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New Methods in the Synthesis of (Meth) Acrylates

Cengiz Soykan

Abstract

Generally, the words “reactive polymers” and “functional polymers” mean the same thing and are used interchangeably in most studies and describe cross-linked (insoluble) bead-structured resins containing chemically reactive functional groups. In this way, reactive polymers are widely used as polymeric reagents or polymer supports in biochemical and chemical applications. Functional (meth) acrylates referred here to supply “functional esters” ruins as a general reactive group precursor. In other sense, the leaving (activating) groups of these monomers may easily react with the alcohols and amines carrying the desired reactive groups and therefore, in general, provide a single reaction step for the synthesis of reactive polymers. In this paper, we suggest new routes for a new (meth)acrylate-based monomers and polymers. Also, the synthesis of a serial new (meth)acrylate esters including amide, dioxolane, benzofuran, and chalcone groups is described.

Keywords: activated (meth)acrylates, α -chloro-N-aryl acetamides, dioxolane, benzofuran, chalcone, functional polymers

1. Introduction

Today, the term “functional polymers” is used to compare the specific properties such as chemical, physicochemical or biochemical functions of polymeric materials and to classify polymers in this field. For the preparation of different purpose polymers, new monomers are obtained by binding the functional group to the structure of certain monomers. Copolymers of commercial monomers and monomers with functional groups are prepared and their properties are investigated. In addition, chemical polymers are chemically modified and functional groups are bonded to produce chemical-reactive polymers in both the industry and polymer-based chemistry. The application of chemical modification to the polymers is used to prepare polymers which cannot be prepared by direct polymerization of the monomer.

There are two ways to synthesize a polymer with the planned pendant reactive group: (1) functionalization of a non-functional polymer by chemical modification; (2) binding of a reactive side group to the monomer and polymerization of this reactive group monomer by chain addition polymerization methods [1]. Both methods have been successfully applied to obtain vinyl polymers. The synthesis and studies on (meth)acrylate polymers have attracted the attention of various groups in recently [2–13]. Acrylate homopolymers along with their copolymers are used in various fields such as thin films, adsorption, fibers, filament coatings, lithography, lacquers, adhesives, printing inks, and binders [14–34].

There are some disadvantages in linking functional groups on polymers:

1. The distribution of bound functional groups on polymer molecules may not be regular.
2. The density of the bound reactive groups is generally low, and therefore, in such polymers, there may be no results in terms of reaction between the functional group and the polymer structure.
3. Polymer functionalization reactions should be carried out in temperate conditions and the efficiency of the reactions should be quantitative. Because it will be a part of the polymer chain in the undesirable groups that may occur by side reactions. Therefore, precautions should be taken in such a way that no side reactions occur as long as possible.
4. The activity of the groups to be bound on the polymer molecules may be different due to the surrounding of the macromolecule compared to similar small molecules. Therefore, more characteristic reaction conditions may be required for a satisfactory transformation.
5. Side reactions during the polymer functionalization reaction will produce impurities in the obtained polymer due to unreacted groups and other functional groups, which will reveal the problem of purification.
6. Due to undesirable side reactions, the chemical and physical properties of the polymer, such as dissolution, cross-linking, halogen and gas release, can be varied.
7. Since the functional groups allow for cross-linking during polymerization and the polymer will not dissolve, there may not be sufficient analytical methods to investigate the properties of the polymer.
8. In particular, where the polymer chain is susceptible to chemical reactions, reactions should be carried out without degradation.

2. Functional methacrylate ester monomer and polymer synthesis from oxirane compounds

2.1 Synthesis of aryloxy-2,3-epoxy propane (oxirane)

The oxirane compound is obtained from the epichlorohydrin with an arylalcohol. The synthesis reaction scheme is given in **Figure 1**.

A typical procedure for the reaction of arylalcohol with epichlorohydrin is as follows: arylalcohol (0.5 mol) and epichlorohydrin (1.5 mol) and sodium hydroxide (0.55 mol) are mixed with magnetic stirrer at 50°C for 10 h, and then

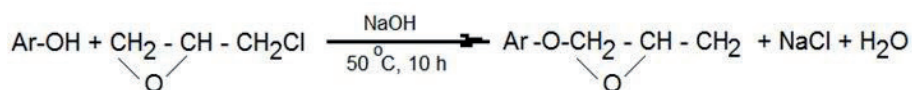


Figure 1.
Reaction scheme of aryloxy-2,3-epoxy propane.

the reaction mixture is stirred at room temperature for 15 h. The organic layer is washed several times with diethylether and dried over magnesium sulfate. After removing diethylether, the excess of epichlorohydrin is distilled at 50°C and 60 mmHg. The remaining reaction mixture is distilled at 110°C and 12 mmHg (oxirane product yield: 87%). The structure of the compound aryloxy-2,3-epoxy propane is identified by the FT-IR techniques. FT-IR (cm⁻¹): 3100–2800 (C—H); 1590 (C=C); 1250 (epoxy C—O); 950–770 (epoxy C—H).

2.2 Synthesis of aryloxy-2-hydroxypropyl methacrylate monomer

Oxirane compound is distilled off again at 110°C and 12 mmHg by vacuum distillation. In a reaction flask, 0.26 mol of oxirane, 0.54 mole of methacrylic acid, 0.30 mol of pyridine, and 100 ppm of hydroquinone are mixed in 200 ml of toluene solvent at 85°C for 24 h with a magnetic stirrer. After the reaction is complete, 30% sodium hydroxide solution is added until the mixture is taken up in ethereal separation funnel and basic. The basic aqueous phase obtained at the end of the extraction is extracted three times with diethylether in another separating funnel. The collected ethereal phases are taken to the separating funnel and extracted until neutral with water. The etheric phases are taken into a collection container and a sufficient amount of anhydrous magnesium sulfate is thrown into it and left to dry for 24 h. At the end of the filtration process, the mixture separated from magnesium sulfate is distilled off the toluene at 45°C and 50 mmHg. To the remaining mixture, 50 ppm of hydroquinone was added and vacuum distillation is carried out with monomer at 150°C and 1 mmHg (monomer yield: 65%). The synthesis reaction scheme is given in **Figure 2**.

The structure of the monomer is confirmed by the FT-IR and ¹H- and ¹³C-NMR spectroscopic techniques. FT-IR (cm⁻¹): 3600–3200 (—OH); 3100–2800 (C—H); 1720 (>C=O); 1630 (CH₂=C); 1580 (aromatic, C=C); 1250 (C—O). ¹H-NMR (CDCl₃, TMS): 8.0–6.8 (aromatics —H); 6.2–5.44 (CH₂=C); 4.25 (O—H); 1.8 (CH₃). ¹³C-NMR (CDCl₃, TMS): 157.2–113.8 (aromatics —C); 134.0–124.4 (CH₂=C); 165.6 (>C=O); 67.8 (CH—OH); 17.2 (CH₃).

2.3 Free radical polymerization of aryloxy-2-hydroxypropyl methacrylate monomer

Appropriate amounts of aryloxy-2-hydroxypropyl methacrylate monomer and chloroform and 2,2'-azobisisobutyronitrile (AIBN) as an initiator (2% of the monomer mass) are disposed in a polymerization tube and liquidated with nitrogen for 10 min. The sealed and waxed polymerization reaction tube is placed at 60 ± 1°C for 24 h in oil bath. The reaction product is poured dropwise into an abundant of diethylether. The obtained polymer is purified by re-precipitation with diethylether from a chloroform solution and the latest operation dried under vacuum oven (conversion 90%). The synthesis reaction scheme is given in **Figure 3**.

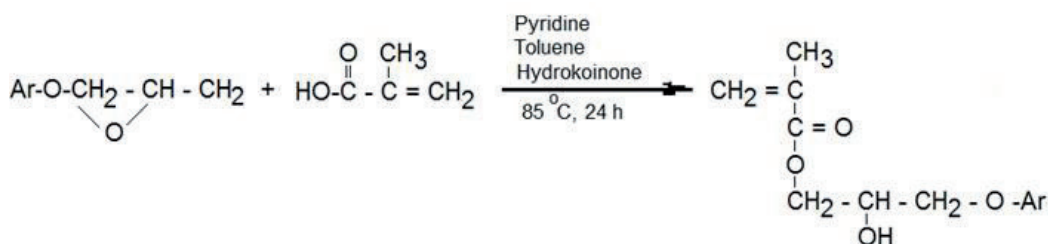


Figure 2.
Reaction scheme of aryloxy-2-hydroxypropyl methacrylate monomer.

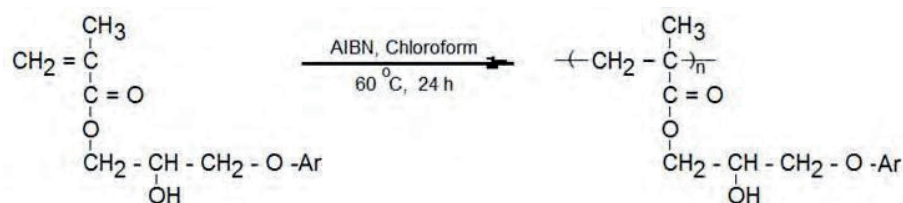


Figure 3.
Reaction scheme of poly aryloxy-2-hydroxypropyl methacrylate.

The formation of the homopolymer of aryloxy-2-hydroxypropyl methacrylate is confirmed by the FT-IR and $^1\text{H-NMR}$ spectroscopic techniques. The main description for the polymerization of the monomer is that the characteristic double bond (vinyl structure double bond) peak signal of the monomer in the FT-IR spectrum is fully depleted and does not peak in this region in the FT-IR spectrum of the polymer. This is because the addition polymerization proceeds through the opening of the pi bond in the vinyl group. This has been effectively observed in the synthesis and characterizations herein. Two signals altered in the FT-IR spectrum of the monomer: the stretching vibration band of the vinyl group $\text{C}=\text{C}$ at 1630 cm^{-1} and the absorption signal at 920 cm^{-1} assigned to the $\text{C}-\text{H}$ bending of geminal $=\text{CH}_2$.

The information is clearly seen in $^1\text{H-NMR}$ spectroscopy on polymer formation. The formation of polymer is clearly evident from the disappearing of the two singlets at 6.3 and 5.4 ppm of the vinyl protons and the wide peaks at 2.4–1.3 ppm due to the conversion to the aliphatic $-\text{CH}_2$ group.

3. Functional methacrylate ester monomer and polymer synthesis from arylacetylhalide compounds

3.1 Synthesis of arylacetylhalide

Arylacetyl chloride is prepared by reacting arylalcohol with chloroacetyl chloride using the K_2CO_3 . A typical procedure for the acylation reaction of arylalcohol with chloroacetyl chloride is as follows: arylalcohol (1 mol) and K_2CO_3 are dissolved in 20 ml of anhydrous benzene at 0°C , and then 1.1 mol of chloroacetyl-chloride is added dropwise to this solution. The reaction mixture is stirred at room temperature for 15 h. The organic layer is washed several times with diethylether and dried over MgSO_4 . After removing diethylether, α -chloro-arylacetyl chloride is crystallized from methanol (yield: 80%). The structure of the compound arylacetylhalide is identified by the FT-IR techniques. FT-IR (cm^{-1}): 3100–2800 ($\text{C}-\text{H}$); 1730 ($>\text{C}=\text{O}$); 1580 (aromatic, $\text{C}=\text{C}$). The synthesis reaction scheme is given in **Figure 4**.

3.2 Synthesis of aryloxycarbonyl methyl methacrylate monomer

Aryloxycarbonyl methyl methacrylate is synthesized as follows: a mixture of arylacetyl chloride (1 mol), sodium methacrylate (1.1 mol) in 100 ml acetonitrile and triethylbenzylammonium chloride (TEBAC) (0.1 mol) as a phase transfer

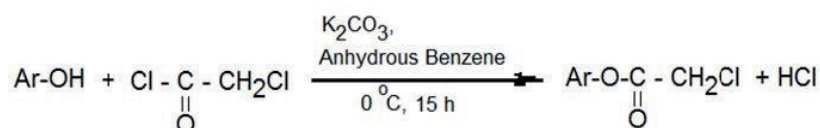


Figure 4.
Reaction scheme of arylacetylhalide.

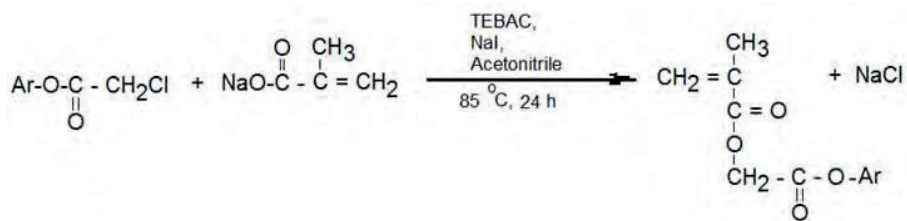


Figure 5.
 Reaction scheme of aryloxycarbonyl methyl methacrylate monomer.

catalyst better and sodium iodide (NaI) (0.1 mol) as catalyst are receipt in a three-neck round bottom flask equipped with a thermometer, magnetic stirrer, and heated to 85°C in a reflux condenser in the presence of 100 ppm hydroquinone. The reaction is continued for an additional 30 h. The reaction mixture is cooled to 20°C and moved to a separating funnel, washed sequentially with diethylether, 5% NaOH, and distilled water. The organic layer are spooled and dried over anhydrous magnesium sulfate (MgSO₄) for 24 h. Magnesium sulfate is filtered and the diethylether is removed from the organic layers with a rotary evaporator. The resulting monomer is purified by recrystallization from ethanol (yield: 85%). The synthesis reaction scheme is given in **Figure 5**.

The structure of the monomer is confirmed by the FT-IR and ¹H- and ¹³C-NMR spectroscopic techniques. FT-IR (cm⁻¹): 3100–2800 (C—H); 1730 (>C=O); 1630 (CH₂=C); 1580 (aromatic, C=C); 1250 (C—O). ¹H-NMR (CDCl₃, TMS): 7.9–6.6 (aromatics —H); 6.2–5.41 (CH₂=C); 1.8 (CH₃). ¹³C-NMR (CDCl₃, TMS): 157.1–113.4 (aromatics —C); 134.4–124.2 (CH₂=C); 165.2 (>C=O); 18.1 (CH₃).

3.3 Free radical polymerization of aryloxycarbonyl methyl methacrylate monomer

Homopolymer of aryloxycarbonyl methyl methacrylate is synthesized using 2,2'-azobisisobutyronitrile (AIBN) as an initiator (2% of the monomer mass) in 1,4-dioxane solution. The reaction mixture is de-aerated by passing nitrogen gas for 10 min, then the tube is tightly sealed and kept in a thermostatic oil bath at 60 ± 1°C for 24 h. The homopolymer is precipitated in excess methanol, purified by dissolution in 1,4-dioxane and reprecipitation in methanol. The homopolymer is dried in vacuum to constant weight (conversion 90%). The synthesis reaction path is given in **Figure 6**.

The formation of the homopolymer of aryloxycarbonyl methyl methacrylate is confirmed by the ¹H-NMR and FT-IR spectroscopic techniques. The information is clearly seen in ¹H-NMR spectroscopy on polymer formation. The formation of polymer is clearly evident from the disappearing of the two singlets at 6.3 and 5.4 ppm of the vinyl protons and the wide peaks at 2.4–1.3 ppm due to the conversion to the aliphatic-CH₂ group. The main description of the polymer is exactly the extinction of some characteristic peaks of the double bond in the FT-IR spectrum, and this has

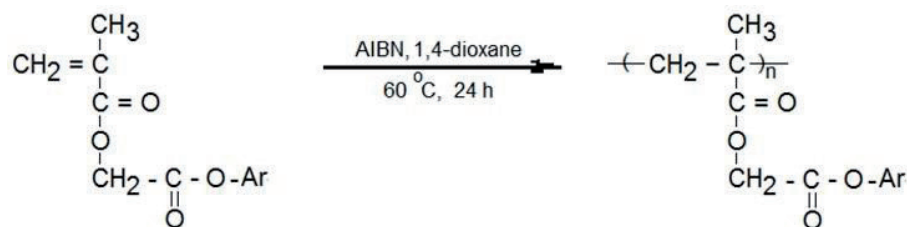


Figure 6.
 Reaction scheme of poly aryloxycarbonyl methyl methacrylate.

been effectively observed in the synthesis and characterizations herein. Two signals altered in the FT-IR spectrum of the monomer: the stretching vibration band of the vinyl group C=C at 1630 cm^{-1} and the absorption signal at 920 cm^{-1} assigned to the C—H bending of geminal=CH₂.

4. Functional methacrylate ester monomer and polymer synthesis from α -chloro-N-arylamide compounds

4.1 Synthesis of α -chloro-N-arylamide

α -chloro-N-arylamide is prepared by reacting arylamine with chloroacetylchloride using the K₂CO₃. A typical procedure is as follows: arylamine (1 mol) and K₂CO₃ were dissolved in 20 ml of anhydrous benzene at 0°C, and then 1.1 mol of chloroacetylchloride are added dropwise to this solution. The reaction mixture is stirred at room temperature for 15 h. The organic phase is washed several times with diethylether and dried over MgSO₄. After removing diethylether, α -chloro-N-arylamide is crystallized from methanol (yield: 80%). The synthesis reaction scheme is given in **Figure 7**.

The structure of the compound α -chloro-N-arylamide is identified by the FT-IR techniques. FT-IR (cm⁻¹): 3340 (NH); 3100–2800 (C—H); 1680 (>C=O); 1580 (aromatic, C=C).

4.2 Synthesis of arylamido methyl methacrylate monomer

Arylamido methyl methacrylate is synthesized as follows: 1.1 mol sodium methacrylate, 1 mol α -chloroacetamide, 0.1 mol NaI and 0.1 mol TEBAC and as catalyst are stirred in 100 ml acetonitrile at 80°C in a reflux condenser for 30 h in the presence of 100 ppm hydroquinone. After the solution is cooled to 20°C and neutralized with a 5% NaOH solution. The organic phase is washed a few times with water, and the water phase is washed with diethylether a several times. The diethyl ether phase and the acetonitrile phase are spooled and dried over anhydrous magnesium sulfate for 24 h. Diethyl ether and acetonitrile are removed with a rotary evaporator. The organic phases are collected and the residue is distilled at 130°C at 5 mmHg to give a colorless liquid (yield: 80%). The synthesis reaction scheme is given in **Figure 8**.

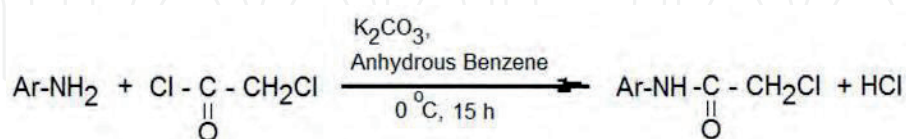


Figure 7.

Reaction scheme of α -chloro-N-arylamide.

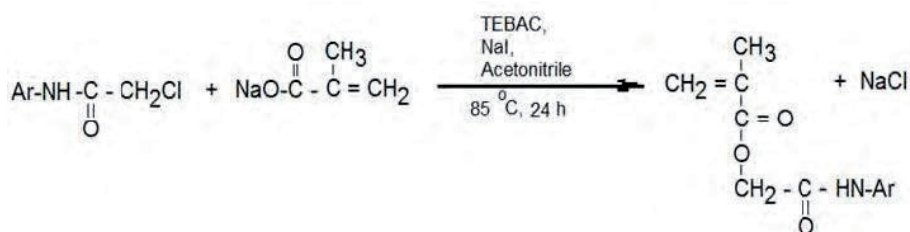


Figure 8.

Reaction scheme of arylamido methyl methacrylate monomer.

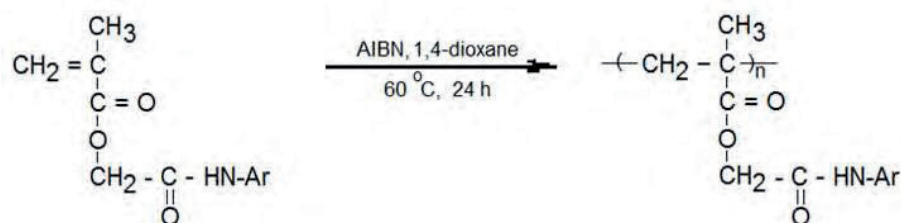


Figure 9.
 Reaction scheme of poly arylamido methyl methacrylate.

The structure of the monomer is confirmed by the FT-IR and ^1H - and ^{13}C -NMR spectroscopic techniques. FT-IR (cm^{-1}): 3325 (NH); 3100–2800 (C—H); 1680 ($>\text{C}=\text{O}$); 1630 ($\text{CH}_2=\text{C}$); 1580 (aromatic, C=C); 1230 (C—O—C). ^1H -NMR (CDCl_3 , TMS): 9.1 (N—H); 8.0–6.7 (aromatics —H); 6.3–5.43 ($\text{CH}_2=\text{C}$); 1.8 (CH_3). ^{13}C -NMR (CDCl_3 , TMS): 157.1–113.4 (aromatics —C); 134.4–124.2 ($\text{CH}_2=\text{C}$); 168.1 ($>\text{C}=\text{O}$); 18.1 (CCH_3).

4.3 Free radical polymerization of arylamido methyl methacrylate monomer

Arylamido methyl methacrylate monomer is freed from inhibitor by washing with a dilute KOH solution followed by distilled water and then drying over MgSO_4 . Appropriate amounts of arylamido methyl methacrylate monomer, 2,2'-azobisisobutyronitrile (AIBN) (2% of the monomer mass) and 1,4-dioxane are placed in a polymerization reaction tube and purged with nitrogen for 15 min. The closed mouth polymerization reaction tube is kept at $60 \pm 1^\circ\text{C}$ for 30 h in oil bath. The reaction product is poured dropwise into an abundant of n-hexane. The obtained polymer is purified by re-precipitation with n-hexane from a 1,4-dioxane solution and the latest operation dried under vacuum oven (conversion 90%). The synthesis reaction scheme is given in **Figure 9**.

The structure of poly arylamido methyl methacrylate is confirmed by the FT-IR and ^1H -NMR spectroscopic techniques. The main description for the polymerization of the monomer is that the characteristic double bond (vinyl structure double bond) peak signal of the monomer in the FT-IR spectrum is fully depleted and does not peak in this region in the FT-IR spectrum of the polymer. This is because the addition polymerization proceeds through the opening of the pi bond in the vinyl group. This has been effectively observed in the synthesis and characterizations herein. Two signals altered in the FT-IR spectrum of the monomer: the stretching vibration band of the vinyl group C=C at 1630 cm^{-1} and the absorption signal at 920 cm^{-1} assigned to the C—H bending of geminal= CH_2 .

The information is clearly seen in ^1H -NMR spectroscopy on polymer formation. The formation of polymer is clearly evident from the disappearing of the two singlets at 6.3 and 5.4 ppm of the vinyl protons and the wide peaks at 2.8–1.4 ppm due to the conversion to the aliphatic — CH_2 group.

5. Functional methacrylate ester monomer and polymer synthesis from aryl-1,3-dioxolane compounds

5.1 Synthesis of (aryl-1,3-dioxolane-4-yl) methanol

(Aryl-1,3-dioxolan-4-yl)methanol is prepared by reacting arylaldehyde with glycerin using the *p*-toluenesulfonic acid as catalyst. A typical procedure is as follows: Arylaldehyde (0.1 mol), glycerin (0.1 mol), *p*-toluenesulfonic acid (*p*-TOS)

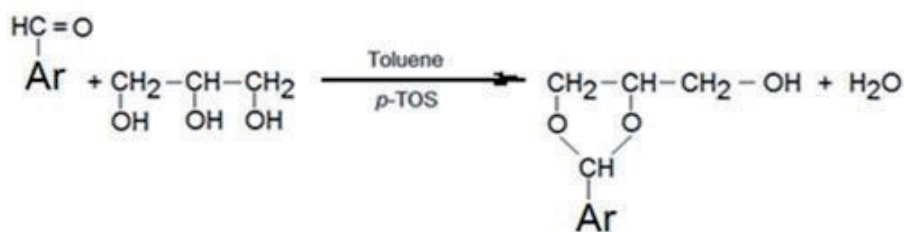


Figure 10.
Reaction scheme of (aryl-1,3-dioxolane-4-yl) methanol.

(0.5 g, as catalyst) and toluene (30 mL) are placed in a 100 mL three-necked reaction balloon fitted with a thermometer, condenser and a stirrer. The reaction mixture is refluxed at 115°C for 2 h with strong mixing. The reaction mixture is extracted a few times with diethyl ether and then 5% KOH solution, diethyl ether and toluene, respectively. The diethyl ether and toluene solvents are evaporated with rotary evaporator. The raw product is washed with water (40 mL × 3) and dried over anhydrous magnesium sulfate at overnight. The synthesis reaction scheme is given in **Figure 10**.

The structure of (aryl-1,3-dioxolane-4-yl) methanol is identified by the FT-IR and ¹H- and ¹³C-NMR spectroscopic techniques. FT-IR (cm⁻¹): 3500–3110 (O—H); 3100–2800 (C—H); 1570 (aromatic, C=C); 1180 (C—O—C). ¹H-NMR (CDCl₃, TMS): 7.48–7.0 (aromatics —H); 6.3–5.52 (CH₂=C); 4.0–3.7 (—O—CH); 4.17–4.11 (O—CH₂); 3.16 (—OH), 3.0 (CH₂). ¹³C-NMR (CDCl₃, TMS): 151.1–116.4 (aromatics —C); 134.4–124.2 (CH₂=C); 63.1 (CH₂); 68.8 (O—CH₂); 77.3 (O—CH).

5.2 Synthesis of (aryl-1,3-dioxolane-4-yl) methyl acrylate monomer

(Aryl-1,3-dioxolan-4-yl)methanol (0.1 mol), triethyl amine (NR₃) (20 mL, as catalyst) and diethyl ether (40 mL) are filled in a 250 mL four-necked reaction balloon fitted with a thermometer, a condenser, a stirrer and an addition funnel including 15 mL acryloyl chloride. The acryloyl chloride is added drop wise to the solution with a dropping funnel. The temperature of the reaction mixture is hold by a cryostat at -5°C for 18 h. The reaction mixture is extracted a few times with 5% KOH solution and after dried over anhydrous magnesium sulfate for 24 h. The solvents are removed by the vacuum evaporator. The synthesis reaction scheme is given in **Figure 11**.

The structure of (aryl-1,3-dioxolane-4-yl) methyl acrylate is confirmed by the FT-IR and ¹H- and ¹³C-NMR spectroscopic techniques. FT-IR (cm⁻¹): 3100–2800 (C—H); 1727 (>C=O); 1630 (CH₂=C); 1570 (aromatic, C=C); 1190 (C—O—C). ¹H-NMR (CDCl₃, TMS): 7.6–7.0 (aromatics —H); 6.3–5.52 (CH₂=C); 5.8 (Ar—CH); 4.2–3.8 (—O—CH); 4.2–4.1 (O—CH₂); 3.0 (CH₂). ¹³C-NMR (CDCl₃, TMS): 166.2 (>C=O); 151.1–116.4 (aromatics —C); 130.4–122.2 (CH₂=C); 103.2 (Ar—CH); 63.1 (CH₂); 68.8 (O—CH₂); 87.2 (O—CH).

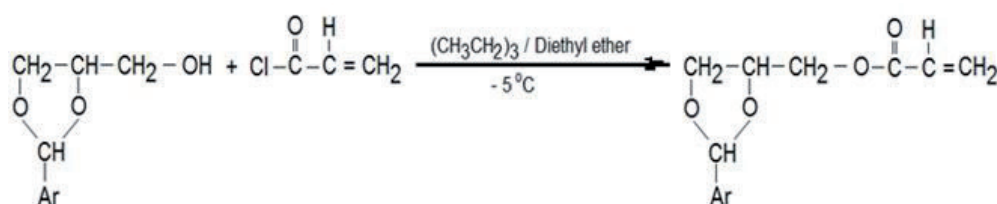


Figure 11.
Reaction scheme of (aryl-1,3-dioxolane-4-yl) methyl acrylate monomer.

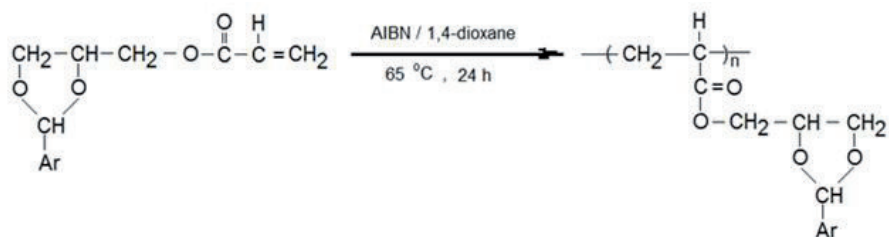


Figure 12.
Reaction scheme of poly(aryl-1,3-dioxolane-4-yl) methyl acrylate.

5.3 Free radical polymerization of arylamido methyl methacrylate monomer

Free radical polymerization reaction of (aryl-1,3-dioxolane-4-yl) methyl acrylate monomer is conducted in a polymerization reaction tube using 2,2'-azo-bis(isobutyronitrile) (AIBN) (1% of the monomer mass) as initiator in 10 mL of 1,4-dioxane, at 65°C with 90% conversion in 6 h. The formed polymer is precipitated in ethyl alcohol. The obtained polymer is dried under vacuum at 45°C for 24 h for constant weight. The synthesis reaction scheme is given in **Figure 12**.

The structure of poly(aryl-1,3-dioxolane-4-yl) methyl acrylate is confirmed by the FT-IR and ¹H-NMR spectroscopic techniques. The information is clearly seen in ¹H-NMR spectroscopy on polymer formation. The formation of polymer is clearly evident from the disappearing of the two singlets at 6.3 and 5.42 ppm of the vinyl protons and the wide peaks at 2.9–1.5 ppm due to the conversion to the aliphatic —CH₂ group. The main description of the polymer is exactly the extinction of some characteristic peaks of the double bond in the FT-IR spectrum, and this has been effectively observed in the synthesis and characterizations herein. Two signals altered in the FT-IR spectrum of the monomer: the stretching vibration band of the vinyl group C=C at 1630 cm⁻¹ and the absorption signal at 920 cm⁻¹ assigned to the C—H bending of geminal=CH₂.

6. Functional methacrylate ester monomer and polymer synthesis from benzofuran compounds

6.1 Synthesis of acetyl benzofuran

Synthesis of acetyl benzofuran is as follows: Potassium carbonate (K₂CO₃) (0.1 mol) and 2-hydroxybenzaldehyde (1 mol) are dissolved in 30 ml of absolute acetone. The reaction mixture is taken in a three-neck round bottom reaction balloon equipped with a magnetic stirrer, a thermometer, and cooled to 0°C. After then chloroacetone (1.1 mol) are added dropwise to this solution at 5°C, and stirred at 20°C for 16 h. The organic phase is washed a few times with distilled water and separation layer is filtered through filter paper and dried over anhydrous MgSO₄ overnight. Acetyl benzofuran compound is crystallized from ethyl alcohol. Yield: 85%. The synthesis reaction scheme is given in **Figure 13**.

The structure of acetyl benzofuran is identified by the FT-IR techniques. FT-IR (cm⁻¹): 3100–2800 (C—H); 1690 (>C=O); 1570 (aromatic, C=C).

6.2 Synthesis of bromo-acetyl benzofuran

Acetyl benzofuran (1 mol) is dissolved in 200 mL acetic acid, and after then bromo is added dropwise to this solution at 25°C for 2 h. After bromination reaction, the mixture is divided into ice-water. The separation layer is filtered through

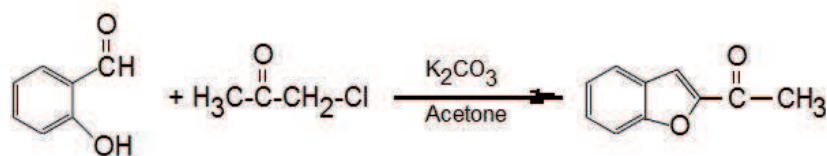


Figure 13.
Reaction scheme of acetyl benzofuran.

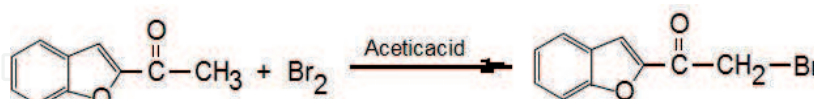


Figure 14.
Reaction scheme of bromo acetyl benzofuran.

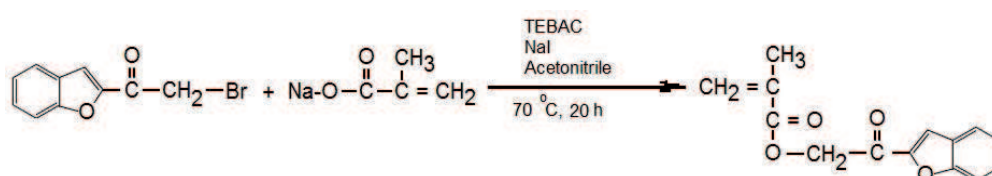


Figure 15.
Reaction scheme of acetyl benzofuryl methyl methacrylate monomer.

filter paper and dried over anhydrous magnesium sulfate (MgSO_4) overnight. Bromo-acetyl benzofuran compound is crystallized from ethyl alcohol. Yield: 85%. The synthesis reaction scheme is given in **Figure 14**.

The structure of bromo acetyl benzofuran is identified by the FT-IR techniques. FT-IR (cm^{-1}): 3100–2800 (C—H); 1690 ($>\text{C}=\text{O}$); 1570 (aromatic, C=C); 780 (CH—Br).

6.3 Synthesis of acetyl benzofuryl methyl methacrylate monomer

Sodium methacrylate (1.1 mol), bromo-acetyl benzofuran (1 mol), sodium iodide (0.1 mol) and triethylbenzylammoniumchloride (TEBAC) (0.1 mol) as catalyst are mixed in 100 mL acetonitrile at 70°C in a reflux condenser for 20 h in the beside of 100 ppm hydroquinone as an inhibitor. After then the solution is cooled to 20°C and neutralized with a 5% NaOH solution. The organic phase is washed with diethyl ether a few times. The diethyl ether and acetonitrile layers are spooled and dried over anhydrous magnesium sulfate (MgSO_4) overnight. Diethyl ether and acetonitrile are evaporated with a rotary evaporator. The organic layers are collected and the residue is crystallized from ethyl alcohol. Yield: 80%. The synthesis reaction scheme is given in **Figure 15**.

The structure of acetyl benzofuryl methyl methacrylate is confirmed by the FT-IR and ^1H - and ^{13}C -NMR spectroscopic techniques. FT-IR (cm^{-1}): 3100–2800 (C—H); 1735 ($>\text{C}=\text{O}$); 1685 (—C=O); 1630 ($\text{CH}_2=\text{C}$); 1580 (aromatic, C=C); 1190 (C—O—C). ^1H -NMR (CDCl_3 , TMS): 7.7–7.2 (aromatics —H); 6.3–5.48 ($\text{CH}_2=\text{C}$); 4.2–4.0 (O— CH_2); 1.5 (CH_3). ^{13}C -NMR (CDCl_3 , TMS): 178.2 (—C=O); 168.1 ($>\text{C}=\text{O}$); 148.1–116.2 (aromatics —C); 130.1–122.0 ($\text{CH}_2=\text{C}$); 68.8 (O— CH_2); 19.1 (CH_3).

6.4 Free radical polymerization of acetyl benzofuryl methyl methacrylate monomer

The preparation of homopolymer of Acetyl benzofuryl methyl methacrylate monomer is synthesized by free radical polymerization in 1,4-dioxane solvent

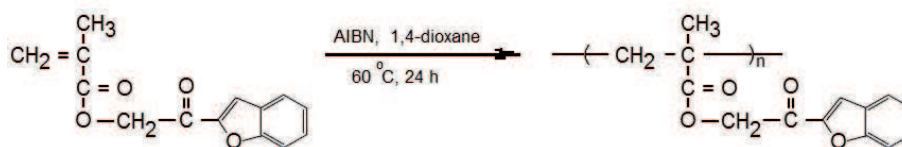


Figure 16.
Reaction scheme of poly acetyl benzofuryl methyl methacrylate.

using 2,2'-azobisisobutyronitrile (AIBN) as a free radical initiator. The homopolymer is purified by repeated reprecipitation from 1,4-dioxane and then filtered and dried until a constant weight is attained. The synthesis reaction path is given in **Figure 16**.

The structure of poly acetyl benzofuryl methyl methacrylate is confirmed by the FT-IR and $^1\text{H-NMR}$ spectroscopic techniques. The information is clearly seen in $^1\text{H-NMR}$ spectroscopy on polymer formation. The formation of polymer is clearly evident from the disappearing of the two singlets at 6.3 and 5.42 ppm of the vinyl protons and the wide peaks at 2.9–1.5 ppm due to the conversion to the aliphatic —CH_2 group. The main description of the polymer is exactly the extinction of some characteristic peaks of the double bond in the FT-IR spectrum, and this real is effectively identified herein. Two signals altered in the FT-IR spectrum of the monomer: the stretching vibration band of the vinyl group $\text{C}=\text{C}$ at 1630 cm^{-1} and the absorption signal at 920 cm^{-1} assigned to the C—H bending of geminal =CH_2 .

7. Functional methacrylate ester monomer and polymer synthesis from photocrosslinkable functional group (pendant chalcone unit) compounds

7.1 Synthesis of hydroxyphenyl-methoxystyryl ketone (hydroxy chalcone)

Substituted benzaldehyde (1 mol) and substituted acetophenone (1 mol) are dissolved in 50 mL of ethyl alcohol and cooled at 18°C . An aqueous NaOH solution (1 mol in 40 mL of distilled water) is then added dropwise with constant mixing and as keeping the temperature constant at 18°C . After stirring the reaction mixture for 12 h at 20°C , it is neutralized with dilute HCl to isolate the compound. The obtained solid matter is filtered through filter paper, washed with ice cold water, dried and recrystallized from ethyl alcohol. Yield: 75%. The synthesis reaction scheme is given in **Figure 17**.

The structure of hydroxyl chalcone is identified by the FT-IR techniques. FT-IR (cm^{-1}): 3500–3200 (O—H); 3100–2800 (C—H); 1690 ($>\text{C}=\text{O}$); 1605 ($\text{—CH}=\text{CH—}$); 1570 (aromatic, $\text{C}=\text{C}$).

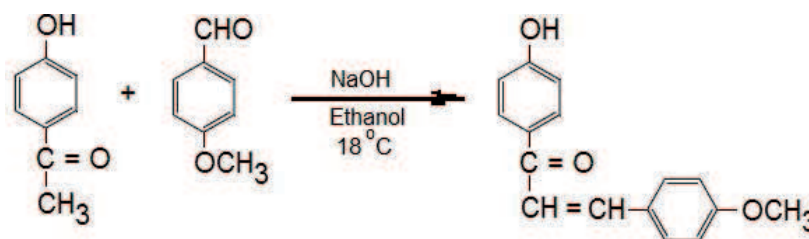


Figure 17.
Reaction scheme of hydroxyl chalcone.

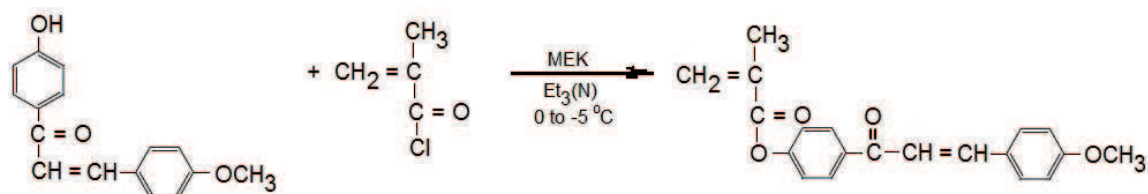


Figure 18.
Reaction scheme of methacryloyloxyphenyl-methoxystyryl ketone.

7.2 Synthesis of methacryloyloxyphenyl-methoxystyryl ketone

In a 250 mL three-necked flask, triethylamine (3 mol) and hydroxyphenyl-methoxystyryl ketone (1 mol) are dissolved in 100 mL of methyl ethyl ketone (MEK) and cooled between 0 and -5°C . Methacryloyl chloride (1.1 mol) in 50 mL of methyl ethyl ketone is then added drop by drop with mixing. After then, the reaction mixture is mixed for 3 h at 20°C and the precipitated quaternary ammonium salt is filtered off. Later, 100 ppm of hydroquinone is added to this solution and the MEK is removed by the vacuum evaporator. The raw product is dissolved in diethyl ether, washed one after another with a 5% aqueous potassium hydroxide solution and distilled water, dried over anhydrous magnesium sulfate (MgSO_4) and the diethyl ether is removed by the evaporator. The obtained material is recrystallized from methyl alcohol to get the shining yellow flakes of substituted methacryloyloxyphenyl-methoxystyryl ketone. Yield: 80%. The synthesis reaction scheme is given in **Figure 18**.

The structure of methacryloyloxyphenyl-methoxystyryl ketone is confirmed by the FT-IR and ^1H - and ^{13}C -NMR spectroscopic techniques. FT-IR (cm^{-1}): 3100–2800 ($\text{C}-\text{H}$); 1740 ($>\text{C}=\text{O}$); 1650 ($-\text{C}=\text{O}$); 1630 ($\text{CH}_2=\text{C}$); 1605 ($-\text{CH}=\text{CH}-$); 1570 (aromatic, $\text{C}=\text{C}$); 1190 ($\text{C}-\text{O}-\text{C}$). ^1H -NMR (CDCl_3 , TMS): 8.1–6.9 (aromatics $-\text{H}$); 6.3–5.78 ($\text{CH}_2=\text{C}$, and $-\text{CH}=\text{CH}-$); 3.84 (OCH_3); 1.8 (CH_3). ^{13}C -NMR (CDCl_3 , TMS): 178.0 ($-\text{C}=\text{O}$); 166.8 ($>\text{C}=\text{O}$); 148.1–116.2 (aromatics $-\text{C}$); 130.1–122.0 ($\text{CH}_2=\text{C}$, and $-\text{CH}=\text{CH}-$); 58.1 (OCH_3); 19.1 (CH_3).

7.3 Free radical polymerization of substituted methacryloyloxyphenyl-methoxystyryl ketone monomer

Substituted methacryloyloxyphenyl-methoxystyryl ketone is polymerized as a 3 molar solution in MEK using 2,2'-azobisisobutyronitrile (AIBN) as initiator at 70°C . The predetermined quantities of substituted methacryloyloxyphenyl-methoxystyryl ketone, the initiator (1 wt.% of monomer) and solvent are placed in a polymerization tube and the mixture is flushed with a slow stream of nitrogen for 20 min. Then, the tube is closed and placed in the thermostated oil bath at 70°C . After the specified time (12 h), the contents are added to excess methyl alcohol to precipitate the polymer. The crude polymer is purified by redissolving in 1,4-dioxane and reprecipitated by methyl alcohol, filtered, washed with methyl alcohol and dried under vacuum at 45°C for constant weight. Yield: 60%. The reaction scheme is shown below (**Figure 19**).

The structure of poly methacryloyloxyphenyl-methoxystyryl ketone is confirmed by the FT-IR and ^1H -NMR spectroscopic techniques. The information is clearly seen in ^1H -NMR spectroscopy on polymer formation. The formation of polymer is clearly evident from the disappearing of the two singlets at 6.3 and 5.78 ppm of the vinyl protons and the wide peaks at 2.7–1.3 ppm due to the conversion to the aliphatic $-\text{CH}_2$ group. The main description of the polymer is exactly the extinction of some characteristic peaks of the double bond in the FT-IR

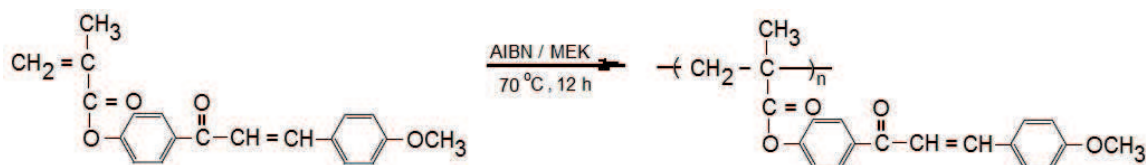


Figure 19.
Reaction scheme of poly methacryloyloxyphenyl-methoxystyryl ketone.

spectrum, and this real is effectively identified herein. Two signals altered in the FT-IR spectrum of the monomer: the stretching vibration band of the vinyl group $\text{C}=\text{C}$ at 1630 cm^{-1} and the absorption signal at 920 cm^{-1} assigned to the $\text{C}=\text{H}$ bending of geminal $=\text{CH}_2$.

8. Conclusion

In this paper, reaction pathway for the synthesis of new methacrylates having pendant amide, dioxolane, benzofuran and chalcone groups are described. Molecular structure information such as reaction scheme, Fourier transform infrared (FT-IR) and nuclear magnetic resonance spectroscopy of all the compounds is given. All of the methacrylates are used as photodegradable packaging materials and photoresists for microlithography. The increasing utility of photosensitive polymers in many applications such as microelectronics, printing and UV-curable lacquers, and inks is provided us with an incentive to obtain novel polymers.

Conflict of interest


The authors declare no conflict of interest.

Author details

Cengiz Soykan
Department of Materials Science and Nanotechnology, Faculty of Engineering,
University of Uşak, Uşak, Turkey

*Address all correspondence to: cengizsoykan@usak.edu.tr

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References

- [1] Sherrington DC. Preparation, functionalization and characteristics of polymer supports. In: Hodge P, Sherrington DC, editors. *Polymer Supported Reactions in Organic Synthesis*. New York: Wiley; 1980. pp. 1-82
- [2] Kalachandra S, Turner DT, Burgess JP, Stejskal EO. Postirradiation reactions of monomer in poly(methyl methacrylate): Analysis by CP/MAS ^{13}C NMR. *Macromolecules*. 1994;**27**(21):5948-5949. DOI: 10.1021/ma00099a003
- [3] Soykan C, Güven Ş, Coşkun R. Copolymers of 2-[(5-methylisoxazol-3-yl)amino]-2-oxo-ethyl methacrylate with ethyl methacrylate: Monomer reactivity ratios, thermal properties and antimicrobial activity. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*. 2006;**43**:1619-1633. DOI: 10.1080/10601320600897031
- [4] Erol İ, Soykan C. Synthesis, characterization and polymerization of new methacrylate esters having pendant amide moieties. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*. 2002;**A39**(5):405-417. DOI: 10.1081/MA-120003963
- [5] Soykan C, Erol İ, Türkmen H, Akçamur Y. New poly(methacrylate)s containing benzylpiperazine and methylpiperidine moieties. *Journal of Polymer Research*. 2004;**11**(3):181-187. DOI: 10.1023/B:JPOL.0000043400.92054.92
- [6] Erol İ, Soykan C. Synthesis and characterization of new aryl-oxycarbonyl methyl methacrylate monomers and their polymers. *Reactive and Functional Polymers*. 2003;**56**:147-157. DOI: 10.1016/S1381-5148(03)00052-X
- [7] İlter Z, Soykan C, Koca M. Synthesis, spectral and thermal properties of copolymers of (2-cyclopentylidene-1,3-dioxolane-4-yl)methyl methacrylate with styrene and acrylonitrile and determination of monomer reactivity ratios. *Journal of Polymer Science Part A: Polymer Chemistry*. 2003;**41**(19):2996-3005. DOI: 10.1002/pola.10892
- [8] İlter Z, Alhanlı F, Doğan F, Kaya İ. Synthesis and characterization of an acrylate polymer containing chlorine-1,3-dioxalane groups in side chains. *Chinese Journal of Polymer Science*. 2012;**30**(5):642-651. DOI: 10.1007/s10118-012-1155-x
- [9] Coşkun M, İlter Z. Copolymerization of (2-phenyl-1,3-dioxolane-4-yl)methyl methacrylate with alkyl methacrylates: Reactivity ratios and copolymer characterization. *Journal of Polymer Science, Part A: Polymer Chemistry*. 2002;**40**(8):1184-1191. DOI: 10.1002/pola.10174
- [10] İlter Z, Coşkun M, Erol İ. Copolymers of (2-cyclohexylidene-1,3-dioxolane-4-yl) methyl methacrylate with acrylonitrile and styrene: Synthesis, characterization, and monomer reactivity ratios. *Journal of Polymer Science, Part A: Polymer Chemistry*. 2001;**39**(13):2326-2331. DOI: 10.1002/pola.1209
- [11] İlter Z, Soykan C, Solmaz A. Copolymers of 7-methoxy-2-acetyl benzofuryl methylmethacrylate with styrene: Synthesis, characterization, reactivity ratios and determination of kinetic parameters with thermogravimetric analysis. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*. 2015;**52**:175-185. DOI: 10.1080/10601325.2015.996937
- [12] Barım G, Altun Ö, Yayla MG. Methacrylate polymers having pendant

- chalcone moieties: Monomer reactivity ratios, thermal and optical properties. *Polymer (Korea)*. 2015;**39**(1):13-22. DOI: 10.7317/pk.2015.39.1.13
- [13] Subramanian K, Krishnasamy V, Nanjundan S, Rami Reddy AV. Photosensitive polymer: Synthesis, characterization and properties of a polymer having pendant photocrosslinkable group. *European Polymer Journal*. 2000;**36**(11):2343-2350. DOI: 10.1016/S0014-3057(00)00008-2
- [14] Brar AS, Malhotra M. Compositional assignments and sequence distribution of vinylidene chloride–methyl acrylate copolymers using one- and two-dimensional NMR spectroscopy. *Macromolecules*. 1996;**29**(23):7470-7476. DOI: 10.1021/ma960363c
- [15] Şahingöz R, Kanbur H, Voigt M, Soykan C. The determination of interface states and series resistance profile of Al/polymer/PEDOT-PSS/ITO heterojunction diode by I-V and C-V methods. *Synthetic Metals*. 2008;**158**:727-731. DOI: 10.1016/j.synthmet.2008.04.023
- [16] Şahingöz R, Soykan C, Yakuphanoglu F, Voigt M, Çetin H. The determination of the conduction mechanism and extraction of diode parameters of ITO/PEDOT-PSS/POLYMER/AL heterojunction diode. *Optical Materials*. 2006;**28**:962-965. DOI: 10.1016/j.optmat.2005.05.009
- [17] Tokaloğlu Ş, Yılmaz V, Kartal Ş, Delibaş A, Soykan C. Synthesis of a novel chelating resin and its use for selective separation and preconcentration of some trace metals in water samples. *Journal of Hazardous Materials*. 2009;**169**:593-598. DOI: 10.1016/j.jhazmat.2009.03.146
- [18] Soykan C, Şahan A, Yakuphanoglu F. Synthesis and semi-conducting properties of novel 2-(4-chloro-1-naphthoxy)-2-oxoethyl methacrylate with 2-(dimethylamino) ethyl methacrylate copolymers, quaternized amino groups. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*. 2011;**48**(2):169-176. DOI: 10.1080/10601325.2011.537537
- [19] Ari H, Soykan C, Özpozan T. Preparation of organic/inorganic hybrid materials using aggregates of poly{2-methyl-N-[2-(phenylthio)phenyl]acrylamide-co-2-(trimethylsilyloxy)ethyl methacrylate} as precursor and vibrational investigation of the polymerization. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*. 2013;**50**(10):1022-1041. DOI: 10.1080/10601325.2013.821847
- [20] Açıkbaş Y, Erdoğan M, Çapan R, Soykan C. Characterization and gas sensing properties of Langmuir-Blodgett thin films of poly(CINOEMA-co-DEAEMA). *Sensor Letters*. 2016;**14**:474-483. DOI: 10.1166/sl.2016.3636
- [21] Açıkbaş Y, Çapan R, Erdoğan M, Bulut L, Soykan C. Optical characterization and swelling behaviour of Langmuir-Blodgett thin films of a novel poly[styrene(ST)-co-glycidyl methacrylate (GMA)]. *Sensors and Actuators B: Chemical*. 2017;**241**:1111-1120. DOI: 10.1016/j.snb.2016.10.025
- [22] Patel MB, Patel SA, Ray A, Patel KH. Synthesis, characterization, and antimicrobial activity of acrylic copolymers. *Journal of Applied Polymer Science*. 2003;**89**(4):895-900. DOI: 10.1002/app.11970
- [23] Patel MP, Shah B, Ray A, Patel KH. Acrylic homo- and co-polymers based on 2,4-dichlorophenyl methacrylate and 8-quinolinyl methacrylate. *Journal of Polymer Science-Taiwan*. 2004;**11**(1):65-73. DOI: 10.1023/B:JPOL.0000021779.30811.48

- [24] Patel MV, Dolia MB, Patel JN, Patel RM. Synthesis and characterization of novel acrylic copolymers: Determination of monomer reactivity ratios and biological activity. *Reactive and Functional Polymers*. 2005;**65**(3):195-204. DOI: 10.1016/j.reactfunctpolym.2005.08.002
- [25] Patel JN, Patel JR, Patel KH, Patel MP, Patel MR. Acrylic copolymers based on phenol: Synthesis, characterization, and antimicrobial activity. *Journal of Macromolecular Science, Part A Pure and Applied Chemistry*. 2007;**44**(4-6):395-402. DOI: 10.1080/10601320601188109
- [26] Patel MG, Patel HJ, Patel JR, Patel KH. Development and applications of novel acrylic copolymers. *International Journal of Polymeric Materials*. 2008;**57**(2):165-176. DOI: 10.1080/00914030701486179
- [27] Patel JR, Patel KH, Patel RM. Reactivity ratio of novel acrylic copolymer by NMR spectroscopy. *Colloid & Polymer Science*. 2009;**287**(1):85-90. DOI: 10.1007/s00396-008-1943-6
- [28] Patel HJ, Patel MG, Patel AK, Patel KH. Synthesis, characterization and antimicrobial activity of important heterocyclic acrylic copolymers. *Express Polymer Letters*. 2008;**2**(10):727-734. DOI: 10.3144/expresspolymlett.2008.86
- [29] Patel RT, Patel KH, Patel AR, Patel RM. Kinetic of 8-quinolinyl methacrylate polymerization by differential scanning calorimetry. *International Journal of Polymeric Materials and Polymeric Biomaterials*. 2000;**46**:71-79. DOI: 10.1080/00914030008054842
- [30] Vijayanand PS, Kato S, Kojima T. Synthesis and characterization of 3,5-dimethoxyphenyl methacrylate and methyl methacrylate copolymers: Determination of monomer reactivity ratios. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*. 2007;**44**(3):277-283. DOI: 10.1080/10601320601077302
- [31] Zhang R, Yang J, Sun W, Shen Z. Synthesis and characterization of poly [4-(2-thiazolylazo) phenyl methacrylate]-co-poly(methyl methacrylate). *Journal of Applied Polymer Science*. 2007;**103**(4):2152-2157. DOI: 10.1002/app.25041
- [32] Thamizharasi S, Gnanasundaram P, Reddy BSR. Copolymerization of 4-acetyl phenylacrylate with methacrylate and butyl methacrylate: Synthesis, characterization and reactivity ratios. *European Polymer Journal*. 1997;**33**(9):1487-1494. DOI: 10.1016/S0014-3057(96)00270-4
- [33] Stanek LG, Heilmann SM, Gleason WB. Synthesis and monomer reactivity ratios of methyl methacrylate and 2-vinyl-4,4'-dimethylazlactone copolymers. *Journal of Polymer Science, Part A: Polymer Chemistry*. 2003;**41**:3027-3037. DOI: 10.1002/pola.10897
- [34] Loubat C, Batt-Coutrot D, Guyot B, Robin JJ, Boutevin B. Synthesis and monomer reactivity ratios of ethyl α -acetoxyacrylate and acrylic acid copolymers. *Polymer International*. 2005;**54**(11):1557-1563. DOI: 10.1002/pi.1884