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https://doi.org/10.37358/Mat.Plast.1964

Green P(AAm-*co*-DADMAC) Copolymeric Material as Catalyst for Synthesis of Potential Phytohormones of Phenylazophenoxy-acetic Acids by Phase Transfer Catalysis

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Abstract. *Several phenylazophenoxyacetic acid derivatives were obtained starting from azophenols and ethyl chloroacetate by an environmentally friendly approach. The synthesis reaction was carried out in heterogeneous medium using P(AAm-co-DADMAC) copolymer. Good results have been obtained thanks to phase transfer catalysis. Retrosynthetic and structural analysis were performed.*

Keywords*: P(AAm-co-DADMAC), phase transfer catalysis, ethyl chloroacetate, spectroscopic analysis*

1. Introduction

Many organic chemical reactions cannot occur because the reactants do not come into contact with each other. A major difficulty is the contacting of an ionic reactant soluble in aqueous inorganic medium with an organic reactant insoluble in the inorganic phase. In such a common case in organic synthesis, the chemist adds to the reaction medium a solvent for both inorganic phase and organic phase. For example an alcohol exhibits lipophilicity by the ethyl group and hydrophilicity by hydroxyl function. However, the reaction rate is slow due to the solvation of the ionic reagent by the newly added solvent [1]. Sometimes dipolar aprotic solvents, that exhibit high dielectric constant and increased dipole moment and have no labile hydrogen atoms, are employed. Solvents such as dimethylformamide, acetonitrile, ethyl acetate, acetone, *N*-methylpyrrolidone, dimethyl sulfoxide, etc., can not form hydrogen bonds [2].

Phase transfer catalysis (PTC) is a modern approach for performing organic chemical reactions between reactants in different chemical phases. To transfer the reagents from one phase to another, i.e. to bring them into contact, a "phase transfer agent", called a phase transfer catalyst, is used [3]. The fundamentals of phase transfer catalysis were developed in the seventh decade of the last century by chemists Starks (1971), Mąkosza (1975), and Brandstrom (1977) [4].

The reactions to which PTC is applicable can be divided into two major categories [5]:

- reactions of anions available as salts;
- reactions of anions that should be generated *in situ.*

In general, the phase transfer catalyst is a quaternary ammonium salt. It carries anions in the form of pairs of lipophilic ions in the organic phase where the reaction takes place.

Phytohormones (plant hormones or auxins) are substances produced by each plant cell, unlike animals in which only a few glands or specialized cells produce them. These biologically active molecules control embryogenesis, stress tolerance, organ size, plant antibodies and its reproduction [6-8]. Phenoxyacetic acids are molecules widely used as plant growth regulators [9, 10]. The Phenoxyacetic acid derivatives are involved in the biosynthesis of auxins during the induction of somatic embryogenesis [6].

Commercially, phenoxyacetic acid derivatives are widely used as important herbicides due to their low price and water solubility. The compounds are applied in agriculture and recreational areas, in grain farms against broadleaf weeds, in parks, on pastures, on golf courses and lawns [11, 12]. Poly(acryl-amide-*co*-diallyldimethylammonium chloride) or P(AAm-*co*-DADMAC), also named poly-

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quaternium-7 copolymer, is a cationic polymer with pyrrolidimium structure. It is obtained by free-radical copolymerization of the water soluble monomer diallyldimethylammonium chloride (DADMAC) and acrylamide (AAm) in presence of potassium persulfate. Its molecular formula is $(C_8H_{16}ClN)_n(C_3H_5NO)_m$ and the chemical structure is shown in Figure 1 [13]. Given its structure and properties, it was selected for our study as phase transfer catalyst in a solventless, environmentally friendly process.

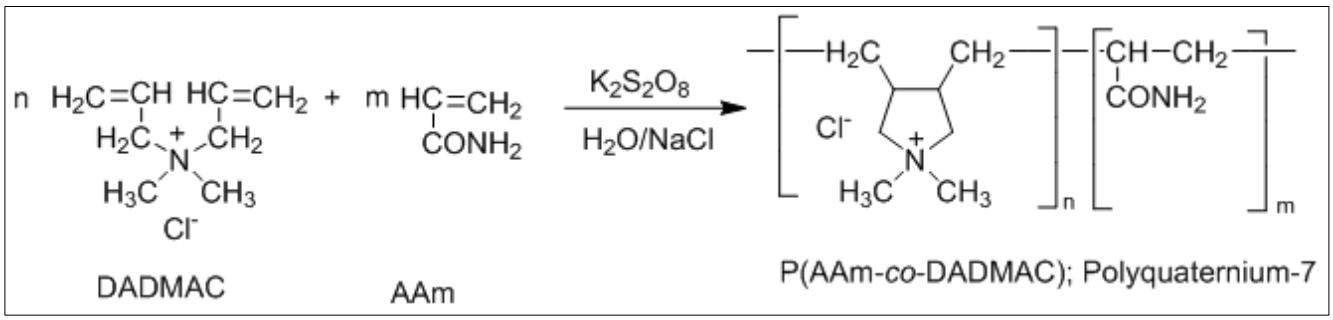


Figure 1. The synthesis and chemical structure of P(AAm-co-DADMAC)

2. Materials and methods

All reagents are commercial products and were used without further purification. The melting temperature of reagents was determined with a Gallenkamp digital melting point apparatus. Ultraviolet-visible spectra were recorded in $2.5x10^{-4}$mol/L 1,4-dioxane solution using a Varian Cary spectrometer. Elemental analysis was performed with an elemental analyzer (Carlo Erba model 1106). ^{1}H-NMR spectra were acquired on Bruker Avance spectrometer at 300 MHz in $CDCl_3$. ^{13}C-NMR analysis was performed using a Bruker Avance spectrometer at 75 MHz with $CDCl_3$ as solvent. Chemical shifts δ were measured in parts per million (ppm) relative to tetramethylsilane (TMS). The infrared spectra were recorded by the means of an Alpha Bruker Optics spectrometer. An Extech EA10 dual input digital thermometer was employed.

2.1. General procedure for synthesis of p-hydroxyazobenzene derivatives

In an acidic solution containing 8 mL H_2O and 2.2 mL HCl solution 37% was added 0.01 mol of aromatic amine. The amine hydrochloride solution was brought to an ice water bath at 0-5°C. A solution of sodium nitrite was prepared by dissolving 0.84 g $NaNO_2$ in 2.5 mL H_2O, and then poured dropwise under stirring into the amine hydrochloride solution so that the temperature did not exceed 0-5°C. The reaction was perfected at the same temperature for 45 min. The resulting suspension of diazonium salt is stable if its temperature is below 5°C.

Separately, another solution was prepared by combining 32mL water, 3.44g NaOH and the corresponding phenol derivative (0.01 mol) and cooled down to 5°C. The diazonium salt solution is added dropwise and with stirring to the phenol derivative solution, verifying that the temperature of the reaction medium, using an Extech EA10 dual-input digital thermometer, does not exceed 12°C. The reaction medium was stirred for 30 min. Whereupon 2.4 mL acetic acid was added, under stiring, until the *p*H becomes weakly acidic (*p*H=6). The precipitate, after being filtered, was air dried, weighed and recrystallized from acetic acid before obtaining the pure compound.

General procedure for synthesis of substituted derivatives of 4-(phenylazo) phenoxyacetic acid by PTC

In a 50 mL two-necked flask, supplied with reflux refrigerant, thermometer and magnetic stirrer, 1.4 mL of H_2O, 1.4 g of KOH, and 5 mmol of aromatic *p*-hydroxyazobenzene derivative were introduced one by one. To this mixture, 0.4725 g of ethyl chloroacetate and 0.5g of 10% P(AAm-co-DADMAC) aqueous solution were added and heated at reflux for 4.5 h. Afterwards, the reaction mixture was cooled at room temperature, 15 mL of water were added to it and the *p*H was adjusted to 3 using a 10% HCl solution. The resulting precipitate is filtered, dried and purified by recrystallization from CH_3COOH.

p-hydroxyazobenzene. Anal. Calc. for $C_{12}H_{10}N_2O$: C 72.72, H 5.05, N 14.14. Found: C 72.68, H 5.00, N 14.08. m.p.=150-151°C; Lit. m.p.=149-151°C [13]; yield 82%.

m-chloro-p-hydroxyazobenzene. Anal. Calc. for $C_{12}H_9N_2OCl$: C 61.93, H 3.87, N 12.04; found: C 61.75, H 3.82, N 11.78; m.p.= 85-85.5°C; Lit. m.p.= 84.5-85.5°C [14]; yield 61%.

m-allyl-p-hydroxyazobenzene. Anal. Calc. for $C_{15}H_{14}N_2O$: C 75.33, H 5.88, N 11.76; found: C 75.21, H 5.73, N 11.62; m.p.= 90-91°C; Lit. m.p.=89-91 [15]; yield 70%.

p'-methyl-p-hydroxyazobenzene. Anal. Calc. for $C_{13}H_{12}N_2O$: C 73.58, H 5.66, N 13.20; found: C 73.38, H 5.28, N 13.11; m.p.= 143-143.5°C; Lit. m.p.= 143-144°C [13]; yield 85%.

4-(phenylazo)phenoxyacetic acid. Anal. Calc. for $C_{14}H_{12}N_2O_3$: C 65.62, H 4.68, N 10.93; found: C 65.59, H 4.57, N 10.33; m.p.= 224-225°C; yield 83%.

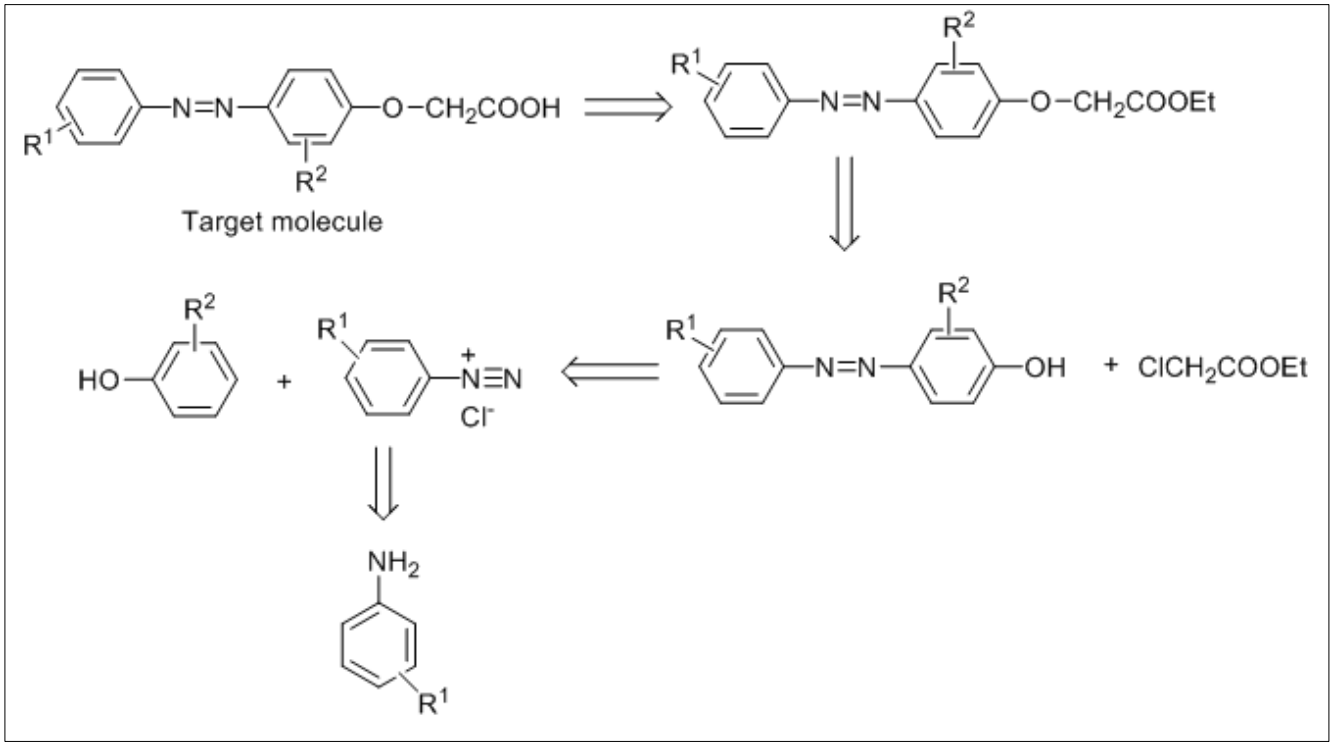
2-chloro-4-(phenylazo)phenoxyacetic acid. Anal. Calc. for $C_{14}H_{11}ClN_2O_3$: C 57.83, H 3.78, N 9.63; found: C 57.67, H 3.71, N 9.52; m.p.=134-135°C; yield 67%.

2-allyl-4-(phenylazo)phenoxyacetic acid. Anal. Calc. for $C_{17}H_{16}N_2O_3$: C 68.91, H 5.40, N 9.45 found: C 68.88, H 5.35, N 9.39; m.p.=82-83°C; yield 71%.

4-(p-methylphenylazo)phenoxyacetic acid. Anal. Calc. for $C_{15}H_{14}N_2O_3$: C 66.66, H 5.18, N 10.37 found: C 66.61, H 5.01, N 10.12; m.p.=216-217°C; yield 80%.

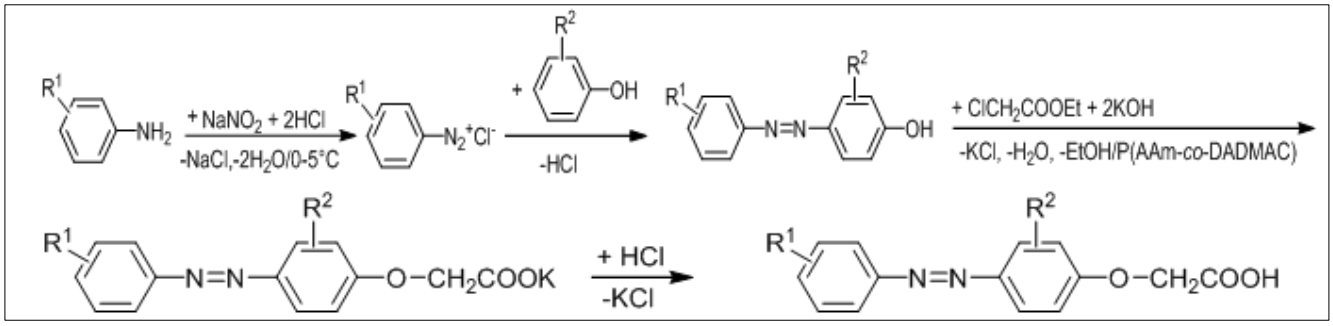
3. Results and discussions

We have synthesized some potential phytohormones that are derivatives of *p*-(phenylazo) phenoxyacetic acid. In order to find the optimal conditions for the synthesis of the compounds, their retrosynthetic analysis was performed. This analysis allows us to identify synthons and their correspondents in potential starting reagents (Scheme 1).



Scheme 1. Retrosynthetic analysis of *p*-(phenylazo) phenoxyacetic acid derivatives

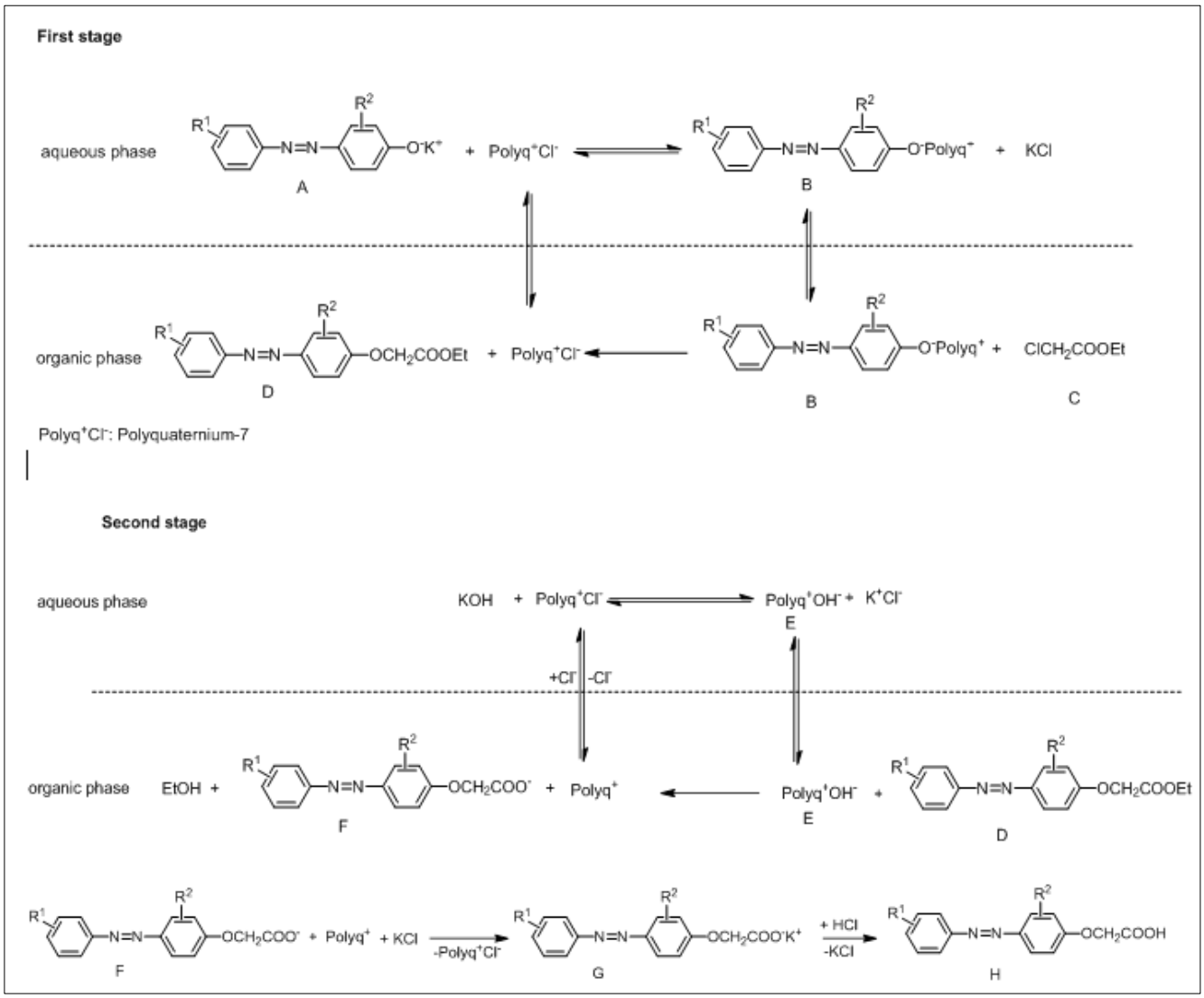
Synthetic pathway starts from substituted anilines that are converted into diazonium salts which couple with phenols to *p*-azophenols. The latter reacts with ethyl chloroacetate in a basic medium and forms ethyl 4-(phenylazo)phenoxyacetate derivatives which by ester hydrolysis followed by acidification generates *p*-(phenylazo) phenoxyacetic acid derivatives (Scheme 2).



Scheme 2. Reactions to obtain *p*-(phenylazo) phenoxyacetic acid derivatives

The reaction system is biphasic: a) aqueous inorganic phase containing azophenoxide anions (A), hydroxylic anions of KOH, and water b) organic phase represented by ethyl chloroacetate (C). The transfer of reagents between the two phases is performed by P(AAm-*co*-DADMAC) (Scheme 3).

In the first stage, P(AAm-*co*-DADMAC) transfers from the aqueous phase to the organic phase the nucleophile, the azophenolate anion (A), by an ionic complex (B). The reaction of (B) with ethyl chloroacetate gives the ethyl 4-(phenylazo) phenoxyacetate derivative (D).



Scheme 3. Mechanism of synthesis of derivatives of *p*-(phenylazo) phenoxyacetic acid using P(AAm-*co*-DADMAC) as catalyst

In the second stage, P(AAm-*co*-DADMAC) transfers the hydroxylic anions from the aqueous phase *via* the ionic species Polyq^{+}OH^{-} (E) to the organic phase represented by ethyl *4*-(phenylazo) phenoxy-acetate derivative (D). The hydrolysis reaction occurs and generates *p*-(phenylazo) phenoxy-acetate salt derivative (F) and, potasium *p*-(phenylazo) phenoxyacetate (G), respectively. Finally, by adding hydrochloric acid solution the salt transforms into *p*-(phenylazo) phenoxyacetic acid derivative (H).

UV-Visible spectra

4-Hydroxyazobenzene derivatives contain azoic chromophore (N=N) and hydroxylic auxochrome (OH). Both of them involved in the aromatic conjugated system. The chromophore and the auxochrome from different molecules interact because the molecules of *4*-hydroxyazobenzene derivatives are associated in pairs (Figure 2) by intermolecular hydrogen bonds [14]:

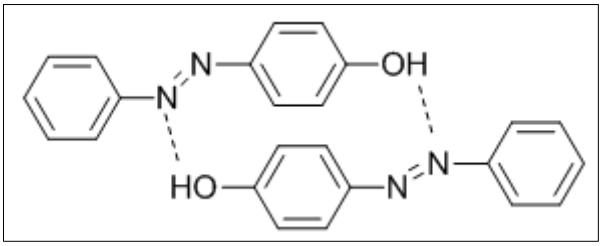


Figure 2. Aromatic conjugation system of two molecules of 4-hydroxyazobenzene

The UV-Vis spectra of 4-hydroxyazobenzene derivatives show two absorption bands. The absorption band in the visible region around 440 nm is due to an n→π* transition prohibited by symmetry and have a low intensity. The strong absorption band centered at about 350 nm is due to the symmetry allowed π→π* transition (Table 1).

The UV-Vis spectra of **4**-(phenylazo) phenoxyacetic acid derivatives reveal three absorption bands. At about 450 nm is a low intensity *R*-band due to the azoic chromophore (N=N). An intense *K*-band absorption of about 350 nm is due to the electronic conjugation of two benzene nuclei. The middle intensity benzenoid type *E* or *B*-bands [15] exhibit at about 230 nm (Table 1).

The formation of intermolecular hydrogen bonds as in the case of 4-hydroxyazobenzene can not be neglected in the case of 4-(phenylazo) phenoxyacetic acids (Figure 3).

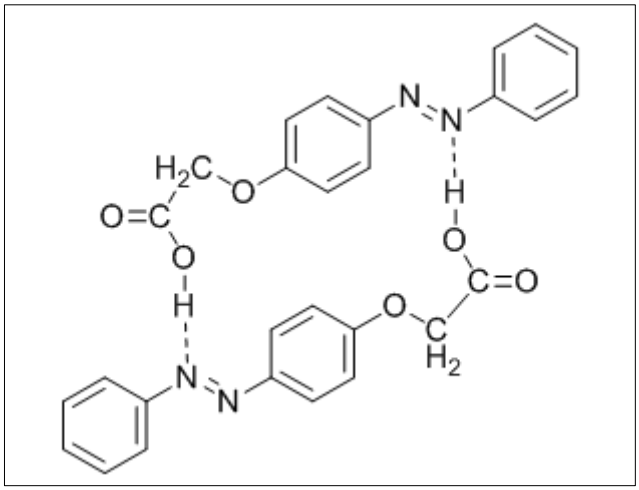


Figure 3. Intermolecular hydrogen bonds formation among molecules of 4-(phenylazo) phenoxyacetic acids

Table 1. IR and UV-VIS absorption bands of the compounds

Compounds	IR, [ν,cm^{-1}]	UV-Vis, [λ, nm]
p-hydroxyazobenzene	3400-3135, 1505, 1488, 1417, 1145, 1108, 806	344 nm ($\pi\rightarrow\pi^*$) 436 nm ($n\rightarrow\pi^*$).
m-chloro-*p*-hydroxy azobenzene	3350-3001, 1510, 1490, 1418, 1139, 1105, 798	350 nm ($\pi\rightarrow\pi^*$) 440 nm ($n\rightarrow\pi^*$)
m-allyl-*p*-hydroxy azobenzene	3450-3250, 1638, 1511, 1495, 1416, 1140, 1100, 800	350 ($\pi\rightarrow\pi^*$) 445 ($n\rightarrow\pi^*$)
p'-methyl-*p*-hydroxyazobenzene	3421-3997, 1562, 1509, 1467, 1412, 1130, 987	350 ($\pi\rightarrow\pi^*$) 447 ($n\rightarrow\pi^*$)
4-(phenylazo) phenoxyacetic acid	3455-3360, 1734, 1617, 1591, 1499, 1428, 1377, 1250, 1153, 1087, 848	238 ($\pi\rightarrow\pi^*$) 350 ($n\rightarrow\pi^*$) 440 ($n\rightarrow\pi^*$).
2-chloro-*4*-(phenylazo) phenoxyacetic acid	3470-3350, 1733, 1588, 1414, 1500, 1262, 1039, 875	241 ($\pi\rightarrow\pi^*$) 349 ($n\rightarrow\pi^*$) 439 ($n\rightarrow\pi^*$)
2-allyl-*4*-(phenylazo) phenoxyacetic acid	3460-3330, 1730, 1569, 1590, 1490, 1416, 1270, 1060, 863	231 ($\pi\rightarrow\pi^*$) 351 ($n\rightarrow\pi^*$) 451 ($n\rightarrow\pi^*$)
4-(*p*-methylphenylazo) phenoxyacetic acid	3430-3250, 3020, 2914, 1731, 1600, 1583, 1497, 1427, 1370, 1240, 1143, 1085, 830	233 ($\pi\rightarrow\pi^*$) 352 ($n\rightarrow\pi^*$) 453 ($n\rightarrow\pi^*$)

FT-IR spectra

The infrared spectra of 4-hydroxyazobenzene derivatives (Table 1) show a broad and intense valence vibration band for the hydroxylic group (OH) at 3400-3000 cm^{-1}. The valence vibration band for the *azo* group was very weak in the *trans* isomer at about 1412 cm^{-1} and intense in the *cis* isomer around 1510 cm^{-1} because it overlaps the deformation vibrations of the methylene group (CH_2).

The infrared spectra of *4*-(phenylazo) phenoxyacetic acids (Table 1) reveals an intense broad valence vibration band for hydroxylic group (OH) at 3470-3250 cm^{-1}. The valence vibration of the C=O group (from COOH) appears at about 1730 cm^{-1} and is very intense. [15] The asymmetric valence vibration band of the ether group appears at about 1250 cm^{-1} and was very intense, and the symmetric valence vibration band of the same group was of medium intensity and appears at about 1100 cm^{-1}. The valence vibration band of the *azo* group occurs at around 1416 cm^{-1} and was intense in the *trans* isomers and very intense in the *cis* isomer at around 1490 cm^{-1}.

NMR spectra

The ^{1}H-NMR spectral data of the *4*-hydroxyazobenzene derivatives, chemical shifts (δ, ppm) and coupling constants (*J, Hz*) are reported in Table 2. The aromatic protons exhibit a multiplet at 6.92-7.89 ppm. The phenolic proton of the hydroxyl group had a broad singlet peak with variable position. The aromatic protons at the two benzene nuclei of the *4*-(phenylazo) phenoxyacetic acid derivatives absorb in the region at about 7.40-8.02 ppm. The proton of the methylene group (CH_2) had a singlet peak at about 4.70 ppm. The peak of the acidic proton of the carboxyl group (COOH) showed a broad singlet at about 10 ppm [15].

The ^{13}C-NMR chemical shifts (δ, ppm) of the peaks of the compounds are displayed in Table 2. The ^{13}C peaks corresponding to the aromatic domain were identified at 114.50-158.70 ppm. The ^{13}C peak from the carboxyl group (COOH) appears at approximately 170 ppm and the peak of the methylene group (CH_2) at around 65 ppm. These signals confirm once again the structure of the synthesized compounds.

Table 2. *^{1}H*-NMR and *^{13}C*-NMR spectral analysis of the compounds

Compounds	*^{1}H*-NMR [δ, ppm; *J*, Hz]	*^{13}C*-NMR [δ, ppm]
p-hydroxyazobenzene	6.92-7.89 (m, *J*=8 Hz, 9H), 9.21 (sbr, 1H)	116.2, 129.9, 125.4, 129.2, 130.8, 146.7, 153.2, 161.1
m-chloro-*p*-hydroxy azobenzene	6.94 (d, *J*= 8.2 Hz, 1H), 7.41-7.51 (m, 3H), 7.60 (dd, *J*= 8.2 Hz, *J*=2.0 Hz, 1H), 7.62–7.70 (m, 3H), 7.77 (sbr, 1H)	117.0, 122.1, 122.5, 122.9, 125.1, 129.2, 130.3, 143.1, 152.7, 153.6
m-allyl-*p*-hydroxy azobenzene	3.49 (d, *J*=7.5 Hz, 2H), 5.08 (dd, *J*=10Hz, *J*=2.1Hz, 2H), 5.14 (dd, *J*=16.6Hz, *J*=2.1Hz, 2H), 6.08 (ddt, *J*=16.6 Hz, *J*=10.1Hz, *J*=7.7Hz, 1H), 8.03–7.03 (m, 6H), 9.25 (sbr, 1H)	34.2, 116.1, 117.1, 122.5, 122.8, 124.1, 127.2, 129.2, 130.3, 136.7, 142.4, 152.6, 156.1
p'-methyl-*p*-hydroxyazobenzene	2.39 (s, 3H), 6.93 (d, *J*=10 Hz, 2H), 7.35 (d, *J*=10 Hz,2H), 7.72 (d, *J*=10 Hz, 2H), 7.77 (d, *J*=10 Hz, 2H), 10.26 (s, 1H)	21.1, 116.5, 120.2, 125, 130.5, 141., 147.1, 148.2, 161.4
4-(phenylazo) phenoxyacetic acid	4.73 (s, 2H), 7.40-7.48 (m, *J*=8 Hz, 4H), 7.83-7.86 (m, 5H), 11.4 (sbr, 1H)	65.2, 115.4, 122.5,123, 129.2, 130.4, 146.9, 152.2, 158.7, 170.1
2-chloro-*4*-(phenylazo) phenoxyacetic acid	4.75 (s, 2H), 7.06 (d, *J*=7.6 Hz, 1H), 7.51–7.39 (m, 2H), 7.60 (dd, *J*= 7.6, *J*=2.2 Hz, 1H), 7.66 (d, *J*=2.3 Hz, 1H), 7.72 – 7.68 (m, 3H); 11 (sbr, 1H)	65.2, 114.7, 121.2, 122.4, 124, 124.3, 129.1, 130.2, 145.6, 152.6, 155.3, 169.5
2-allyl-*4*-(phenylazo) phenoxyacetic acid	4.69 (s, 2H), 3.48 (d, *J*=7.5 Hz, 2H), 5.07 (dd, *J*=10 Hz, *J*=2.1 Hz, 2H), 5.14 (dd, *J*=16.6 Hz, *J*=2.1 Hz, 2H), 6.09 (ddt, *J*=16.6 Hz, *J*=10.1Hz, *J*=7.7Hz, 1H), 7.04-8.02 (m, 6H), 11.8 (sbr, 1H)	33.4, 66.3, 114.5, 116.2, 121.2, 122.7, 123.2, 127.2, 129.1, 130.3, 136.6, 144.7, 152.8, 157.2, 171.6
4-(*p*-methylphenylazo) phenoxyacetic acid	4.72 (s, 2H), 2.40 (s, 3H), 7.76 (m, *J*=7.8 Hz, *J*=1.2 Hz, 2H), 7.27 (m, 2H), 7.01 (m, J=6.6 Hz, *J*=3.6 Hz, 2H), 7.27 (m, 2H), 11.5 (sbr, 1H)	21.2, 65.1, 115.4, 120.1, 129.8, 130.5, 141.2, 146.9, 148.4, 158.7, 170.1

4. Conclusions

An environmentally friendly method involving phase transfer catalysis (PTC) was implemented for the synthesis of *4*-(phenylazo) phenoxyacetic acid derivatives. The method does not require organic solvent. A green copolymer material P(AAm-*co*-DADMAC) was employed as catalyst. The facile experimental protocol, the simplicity of installation, the absence of waste and good efficiency of the process are assets which make this method friendly to the environment.

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Manuscript received: 14.03.2021