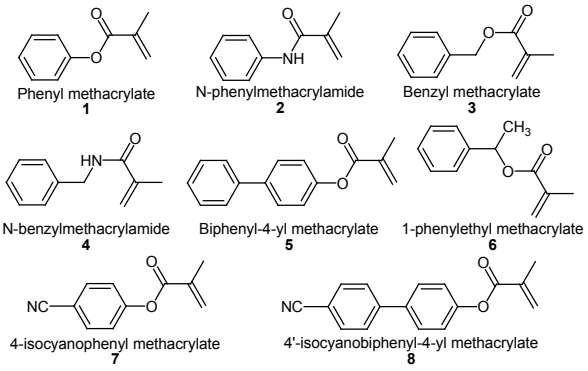


Figure 2. Monomethacrylated monomers.

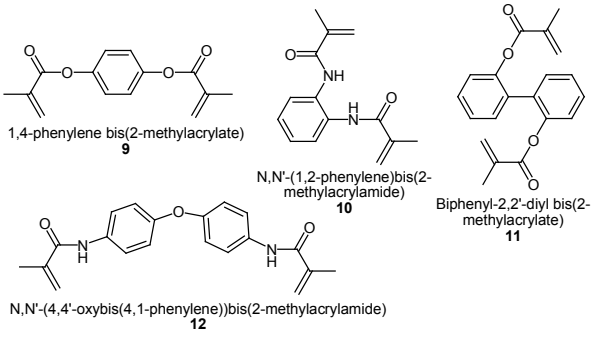


Figure 3. Bis-methacrylated monomers.

The experimental conditions and results are listed in Tables 1-5. The structure and purity of all isolated compounds were proven by ^{1}H and ^{13}C NMR, DEPT, COSY, HMQC, FTIR, elemental analyses and melting point (see Supplemental Information).

Five-carbon spacer arm was introduced to the structures **13-24** to increase the flexibility (Scheme 3) and this was carried out as follows. To a mixture of the substrate (mono or bi-phenol) and K_2CO_3 in the minimum amount of DMF necessary to homogenize the reaction mixture, was added 1,5-dibromopentane, and the mixture was subjected to MW irradiation to produce the bromo derivative, after purification. This intermediate was added to an equimolar mixture of K_2CO_3 and methacrylic acid in DMF, and then subjected to MW irradiation using a preprogrammed potency/

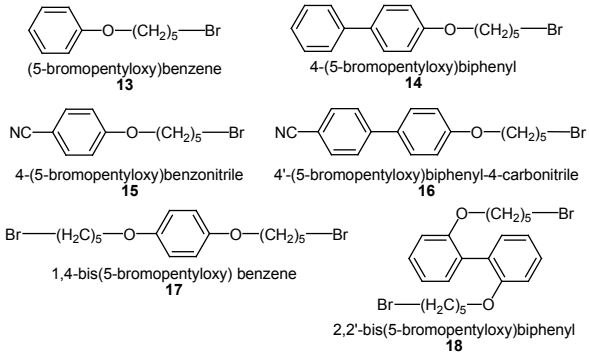


Figure 4. Br-intermediates with spacer arm.

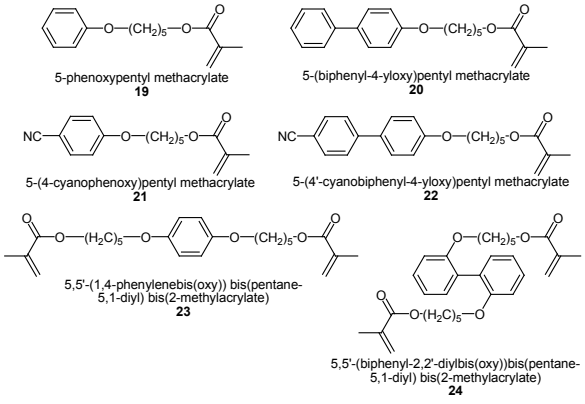


Figure 5. Methacryl esters and amides with spacer arm.

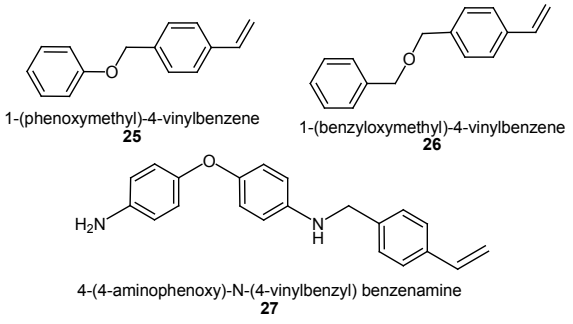
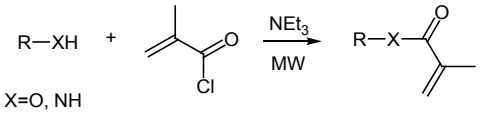


Figure 6. Monovinylbenzene monomers.

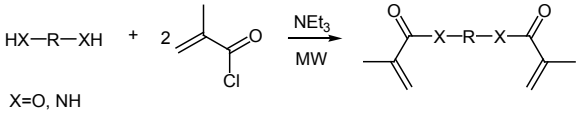
time protocol (Tables 3, 4). During this procedure it was necessary to add a small amount of DMF as solvent (1 mL) because both reagents were solid compounds. DMF was chosen because of its dipolar nature and ability to dissolve the starting compounds and the products of the reactions coupled with a comparatively high boiling point (153°C).

For the reaction of vinylbenzenes the common method is by treating the corresponding substrate with sodium hydride, and then adding the 4-vinylbenzyl chloride (Scheme 4; Table 5) [22].

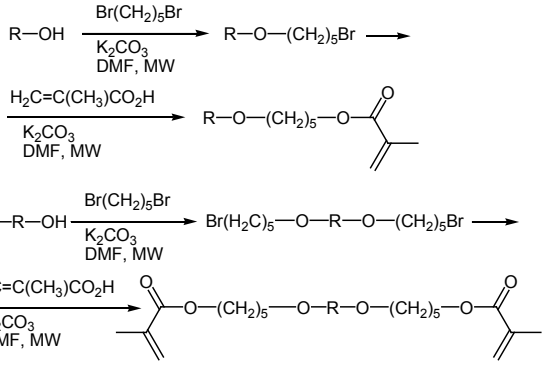
In some of the examples we have applied the method to obtain known compounds, as in the case of compounds **1** [23], **2** [24], **3** [23], **5** [25], **6** [26], **7** [27]



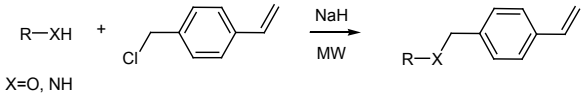
Scheme 1. General scheme for the synthesis of monomethacrylated monomers from the corresponding phenols or amines.



Scheme 2. General scheme for the synthesis of bismethacrylated monomers.



Scheme 3. General scheme for the synthesis with introducing of spacer arm between the aromatic system and the methacrylate group.



Scheme 4. General scheme for the synthesis of monovinylbenzene monomers.

and **14** [28]. Some others have been mentioned in the chemical literature, but were lacking full characterization, which have been provided here, as **4** [29], **9** [30], **10** [25], **11** [31], **13** [32], **15** [33], **16** [34], **25** [35], **26** [36]. The compounds **8, 12, 17, 18, 19, 20, 21, 22, 23, 24** and **27** were new compounds.

The experimental results showed that microwave irradiation efficiently promoted the reactions and the reaction times were remarkably shortened. In some cases, as compounds **12** and **27,** the faster heating favoured side reactions and/or steric hindrance, resulting in decreased yields. The procedures for introducing the 5-C spacer unit (Tables 3 and 4) proceeded smoothly with phenols, but the formation of vinylbenzyl monomers (Table 5) took place accompanied with side reactions, and resulted in comparatively lower yields. In this case, the highest yield achieved was for the monomer **26** (64%).

Table 1. Monomethacrylated monomers: 1 eq CH_2=C(CH_3)COCl, 2 eq Et_3N, MW 200 W.

Product	Substrate	Reaction time [min]	Yield [%]
1	Phenol	1	95
2	Aniline	5	70
3	Benzyl alcohol	1	96
4	Benzylamine	5	68
5	4-Phenylphenol	1	76
6	1-Phenylethanol	5	49
7	4-Cyanophenol	2	70
8	4'-Hydroxy-4-biphenylcarbonitrile	1	88

Additionally, in Table 6 we have compared the microwave conditions with classical synthetic methods found in the literature, for the compounds **2, 5, 6, 7** and **14**. When using microwave irradiation, the yields obtained were not always higher, but once again, the results highlight the efficiency of microwave irradiation to promote chemical reactions and to reduce reaction time from hours to minutes.

In summary, we have provided a simple and effective method for the synthesis of structurally diverse functionalized monomers. The general approach to synthesize a diverse compound collection from a common substrate with different reagents provided efficient access to collections of small molecules bearing double bond to be screened as monomers for obtaining new type of PDLC films.

2. Experimental Procedure

2.1. General Methods

Reagents and solvents were purified before use [38] NMR spectra were recorded at 400 MHz on a Bruker AMX-400 instrument in $CDCl_3$ with chemical shift values (δ) reported in ppm downfield from TMS. FTIR spectra were recorded on Perkin-Elmer Spectrum BX apparatus in KBr dispersions. The reactions were performed using a MicroSynth Labstation (MileStone, USA) in open flasks, equipped with a temperature control sensor and under magnetic stirring [39]. The reactions were followed by TLC every 1 min and stopped when no starting material was observed or undesired products started to form.

2.2. Monomers Synthesis

2.2.1. Synthesis of monomethacrylated monomers 1-8

To 1.000 g of the corresponding phenol or amine under Ar were added 2 eq triethylamine. The mixture was cooled to 0°C in an ice bath, and 1 eq methacryl chloride was added slowly. The reaction mixture was placed in the microwave cavity, and subjected to MW irradiation of 200 W for the required time (Table 1). After that the mixture was dissolved in CH_2Cl_2 and washed with water to neutral pH. The organic phase was dried, filtered, and concentrated. The residue was purified by flash column chromatography with hexane/ethyl acetate (gradient from 1:1 to 1:2) to afford monomers **1, 2, 3** and **4** and (gradient from 5:1 to 1:1) to afford monomers **5, 6, 7** and **8**.

Table 2. Bis-methacrylated monomers: 2 eq CH_2=C(CH_3)COCl, 4 eq Et_3N, MW 200 W.

Product	Substrate	Reaction time [min]	Yield [%]
9	Hydroquinone	1	85
10	1,2-Phenylenediamine	1	80
11	2,2'-Biphenol	1	86
12	4,4'-Oxydianiline	3	40

Table 3. Introducing of spacer arm between the aromatic system and the methacrylate group – synthesis of Br-intermediates: $Br(CH_2)_5Br$, K_2CO_3, DMF, MW 200 W.

Product	Substrate	Reaction time [min]	Yield [%]
13	Phenol	5	81
14	4-Phenylphenol	3	79
15	4-Cyanophenol	5	70
16	4'-Hydroxy-4-biphenylcarbonitrile	2	75
17	Hydroquinone	5	50
18	2,2'-Biphenol	5	62

Phenyl methacrylate 1

1.64 g, 95%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.39 (t, *J* = 7.9 Hz, 2H, Ar-*H*), 7.23 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.12 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 6.35 (s, 1H, C*H$_{2a}$*), 5.75 (s, 1H, C*H$_{2b}$*), 2.06 (s, 3H, C*H$_3$*). ^{13}C-RMN ($CDCl_3$) δ 165.8 (*C*=O), 150.9 (*C$_q$*-Ar), 135.9 (*C$_q$*), 129.4 (*C*-Ar), 127.1 (*CH$_2$*=), 125.7 (*C*-Ar), 121.6 (*C*-Ar), 18.4 (*CH$_3$*). White oil. The data were according to Aldrich® (reference 392162-15 mL).

N-phenylmethacrylamide 2 [24]

1.21 g, 70%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.56 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.36-7.30 (m, 2H, Ar-*H*), 7.14-7.09 (m, 1H, Ar-*H*), 5.79 (s, 1H, C*H$_{2a}$*), 5.45 (s, 1H, C*H$_{2b}$*), 2.06 (s, 3H, C*H$_3$*). ^{13}C-RMN ($CDCl_3$) δ 166.6 (*C*=O), 140.9 (*C$_q$*=), 137.8 (*C$_q$*-Ar), 129.0 (*C*-Ar), 124.4 (*C*-Ar), 120.0 (*CH$_2$*=), 119.8 (*C*-Ar), 18.7 (*CH$_3$*). FTIR (NaCl, cm^{-1}): ν 3290 (NH), δ 1595 (NH), γ 891(NH), ν 1660 (C=O), ν 1620 (CH_2=C) and 1494 (aromatic C=C), ν 1436 (C-N), ν 1373 (CH_3). White solid, mp: 180-189ºC. Anal. Calcd for $C_{10}H_{11}NO$: C,73.92; H,6.96; N,8.61. Found: C,74.01; H,6.88; N,8.69. The data were corresponding to the literature [24].

Table 4. Synthesis of methacryl esters with spacer arm: $CH_2=C(CH_3)CO_2H$, K_2CO_3, DMF, MW 200W.

Product	Substrate	Reaction time [min]	Yield [%]
19	13	5	70
20	14	1	75
21	15	5	65
22	16	1	65
23	17	5	85
24	18	5	68

Benzyl methacrylate 3

1.56 g, 96%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.34 (m, 5H, Ar-*H*), 6.16 (s, 1H, =C*H$_{2a}$*), 5.58 (s, 1H, =C*H$_{2b}$*), 5.19 (s, 2H, C*H$_2$*), 1.97 (s, 3H, C*H$_3$*). ^{13}C-RMN ($CDCl_3$) δ 167.2 (*C*=O), 136.2 (C_q-Ar), 136.1 (C_q), 128.5 (*C*-Ar), 128.1 (*C*-Ar), 127.9 (*C*-Ar), 125.7 (*C*H$_2$=), 66.3 (*C*H$_2$), 18.3 (*C*H$_3$). White oil. The data were according to Aldrich® (reference 409448-250 mL).

N-benzylmethacrylamide 4 [29]

1.11 g, 68%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.32 (m, 5H, Ar-*H*), 5.72 (s, 1H, =C*H$_{2a}$*), 5.35 (s, 1H, =C*H$_{2b}$*), 4.50 (d, *J* = 5.5 Hz, 2H, C*H$_2$*), 1.99 (s, 3H, C*H$_3$*). ^{13}C-RMN ($CDCl_3$) δ 168.3 (*C*=O), 139.8 (C_q), 138.2 (C_q-Ar), 128.7 (*C*-Ar), 127.8 (*C*-Ar), 127.5 (*C*-Ar), 119.7 (=*C*H$_2$), 43.7 (*C*H$_2$), 18.7 (*C*H$_3$). FTIR (NaCl, cm^{-1}): ν 3450 (NH), δ 1515 (NH), γ 736 (NH), ν 1667 (C=O), ν 1625 (CH_2=C) and (aromatic C=C), ν 1454 (CN), ν 1422 (CH_2), ν 1375 (CH_3). White solid, mp 79-84ºC. Anal. Calcd for $C_{11}H_{13}NO$: C,75.40; H,7.48; N,7.99. Found: C,74.94; H,7.60; N,8.15.

Biphenyl-4-yl methacrylate 5 [25]

1.15 g, 76%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.59 (dd, *J* = 10.6, 8.45 Hz, 4H, Ar-*H*), 7.44 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.36 (d, *J* = 7.3 Hz, 1H, Ar-*H*), 7.22 (t, *J* = 12.3 Hz, 2H, Ar-*H*), 6.38 (s, 1H, =C*H$_{2a}$*), 5.78 (s, 1H, =C*H$_{2b}$*), 2.09 (s, 3H, C*H$_3$*). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 165.9 (*C*=O), 150.3 (C_{qAr}-O), 140.4 (C_q-Ar), 138.9 (C_q=), 135.9 (C_q-Ar), 128.8 (*C*-Ar), 128.1 (*C*-Ar), 127.3 (*C*-Ar), 127.1 (*C*-Ar), 121.9 (=*C*H$_2$), 18.4 (*C*H$_3$). FTIR (NaCl, cm-1): ν 1734 (C=O), ν 1638 and 1485 (aromatic C=C), ν 1638 (CH_2=C), ν 1378 (CH_3), ν 1128 (C-O). White solid, mp:101-106ºC. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found C, 80.70; H, 6.05. The data were corresponding to the literature [37].

1-phenylethyl methacrylate 6 [26]

0.76 g, 49%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.31 (m, 5H, Ar-*H*), 6.16 (s, 1H, =C*H$_{2a}$*), 5.94 (q, *J* = 6.6 Hz, 1H, =C*H$_{2b}$*), 5.64-5.53 (m, 1H, C*H*), 1.96 (s, 3H, C*H$_3$*-C=), 1.57 (d, *J* = 6.6 Hz, 3H, C*H$_3$*-CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.6 (*C*=O), 141.9 (C_q-Ar), 136.6 (C_q=), 128.4 (*C*-Ar), 127.7 (*C*-Ar), 125.9 (*C*-Ar), 125.4 (*C*H$_2$=), 72.5 (*C*H), 22.3 (*C*H$_3$-CH), 18.4 (*C*H$_3$-C=). FTIR (NaCl, cm^{-1}): ν 1713 (C=O), ν 1637 and 1495 (aromatic C=C), ν 1637 (CH_2=C), ν 1378 (CH_3). White oil. Anal. Calcd for $C_{12}H_{14}O_2$: C, 76.17; H, 6.92. Found: C, 76.24; H, 7.07. The data were corresponding to the literature [26].

Table 5. Monovinylbenzene monomers: $CH_2=CHC_6H_4CH_2Cl$, NaH, DMF, MW 200W.

Product	Substrate	Reaction time [min]	Yield [%]
25	Phenol	1	63
26	Benzyl alcohol	2	64
27	4,4'-Oxydianiline	5	27

Table 6. Comparison between the results of the MW and conventional conditions described in the literature.

Nº	Reaction conditions	Yield [%]	Conventional conditions, reference	Yield [%]
2	200 W, 5 min	70	0°C for 1 h and r.t. for 4 h [24]	70
5	200 W, 1 min	76	0°C for 2 h and r.t. for 1 h [37]	70
6	200 W, 5 min	49	enzyme, r.t. [26]	50
7	200 W, 2 min	70	0°C for 2 h and r.t. for 1 h [27]	75
14	200 W, 3 min	79	Reflux for 20 h [28]	37

4-isocyanophenyl methacrylate 7 [27]

1.10 g, 70%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.71 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.30-7.25 (m, 2H, Ar-*H*), 6.38 (s, 1H, =C*H$_{2a}$*), 5.83 (s, 1H, =C*H$_{2b}$*), 2.07 (s, 3H, C*H$_3$*). ^{13}C NMR (100 MHz, *CDCl$_3$*) δ ppm 164.8 (*C*=O), 154.2 (C_{qAr}-O), 135.2 (C_q=), 133.7 (*C*-Ar), 128.4 (=*C*H$_2$), 123.6 (*C*-Ar), 118.2 (*C*N), 109.7 (C_{qAr}-CN), 18.2 (*C*H$_3$). FTIR (NaCl, cm^{-1}): ν 2232 (CN), ν 1736 (C=O), ν 1637 (CH_2=C), ν 1602 and 1451 (aromatic C=C), ν 1378 (CH_3), ν 1266 (C-O). Yellow solid, mp: 78-85ºC Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.45; H, 5.01; N, 7.35. The data were corresponding to the literature [27].

4'-isocyanobiphenyl-4-yl methacrylate 8

1.19 g, 88%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.69 (dd, J_1 = 8.19 Hz, J_2 = 23.74 Hz, 4H, Ar-*H*), 7.60 (d, *J* = 8.48 Hz, 2H, Ar-*H*), 7.24 (d, *J* = 8.51 Hz, 1H, Ar-*H*), 6.38 (s, 1H, =C*H$_{2a}$*), 5.80 (s, 1H, =C*H$_{2b}$*), 2.08 (s, 3H, C*H$_3$*). ^{13}C NMR (100 MHz, *CDCl$_3$*) δ ppm 165.7 (*C*=O), 151.4 (C_{qAr}-O), 144.7 (C_{qAr}-Ar), 136.7 (C_{qAr}-Ar), 135.6 (C_q=), 132.6 (*C*-Ar), 128.3 (*C*-Ar), 127.6 (*C*H$_2$=), 122.3 (*C*-Ar), 118.8 (*C*N), 110.9 (C_{qAr}-CN), 18.3 (*C*H$_3$). FTIR (NaCl, cm^{-1}): ν 2229 (NC), ν 1732 (C=O), ν 1608 and 1421 (aromatic C=C), ν 1320 (CH_3), ν 1169 (C-O). White solid, mp 124-129ºC Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32; O 12.15. Found: C, 77.70; H, 5.10; N, 5.43.

2.2.2. Synthesis of bis-methacrylated monomers 9-12

To 1.000 g of the corresponding biphenol or diamine under Ar were added 4 eq triethylamine. The mixture was cooled to 0°C in ice bath, and 2 eq methacryl chloride or anhydride was added slowly. The reaction mixture was placed in the microwave cavity, and subjected to MW irradiation of 200 W for the required time (Table 2). After that the mixture was dissolved in CH_2Cl_2 and washed with water to neutral pH. The organic phase was dried, filtered, and concentrated. The residue was purified by flash column chromatography with hexane/ethyl acetate (gradient from 1:1 to 1.2) to afford monomers **9, 12** and gradient from 5:1 to 1:1 to afford monomers **10, 11**.

1,4-phenylene bis(2-methylacrylate) 9 [30]

1.90 g, 85%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.14 (s, 4H, Ar-*H*), 6.34 (s, 2H, =C*H$_{2a}$*), 5.75 (s, 2H, =C*H$_{2a}$*), 2.05 (s, 6H, C*H$_3$*). ^{13}C NMR (100 MHz, *CDCl$_3$*) δ ppm 165.6 (*C*=O), 148.2 (*C$_{qAr}$*-O), 135.6 (*C$_q$*=), 127.3 (*C*H$_2$=), 122.3 (*C*-Ar), 18.3 (*C*H$_3$). FTIR (NaCl, cm^{-1}) ν 1736 (C=O), ν 1638 (CH$_2$=C) ν 1638 and 1502 (aromatic C=C), ν 1380 (CH$_3$), ν 1265 (C-O). White solid, mp: 86-93ºC. Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73.Found: C, 68,17; H 5.86.

N,N'-(1,2-phenylene)bis(2-methylacrylamide) 10 [25]

1.81 g, 80%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 8.86 (s, 2H, N*H*), 7.28 (dd, *J* = 5.75, 3.74 Hz, 2H, Ar-*H*), 7.07 (dd, *J* = 5.83, 3.56 Hz, 2H, Ar-*H*), 5.92 (s, 2H, =C*H$_{2a}$*), 5.48 (s, 2H, =C*H$_{2b}$*), 2.00 (s, 6H, C*H$_3$*). ^{13}C-RMN (CDCl$_3$) δ ppm 167.3 (*C*=O), 139.1 (*C$_q$*=), 130.6 (*C$_q$*-Ar), 125.9 (*C*-Ar), 125.7 (*C*H$_2$=), 121.8 (*C*-Ar), 18.5 (*C*H$_3$). FTIR (NaCl,cm^{-1}) ν 3419 (NH), δ 1509 (NH), γ 739 (NH), ν 1654 (C=O), ν 1626 and 1478 (aromatic C=C), ν 1626 (C=C), ν 1446 (C-N), ν 1375 (CH$_3$). Yellow solid, mp: 119-123ºC Anal. Calcd for: $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.75; H, 6.68; N, 11.53.

Biphenyl-2,2'-diyl bis(2-methylacrylate) 11 [31]

1.49 g, 86%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.19-7.39 (m, 8H, Ar-*H*), 6.02 (s, 2H, =C*H$_{2a}$*), 5.53 (s, 2H, =C*H$_{2b}$*), 1.83 (s, 6H, C*H$_3$*). ^{13}C NMR (100 MHz, *CDCl$_3$*) δ ppm 165.4 (*C*=O), 148.3 (*C$_{qAr}$*-O), 135.4 (*C$_q$*=), 131.1 (*C$_{qAr}$*-Ar), 128.8 (*C*-Ar), 126.9 (*C*H$_2$=), 125.6 (*C*-Ar), 122.2 (*C*-Ar), 18.1 (*C*H$_3$). FTIR (NaCl, cm^{-1}) ν 1734 (C=O), ν 1678 (CH$_2$=C), ν 1638 and 1504 (aromatic C=C), ν 1378 (CH$_3$), ν 1267 (C-O). White oil. Anal. Calcd for $C_{20}H_{18}O_4$:C, 74.52; H, 5.63. Found: C, 74.68; H, 5.69.

N,N'-(4,4'-oxybis(4,1-phenylene))bis(2-methylacrylamide) 12

0.67 g, 40%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ 7.72 ppm (d, *J* = 8.96 Hz, 4H, Ar-*H*), 6.95 (d, *J* = 8.97 Hz, 4H, Ar-*H*), 5.81 (s, 2H, =C*H$_{2a}$*), 5.45 (s, 2H, =C*H$_{2b}$*), 1.99 (s, 6H, C*H$_3$*). ^{13}C-RMN (CDCl$_3$) δ ppm 166.5 (*C*=O), 153.9 (*C$_{qAr}$*-O), 140.8 (*C$_q$*=), 133.1 (*C$_{qAr}$*-N), 121.8 (*C*-Ar), 119.8 (*C*H$_2$=), 119.2 (*C*-Ar), 18.7 (*C*H$_3$). FTIR (KBr, cm-1) ν 3281 (NH), δ 1529 (NH), γ 837(NH), ν 1663 (C=O) and (CH$_2$=C), ν 1625 and 1452 (aromatic C=C), ν 1371 (CH$_3$), ν 1226 (C-O). White solid, mp: 78-83ºC. Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.55; H, 6.04; N, 8.24.

2.2.3. Synthesis of brominated intermediates 13-18

To a suspension of 2 eq (mono-) or 4 eq K_2CO_3 (bi-substituted derivatives) in 1 mL DMF was added 1.000 g of the corresponding phenol, then 1 eq for mono- or 2 eq for bi-substituted derivatives of 1,5-dibromopentane was added slowly. Thus obtained mixture was subjected to MW irradiation of 200 W for the required time (Table 3). After that the reaction mixture was dissolved in diethyl ether, washed with dist. water, and the organic phase was dried, filtered and concentrated. The residue was purified by flash column chromatography with hexane/ethyl acetate (gradient from 5:1 to 1:1) to afford the compounds **13-18.**

(5-bromopentyloxy)benzene 13 [32]

2.09 g, 81%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.36-7.18 (m, 2H, Ar-*H*), 6.95-6.86 (m, 3H, Ar-*H*), 4.01-3.92 (m, 2H, C*H$_2$*-O), 3.46-3.41 (m, 2H, C*H$_2$*-Br), 1.97-1.89 (m, 2H, C*H$_2$*), 1.86-1.76 (m, 2H, C*H$_2$*), 1.67-1.57 (m, 2H, C*H$_2$*). ^{13}C NMR (100 MHz, *CDCl$_3$*) δ 159.0 (*C$_{qAr}$*), 129.4 (*C*-Ar), 120.6 (*C*-Ar), 114.4 (*C*-Ar), 67.4 (*C*H$_2$-O), 33.5 (*C*H$_2$-Br), 32.5 (*C*H$_2$), 28.4 (*C*H$_2$), 24.8 (*C*H$_2$). FTIR (NaCl,cm^{-1}) ν 1598 and 1473 (aromatic C=C), ν 1389(CH$_2$), ν 1171(C-O), ν 1152 (CH$_2$-Br). White oil. Anal. Calcd for $C_{11}H_{15}BrO$: C, 54.34; H, 6.22; Br, 32.86; Found: C, 54.40; H, 6.34; Br, 32.92.

4-(5-bromopentyloxy)biphenyl 14 [28]

1.60 g, 79%

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.52 (dd, *J* = 13.54, 8.06 Hz, 4H, Ar-*H*), 7.40 (t, *J* = 7.60 Hz, 2H, Ar-*H*), 7.28 (t, *J* = 7.30 Hz, 1H, Ar-*H*), 6.94 (d, *J* = 8.63 Hz, 2H, Ar-*H*), 3.98 (t, *J* = 6.29 Hz, 2H, C*H$_2$*-O), 3.40 (td, *J* = 16.62, 6.72 Hz, 2H, C*H$_2$*-Br), 2.01-1.88 (m, 2H, C*H$_2$*), 1.88-1.76 (m, 2H, C*H$_2$*), 1.59 (tdd, *J* = 14.97, 9.58, 7.64 Hz, 2H, C*H$_2$*). ^{13}C NMR (100 MHz, *CDCl$_3$*) δ ppm 158.5 (*C$_{qAr}$*-O), 140.8 (*C$_{qAr}$*-Ar), 133.6 (*C$_{qAr}$*-Ar), 128.7 (*C*-Ar), 128.1 (*C*-Ar), 126.6 (*C*-Ar), 114.7 (*C*-Ar), 67.58 (*C*H$_2$-O), 33.6 (*C*H$_2$-Br), 32.4 (*C*H$_2$), 28.4 (*C*H$_2$), 24.8 (*C*H$_2$). FTIR (NaCl, cm^{-1}): ν 1610 and 1519 (aromatic C=C), 1487 ν (CH$_2$), 1285 ν (CH$_2$-Br), 1246 ν (C-O). White solid, mp: 50-53ºC Anal. Calcd for $C_{17}H_{19}BrO$: C, 63.96; H, 6.00; Br, 25.03. Found: C, 64.00; H, 6.09, Br, 25.07. Which were corresponding to the literature [28].

4-(5-bromopentyloxy)benzonitrile 15 [33]
0.94 g, 70%
^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.58 (d, *J* = 8.57 Hz, 2H, Ar-*H*), 6.93 (d, *J* = 8.57 Hz, 2H, Ar-*H*), 4.02 (t, *J* = 6.25 Hz, 2H, C*H*$_2$-O), 3.45 (t, *J* = 6.65 Hz, 2H, C*H*$_2$-Br), 2.00-1.90 (m, 2H, C*H*$_2$), 1.89-1.79 (m, 2H, C*H*$_2$), 1.71-1.58 (m, 2H, C*H*$_2$). ^{13}C NMR (100 MHz, *CDCl$_3$*) δ ppm 162.2 (*C*$_{qAr}$-O), 133.9 (*C*-Ar), 119.2 (*C*N), 115.1 (*C*-Ar), 103.8 (*C*$_{qAr}$-CN), 67.9 (*C*H$_2$-O), 33.4 (*C*H$_2$-Br), 32.3 (*C*H$_2$), 28.1 (*C*H$_2$), 24.7 (*C*H$_2$). FTIR (NaCl, cm^{-1}) ν 2226 (NC), ν 1606 and 1508 (aromatic C=C), ν 1470 (CH$_2$), ν 1264 (C-O), ν 1172 (CH$_2$-Br). White solid, mp: 53-56ºC Anal. Calcd for $C_{12}H_{14}BrNO$: C, 53.75; H, 5.26; Br, 29.80; N, 5.22. Found: C, 53.79; H, 5.27; Br, 29.88; N, 5.20.

4'-(5-bromopentyloxy)biphenyl-4-carbonitrile 16 [34]
1.32 g, 75%
^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.60-7.54 (m, 4H, Ar-*H*), 6.94 (d, *J* = 8.33 Hz, 4H, Ar-*H*), 4.02 (t, *J* = 6.17 Hz, 2H, C*H*$_2$-O), 3.44 (t, *J* = 6.59 Hz, 2H, C*H*$_2$-Br), 2.01-1.89 (m, 2H, C*H*$_2$), 1.85 (td, *J* = 13.84, 9.30 Hz, 2H, C*H*$_2$), 1.65 (m, 2H, C*H*$_2$). ^{13}C NMR (100 MHz, *CDCl$_3$*) δ ppm 162.1 (*C*$_{qAr}$-O), 145.1 (*C*$_{qAr}$-Ar), 133.8 (*C*-Ar), 132.7 (*C*$_{qAr}$-Ar), 128.8 (*C*-Ar), 119.1 (*C*N), 115.1 (*C*-Ar), 103.6 (*C*$_{qAr}$-CN), 67.9 (*C*H$_2$-O), 33.4 (*C*H$_2$-Br), 32.2 (*C*H$_2$), 28.0 (*C*H$_2$), 24.6 (*C*H$_2$). FTIR (NaCl, cm^{-1}) ν 2226 (NC), ν 1604 and 1494 (aromatic C=C), ν 1472 (CH$_2$), ν 1265 (C-O), ν 1179 (CH$_2$-Br). White solid, mp 82-84ºC. Anal. Calcd for $C_{18}H_{18}BrNO$: C, 62.80; H, 5.27; Br 23.21; N, 4.07. Found: C, 62.78; H, 5.37; Br 23.29; N,3.97.

1,4-bis(5-bromopentyloxy)benzene 17
1.85 g, 50%
^{1}H NMR (400 MHz, *CDCl$_3$*) δ 6.82 (s, 4H, Ar-*H*), 3.92 (t, *J*=6.2 Hz, 4H, C*H*$_2$-O), 3.43 (q, *J*=6.9 Hz, 4H, C*H*$_2$-Br), 1.95-1.88 (m, 4H, C*H*$_2$), 1.80-1.75 (m, 4H, C*H*$_2$), 1.63-1.58 (m, 4H, C*H*$_2$).^{13}C NMR (100 MHz, *CDCl$_3$*) δ 153.1 (*C*$_{qAr}$-O), 115.4 (*C*-Ar), 68.2 (*C*H$_2$-O), 33.6 (*C*H$_2$-Br), 32.5 (*C*H$_2$), 28.6 (*C*H$_2$), 24.9 (*C*H$_2$). FTIR (NaCl, cm^{-1}) ν 1637 and 1508 (aromatic C=C), ν 1420 (CH$_2$), ν 1265 (C-O), ν 1170 (CH$_2$-Br). White solid, mp 94-99ºC Anal. Calcd for $C_{16}H_{24}Br_2O_2$: C, 47.08; H, 5.93; Br, 39.15; Found: C, 46.99; H, 6.00; Br, 39.19.

2,2'-bis(5-bromopentyloxy)biphenyl 18
1.61 g, 62%
^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.31-7.20 (m, 4H, Ar-*H*), 7.01-6.88 (m, 4H, Ar-*H*), 3.90 (t, *J* = 6.12 Hz, 4H, C*H*$_2$-O), 3.27 (t, *J* = 6.72 Hz, 4H, C*H*$_2$-Br), 1.80-1.68 (m, 4H, C*H*$_2$), 1.67-1.57 (m, 4H, C*H*$_2$), 1.41 (m, 4H, C*H*$_2$). ^{13}C NMR (100 MHz, *CDCl$_3$*) δ ppm 156.4 (*C*$_{qAr}$-O), 131.4 (*C*$_{qAr}$-Ar, *C*-Ar), 128.3 (*C*-Ar), 120.2 (*C*-Ar), 112.2 (*C*-Ar), 68.1 (*C*H$_2$-O), 33.8 (*C*H$_2$-Br), 32.2 (*C*H$_2$), 28.3 (*C*H$_2$), 24.8 (*C*H$_2$). FTIR (NaCl, cm^{-1}) ν 1637 and 1498 (aromatic C=C), ν 1443 (CH$_2$), ν 1266 (C-O), ν 1127 (CH$_2$-Br). White oil. Anal. Calcd for $C_{22}H_{28}Br_2O_2$: C, 54.56; H, 5.83; Br, 33.00; Found:C, 54.50; H, 5.49; Br, 33.04.

2.2.4. Synthesis of methacryl esters with spacer arm 19-24

1.000 g of the intermediates **13-18** were added slowly to equimolar mixture of K_2CO_3 and methacrylic acid in 1 mL DMF while stirring. The mixture was subjected to MW irradiation of 200W for the required time (Table 4). After that the reaction mixture was dissolved in diethyl ether and washed with dist. water. The organic phase was dried, filtered and concentrated. The residue was purified by flash column chromatography with hexane/ethyl acetate (gradient from 1:1 to 1:2) to afford monomer **19** and gradient from 5:1 to 1:1 to afford monomers **20-24**.

5-phenoxypentyl methacrylate 19
0.71 g, 70%
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.20 (m, 2H, Ar-*H*), 6.94-6.87 (m, 3H, Ar-*H*), 6.10 (s, 1H, C*H*$_{2a}$), 5.55 (s, 1H, C*H*$_{2b}$), 4.21-4.15 (m, 2H, C*H*$_2$-OOC), 3.99-3.95 (m, 2H, C*H*$_2$-OAr), 1.95 (s, 3H, C*H*$_3$), 1.87-1.80 (m, 2H, C*H*$_2$), 1.79-1.73 (m, 2H, C*H*$_2$), 1.62-1.55 (m, 2H, C*H*$_2$). ^{13}C NMR (100 MHz, *CDCl$_3$*) δ 167.4 (*C*=O), 159.0 (*C*$_{qAr}$-O), 136.4 (*C*$_q$=); 129.4 (*C*-Ar), 125.2 (*C*H$_2$=), 120.5 (*C*-Ar), 114 (*C*-Ar), 67.4 (*C*H$_2$-O), 64.5 (*C*H$_2$-OOC), 29.0 (*C*H$_2$), 28.3 (*C*H$_2$), 22.6 (*C*H$_2$), 18.3 (*C*H$_3$). FTIR (NaCl,cm^{-1}) ν 1637 (C=O), ν 1599 and 1454 (aromatic C=C), ν 1401 (CH$_2$), ν 1168(C-O). White oil, Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12; Found: C, 72.50; H, 8.04.

5-(biphenyl-4-yloxy)pentyl methacrylate 20
0.76 g, 75%
^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.53 (dd, *J* = 13.46, 8.05 Hz, 4H, Ar-*H*), 7.41 (t, *J* = 7.57 Hz, 2H, Ar-*H*), 7.29 (t, *J* = 7.24 Hz, 1H, Ar-*H*), 6.96 (d, *J* = 8.52 Hz, 2H, Ar-*H*), 6.11 (s, 1H, =C*H*$_{2a}$), 5.55 (s, 1H, =C*H*$_{2b}$), 4.19 (t, *J* = 6.49 Hz, 2H, C*H*$_2$-OOC), 4.01 (t, *J* = 6.29 Hz, 2H, C*H*$_2$-OAr), 1.95 (s, 3H, C*H*$_3$), 1.90-1.81 (m, 2H, C*H*$_2$), 1.81-1.71 (m, 2H, C*H*$_2$), 1.59 (m, 2H, C*H*$_2$). ^{13}C NMR (100 MHz, *CDCl$_3$*) δ ppm 167.5 (*C*=O), 158.6 (*C*$_{qAr}$-O), 140.8 (*C*$_{qAr}$-Ar), 136.4 (*C*$_q$=), 133.6 (*C*$_{qAr}$-Ar), 129.4 (*C*-Ar), 128.8 (*C*-Ar), 128.0 (*C*-Ar), 127.4 (*C*-Ar), 125.9 (*C*H$_2$=), 115.4 (*C*-Ar), 114.1 (*C*-Ar), 67.7 (*C*H$_2$-O), 64.5 (*C*H$_2$-OOC), 28.9 (*C*H$_2$), 28.4 (*C*H$_2$), 22.6 (*C*H$_2$), 17.8 (*C*H$_3$). FTIR (NaCl, cm^{-1}) ν 1710 (C=O), ν 1654 (CH$_2$=C), ν 1638 and 1518 (aromatic C=C), ν 1420 (CH$_2$), ν 1321 (CH$_3$), ν 1265 (C-O). White solid, mp: 30-34ºC. Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.86; H, 7.56.

5-(4-cyanophenoxy)pentyl methacrylate 21
0.66 g, 65%
^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.57 (d, *J* = 8.75 Hz, 2H, Ar-*H*), 6.94 (d, *J* = 8.75 Hz, 2H, Ar-*H*), 6.10 (s, 1H, =C*H*$_{2a}$), 5.56 (s, 1H, =C*H*$_{2b}$), 4.19 (t, *J* = 6.50 Hz, 2H,

CH_2-OOC), 4.02 (t, *J* = 6.30 Hz, 2H, CH_2-O), 1.95 (s, 3H, CH_3), 1.91-1.81 (m, 2H, CH_2), 1.81-1.72 (m, 2H, CH_2), 1.59 (dd, *J* = 15.31, 8.12 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, *CDCl$_3$)* δ ppm 167.3 (*C*=O), 162.1 (C_{qAr}-O), 136.3 (C_q=), 133.3 (*C*-Ar), 125.2 (=CH_2), 119.2 (*C*N), 115.0 (*C*-Ar), 109.9 (C_{qAr}-CN), 67.9 (CH_2-O), 64.3 (CH_2-OOC), 28.5 (CH_2), 28.2 (CH_2), 22.4 (CH_2), 18.8 (CH_3). FTIR (NaCl, cm-1) v 2226 (NC), v 1712 (C=O), v 1607 and 1508 (aromatic C=C), v 1421 (CH_2), v 1321 (CH_3), v 1266 (C-O). White solid, mp 41-50ºC. Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.41; H, 7.06; N, 5.14.

5-(4'-cyanobiphenyl-4-yloxy)pentyl methacrylate 22

0.66 g, 65%

^{1}H NMR (400 MHz, *CDCl$_3$)* δ ppm 7.65 (dd, *J* = 19.01, 8.16 Hz, 4H, Ar-*H*), 7.52 (d, *J* = 8.43 Hz, 2H, Ar-*H*), 6.98 (d, *J* = 8.44 Hz, 2H, Ar-*H*), 6.11 (s, 1H, =CH_{2a}), 5.56 (s, 1H, =CH_{2b}), 4.19 (t, *J* = 6.48 Hz, 2H, CH_2-OOC), 4.02 (t, *J* = 6.25 Hz, 2H, CH_2-O), 1.95 (s, 3H, CH_3), 1.92-1.82 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 1.60 (dd, *J* = 15.09, 7.99 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, *CDCl$_3$)* δ ppm 167.4 (*C*=O), 159.6 (C_{qAr}-O), 145.1 (C_{qAr}-Ar), 136.4 (C_q=), 132.44 (C_{qAr}-Ar, *C*-Ar), 131.2 (*C*-Ar), 128.2 (*C*-Ar), 127.0 (*C*-Ar), 125.2 ((=CH_2), 119.0 (*C*N), 115.0 (*C*-Ar), 109.9 (C_{qAr}-CN), 67.7 (CH_2-O), 64.4 (CH_2-OOC), 28.7 (CH_2), 28.3 (CH_2), 22.5 (CH_2), 18.2 (CH_3). FTIR (NaCl, cm^{-1}) v 2227 (NC), v 1711 (C=O), v 1604 and 1494 (aromatic C=C), v 1471(CH_2), v 1265 (C-O). White solid, mp 74-78ºC. Anal. Calcd for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.63; H, 6.62; N, 4.05.

5,5'-(1,4-phenylenebis(oxy))bis(pentane-5,1-diyl) bis(2-methylacrylate) 23

0.87 g, 85%

^{1}H NMR (400 MHz, *CDCl$_3$)* δ 6.81 (s, 4H, Ar-*H*), 6.10 (s, 2H, =CH_{2a}), 5.55 (s, 2H, =CH_{2b}), 4.20-4.14 (m, 4H, CH_2-OOC), 3.94-3.89 (m, 4H, CH_2-O), 1.94 (s, 6H, CH_3), 1.84-1.70 (m, 8H, CH_2), 1.60-1.53 (m, 4H, CH_2). ^{13}C-RMN ($CDCl_3$) δ 167.4 (*C*=O), 153.1 (C_{qAr}-O), 136.5 (C_q=), 125.2 (CH_2=), 115.4 (*C*-Ar), 68.3 (CH_2-O), 64.5 (CH_2-OOC), 29.0 (CH_2), 28.4 (CH_2), 22.6 (CH_2), 18.3 (CH_3). FTIR (NaCl, cm^{-1}) v 1716 (C=O), v 1636 and 1508 (aromatic C=C), v 1406 (CH_2), v 1165 (C-O). White oil. Anal. Calcd for $C_{23}H_{32}O_7$: C, 68.87; H, 8.19. Found: C, 68.80; H, 8.13.

5,5'-(biphenyl-2,2'-diylbis(oxy))bis(pentane-5,1-diyl) bis(2-methylacrylate) 24

0.70 g, 68%

^{1}H NMR (400 MHz, *CDCl$_3$)* δ ppm 7.25 (dd, *J* = 15.18, 7.40 Hz, 4H, Ar-*H*), 7.00-6.88 (m, 4H, Ar-*H*), 6.06 (s, 2H, =CH_{2a}), 5.53 (s, 2H, =CH_{2b}), 4.10-3.98 (m, 4H, CH_2-OOC), 3.90 (t, *J* = 6.21 Hz, 4H, CH_2-O), 1.92 (s, 6H, CH_3), 1.69-1.62 (m, 4H, CH_2), 1.62-1.52 (m, 4H, CH_2), 1.35 (m, 4H, CH_2). ^{13}C NMR (100 MHz, *CDCl$_3$)* δ ppm 167.3 (*C*=O), 156.4 (C_{qAr}-O), 136.4 (C_q=), 131.4 (C_{qAr}-Ar, *C*-Ar), 128.3 (*C*-Ar), 125.1 (CH_2=), 120.1 (*C*-Ar), 112.2 (*C*-Ar), 68.1 (CH_2-O), 64.5 (CH_2-OOC), 28.8 (CH_2), 28.2 (CH_2), 22.6 (CH_2), 18.2 (CH_3). FTIR (NaCl, cm^{-1}) v 1720 (C=O), v 1600 and 1503 (aromatic C=C), v 1636 (CH_2=C), v 1443 (CH_2), v 1359 (CH_3), v 1296 (C-O). White oil. Anal. Calcd for $C_{30}H_{38}O_6$: C, 72.85; H, 7.74. Found: C, 72.80; H, 7.70.

2.2.5. Synthesis of vinylbenzene monomers 25-27

To a cooled to 0°C in an ice bath mixture of 1.000 g of the corresponding phenol or amine with a catalytic amount of $Bu_4N^+I^-$ and 1 mL DMF, were added 2 eq NaH, and stirred under Ar. After 20 min were added 2 eq 1-(chloromethyl)-4-vinylbenzene slowly. The reaction mixture was placed in the microwave cavity, and subjected to MW irradiation of 200 W for the required time (Table 5). After that the mixture was dissolved in CH_2Cl_2, and washed with water to neutral pH. The organic phase was dried, filtered, and concentrated. The residue was purified by flash column chromatography with hexane/ethyl acetate (gradient from 1:1 to 1:2) to afford monomer **27** and gradient from 5:1 to 1:1 to afford monomers **25, 26**.

1-(phenoxymethyl)-4-vinylbenzene 25 [35]

1.41 g, 63%

^{1}H RMN (400 MHz, *CDCl$_3$)* δ ppm 7.41 (q, *J* = 8.21 Hz, 4H, Ar-*H*), 7.28 (m, 2H, Ar-*H*), 6.96 (t, *J* = 8.39 Hz, 3H, Ar-*H*), 6.72 (dd, *J* = 17.59, 10.89 Hz, 1H, C*H*=), 5.76 (d, *J* = 17.59 Hz, 1H, =CH_{2a}), 5.25 (d, *J* = 10.88 Hz, 1H, =CH_{2b}), 5.05 (s, 2H, CH_2). ^{13}C RMN ($CDCl_3$) δ 158,7 (C_{qAr}-O), 136,5 (C_{qAr}-C=), 136,4 (C_{qAr}-CH_2, *C*H=), 129,5 (*C*-Ar), 127,7 (*C*-Ar), 126,4 (*C*-Ar), 121,7 (*C*-Ar), 114,8 (*C*-Ar), 114,0 (CH_2=), 69,6 (CH_2). FTIR (NaCl, cm^{-1}) v 1630 (CH_2=C), v 1600 and 1495 (aromatic C=C), v 1421 (CH_2), v 1379 (CH_3), v 1266 (C-O). White solid, mp 109-114ºC. Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.66; H, 6.78.

1-(benzyloxymethyl)-4-vinylbenzene 26 [36]

1.33 g, 64%

^{1}H NMR (400 MHz, *CDCl$_3$)* δ ppm 7.40-7.28 (m, 9H, Ar-*H*), 6.70 (dd, *J* = 17.59, 10.88 Hz, 1H, C*H*=), 5.74 (d, *J* = 17.59 Hz, 1H, =CH_{2a}), 5.23 (d, *J* = 10.88 Hz, 1H, =CH_{2b}), 5.08 (s, 2H, CH_2), 5.06 (s, 2H, CH_2). ^{13}C-RMN ($CDCl_3$) δ 137,3 (C_{qAr}-C), 136,1 (C_{qAr}-C), 135,8 (C_{qAr}-C), 135.3 (*C*H=), 128,3 (*C*-Ar), 128,0 (*C*-Ar), 126,1 (*C*-Ar), 114,0 (CH_2=), 66,0 (CH_2), 65,7 (CH_2). FTIR (NaCl, cm^{-1}) v 1631 and 1513 (aromatic C=C), v 1631 (CH2=C), v 1454 (CH_2), v 1361 (C-O). Yellow oil. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C,85.60; H, 7.26.

4-(4-aminophenoxy)-N-(4-vinylbenzyl) benzenamine 27

0.43 g, 27%

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38 (d, J = 7.99 Hz, 2H, Ar-*H*), 7.32 (d, J = 7.87 Hz, 2H, Ar-*H*), 6.81 (dd, J = 12.76, 8.74 Hz, 4H, Ar-*H*), 6.70 (dd, J = 17.60, 10.90 Hz, 1H, C*H*=), 6.60 (dd, J = 17.39, 8.66 Hz, 4H, Ar-*H*), 5.73 (d, J = 17.60 Hz, 1H, =CH_{2a}), 5.23 (d, J = 10.85 Hz, 1H, =CH_{2b}), 4.27 (s, 2H, CH_2). ^{13}C-RMN ($CDCl_3$) δ ppm 150.8 (C_{qAr}-O), 149.9 (C_{qAr}-O), 143.8 (C_{qAr}-N), 141.5 (C_{qAr}-N), 139.0 (C_{qAr}-N), 136.4 (*C*H=), 127.7 (*C*-Ar), 126.4 (*C*-Ar), 116.2 (*C*H_2=), 113.9 (*C*-Ar), 113.7 (*C*-Ar), 48.7 (*C*H_2). FTIR (NaCl, cm-1) ν 3053 (NH), δ 1504 (NH), γ 736 (NH), ν 1622 (aromatic C=C and CH_2=C), ν 1407 (CH_2). Brown solid, mp 100-105ºC. Anal. Calcd for $C_{30}H_{28}N_2O$: C, 79.72; H, 6.37; N, 8.85. Found: C, 79.72; H, 6.30; N, 8.89.

Supporting Information

Supporting information for this article, including experimental procedures, characterization data and copies of NMR and FTIR spectra of all products, is available online.

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