ACTA CHEMICA IASI, **19**, 101-115 (2011)

Anthracene-based Acrylamides and Methacrylamides as Functional Monomers: Synthesis and Characterization

Oana-Iuliana Negru, Virgil Barboiu and Mircea Grigoras*

Electroactive Polymers Department, "P.Poni" Institute of Macromolecular Chemistry, 41 A G.Ghica Voda Aleey, Iasi, 700478, Romania

Abstract: Six novel anthracene – based monomers, i.e., 1-anthryl acrylamide, 1-anthryl methacrylamide, 2-anthryl acrylamide, 2-anthryl methacrylamide, 9-anthryl acrylamide and 9-anthryl methacrylamide were synthesized and characterized. Reaction of acryloyl- and methacryloyl chloride, in presence of triethylamine, with 1-, 2- and 9-anthryl amine led to the corresponding acrylamide and methacrylamide monomers. Their structure was proved by elemental analysis, ESI-MS, FTIR, ^{1}H-NMR and UV spectroscopy. Due to their strong fluorescent properties there monomers can be used to label usual polymers.

Keywords: Anthracene Acrylamides and Methacrylamides, Functional Monomers, FTIR, NMR, UV Characterisation.

Introduction

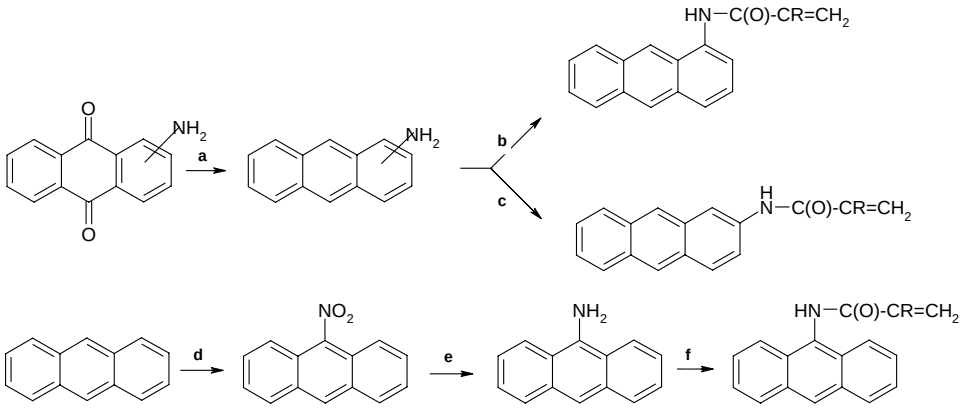
The interest for vinyl monomers and polymers containing bulky

*Oana–Iuliana Negru, tel: +40-0232-217454, Fax: +40-0232-211299, e-mail: irimia.oana@icmpp.ro

aromatic substituents started particularly since the charge transfer complex, poly *N*-vinylcarbazole-2,4,7-trinitro-9-fluorenone (PVK/TNF) was used as a photoconducting material in electrophotography.[1] Anthracene is known as a strong electron donor and highly efficient and stable fluorophore molecule while polymers containing anthracene groups preserve these characteristics. In addition, anthracene-based oligomers and polymers combine the specific properties of aromatic compound with those of macromolecular state. These polymers may have potential applications as organic semiconductors and photoconductors,[2] photoreactive materials,[3] light emitting materials and solar cells,[4] organic field effect transistors,[5] photon harvesters.[6] Polymerization of anthracene monomers is also an interesting research topic. In the most cases, the polymerization yields oligomers with random structure due to the inhibition effect of the anthryl group, the isomerization reactions of carbenium ions and carbanions, the chain transfer reaction and the "wrong" monomer additions.[7] Also, anthracene groups can participate in Diels-Alder cycloaddition, photodimerization and photooxidation reactions with applications in formation of thermally reversible networks and photorezists.[8] In this paper we report the synthesis of six new anthracene-based monomers containing acrylamide and methacrylamide function as polymerizable group. The monomers are: 1-anthryl acrylamide (1-AA), 1-anthryl methacrylamide (1-AM), 2-anthryl acrylamide (2-AA), 2-anthryl methacrylamide (2AM), 9-anthryl acrylamide (9-AA) and 9-anthryl methacrylamide (9-AM). The monomers can be used to obtain functionalized polymers or to label the usual polymers by copolymerization using small quantities of anthracene groups (1-5%) as a fluorescent probe to study macromolecular dynamics.

Results and discussions

Six new anthracene-based acrylamide and methacrylamide monomers were synthesized through a coupling reaction between acyl chloride and corresponding anthracene amine, in presence of triethylamine used as neutralizing agent for HCl formed as secondary product. Scheme 1 shows the chemical structure and the synthetic strategies leading to the anthracene monomers. First, 1- and 2-aminoanthracene were obtained by reduction of the commercial 1- and 2-aminoanthraquinone with Zn/NaOH.[9] 9-Aminoanthracene was synthesized by nitration of anthracene with HNO_3 and reducing of 9-nitroanthracene with $SnCl_2$.[10] All amine derivatives are crystalline products, yellow colored and having a strong fluorescence in diluted solution.



a) 1-amino, and 2-aminoanthraquinone, Zn/NaOH, b) methacryloyl chloride, TEA, toluene, c) acryloyl chloride, TEA, toluene, d) HNO_3, e) $SnCl_2$/HCl, f) acryloyl and methacryloyl chloride, TEA, toluene.

Scheme 1. Synthesis of anthryl acrylamides (R=H) and methacrylamides (R=CH_3)

Anthracene- acrylamide and methacrylamide monomers are obtained as crystalline and colored products with high melting points and good thermal stability. Table 1 gives the melting points, yields and elemental analysis results for the synthesized monomers.

Table 1. The melting points, the yields and results of elemental analysis of the monomers

M [a]	Yield [b] %	Melting point (°C)	C (%)		H (%)		N (%)		Color [c]
			Calcd	Found	Calcd	Found	Calcd	Found	
1-AA	62.6	158	82.57	82.40	5.30	5.24	5.66	5.70	T
1-AM	75.7	160	82.73	82.85	5.79	5.70	5.36	5.28	T
2-AA	92.0	215	82.57	82.47	5.30	5.27	5.66	5.78	Y
2-AM	95.0	233	82.73	82.58	5.79	5.62	5.36	5.42	Y
9-AA	58.4	150	82.57	82.41	5.30	5.36	5.66	5.50	O
9-AM	61.2	164	82.73	82.68	5.79	5.68	5.36	5.49	O

[a] 1-AA, N-1-anthrylacrylamide; 1-AM, N-1-anthrylmethacrylamide; 2-AA, N-2-anthrylacrylamide; 2-AM, N-2-anthrylmethacrylamide; 9-AA, N-9-anthrylacrylamide; 9-AM, N-9-anthrylmethacrylamide.

[b] Based on the corresponding anthrylamine

[c] T, tan, O, orange, Y, yellow.

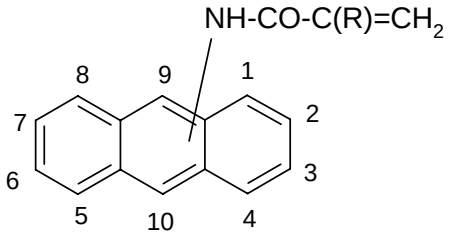
FTIR Studies

The amine compounds show IR bands at 3500 cm^{-1} (ν NH asym.) and 3400 cm^{-1} (ν NH sym.), ν C=C (1600-1610 cm^{-1}) and γC-H for 1-, 2- or 9-substituted anthryl ring (700-900 cm^{-1}). By coupling with acyl chloride the characteristic bands of amine group are replaced with amide group vibrations. The FTIR spectra of all monomers show the main characteristic peaks assigned as follows (Table 2): ν NH (3210-3300 cm^{-1}), ν C=O of amide moiety (1645-1660 cm^{-1}) and (1485-1520 cm^{-1}), ν C=C (1610-1620 cm^{-1}) and γC-H for 1-, 2- or 9-substituted anthryl ring (700-900 cm^{-1}). The differences between IR spectra in the 700-900 cm^{-1} region are due to a combination of γC-H from 1,2- disubstituted, 1,2,3- or 1,2,4-trisubstituted, 1,2,4,5-tetrasubstituted or 1,2,3,4,5-pentasubstituted benezene rings from anthracene compounds.

^{1}H-NMR Studies

Figure 1 shows ^{1}H-NMR spectra obtained for 1-anthrylamine (1-A), 2-anthrylamine (2-A) and 9-anthrylamine (9-A) and the corresponding acrylamide and methacrylamide monomers. The amine protons appear as broad signals at 4.30 ppm (1-A), 3.90 ppm (2-A) and 4.38 ppm (9-A). After reaction with acyl chloride this signal disappears and another broad signal appears after 9 ppm due to amide proton (-NH-CO-) while vinyl protons appear as distinct signals between 5.5-6.6 ppm. Methyl group from methacrylamide monomers appears as a singlet at 2.02-2.25 ppm. Therefore, the NMR spectra prove the formation of acrylamide and methacrylamide monomers (Table 2).

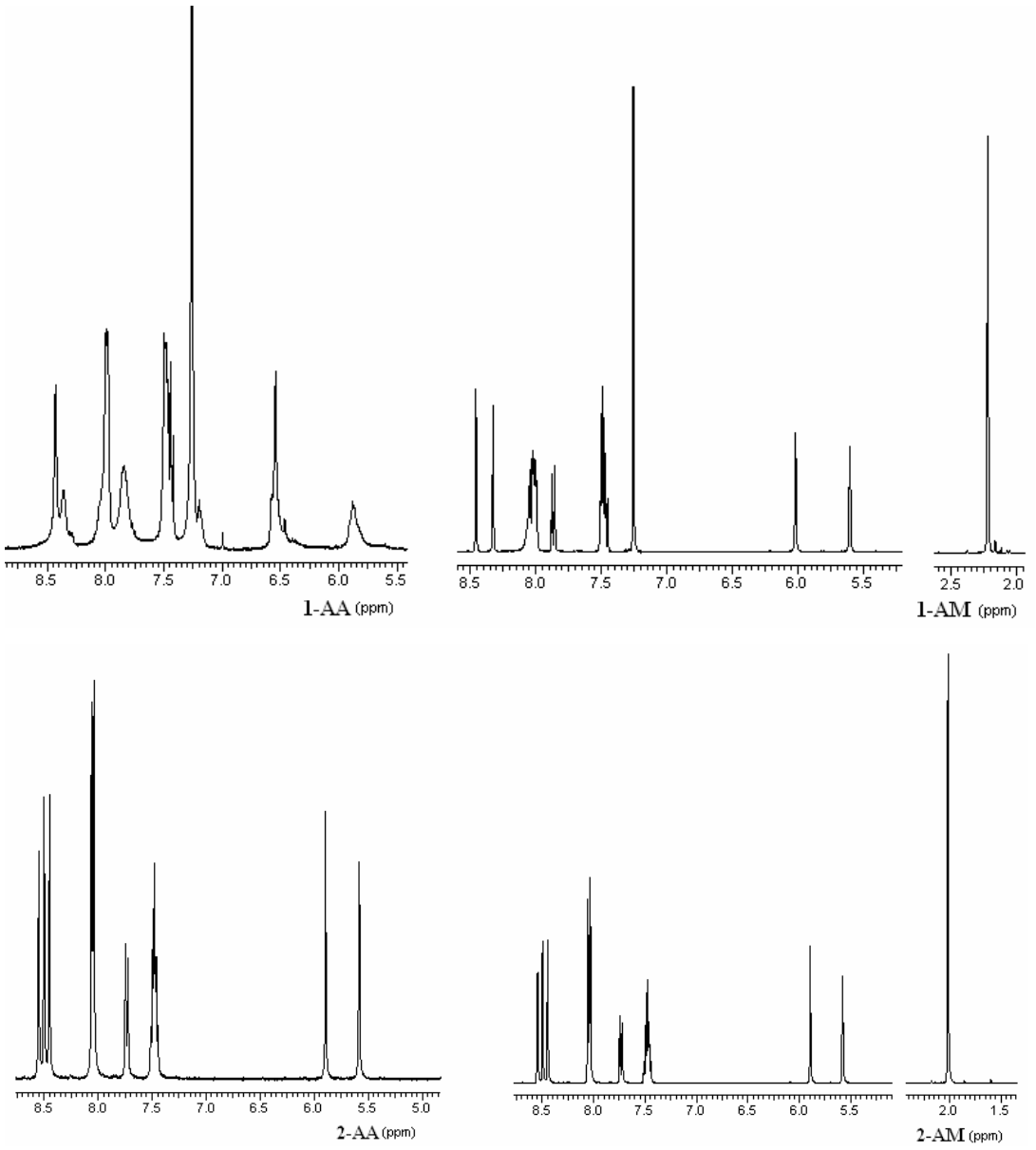
Table 2. Spectral characteristics of the monomers



Monomer	**^{1}H-NMR (400 MHz) δ, ppm**	**IR (KBr pellet) cm^{-1}**	**UV ($CHCl_3$) λ_{max}, nm**	**ESI-MS (m/z)**
1-AA	$CDCl_3$, 5.9 (1H) and 6.54 (2H) for vinyl protons, 7.42-7.50 (m, 3H, H_3, H_6 and H_7), 7.84 (1H, H_2), 7.99 (m, 3H, H_4, H_5 and H_8), 8.36 (1H) and 8.43 (1H) for H_9 and H_{10}.	725,740, 775 and 870 (γC-H, 1-substituted anthryl group), 1615 (υC=C), 3240 (υNH), 1520 and 1650 (amide group)	258, 366, 378, 396	270.18 $[M+Na]^+$
1-AM	$CDCl_3$, 2.22 (s, 3H, -CH_3), 5.60 (s, 1H) and 6.02 (s, 1H) for vinyl protons, 7.45-7.52 (m, 3H, H_3, H_6 and H_7), 7.87 (d, J = 8.4 Hz, H_2), 8.00 (d, J = 8.4 Hz, 1H), 8.01 (d, J =	732, 740, 780, 875 (γC-H,1-substituted anthryl group), 1615 (υC=C), 1500 and 1650 (-CO-NH-), 3300 (υNH)	258, 365, 376, 396	284.14 $[M+Na]^+$

	8.4 Hz, 1H) and 8.04 (d, J = 8.4 Hz, 1H) for H_4, H_5 and H_8, 8.33 (s, 1H) and 8.46 (s, 1H) for H_9 and H_{10}.			
2-AA	DMSO-D_6, 5.6-5.8 (m, 1H), 6.3-6.5 (2H, m) for vinyl protons, 7.2-7.5 (m, 2H, H_6 and H_7), 7.7 (d, 1H, H_3), 7.9-8.1 (m, 3H, H_4, H_5 and H_8), 8.3-8.5 (m, 3H, H_1, H_9 and H_{10}).	735, 750, 810 and 890 (γC-H, 2-substituted anthryl group), 1515 and 1650 (CO-NH), 1615 (υC=C), 3210 (υNH)	258, 280, 356, 372, 392	270.15 $[M+Na]^+$
2-AM	DMSO-D_6, 2.02 (3, 3H, -CH_3), 5.58 (s, 1H) and 5.89 (s, 1H) for vinyl protons, 7.46 and 7.50 (dd, J = 8.4 and 8.8 Hz, H_6 and H_7), 7.73 (d, J = 8.4 Hz, 1H, H_3), 8.05 (d, J = 8.4 Hz, 3H, H_4, H_5 and H_8), 8.45 (s, 1H), 8.50 (s, 1H) and 8.55 (s, 1H) for H_1, H_9 and H_{10}.	735, 750, 810 and 890 (γC-H, 2-substituted anthryl group), 1515 and 1650 (CO-NH), 1620 (υC=C) and 3230 (υNH)	258, 280, 355, 372, 391	284.14 $[M+Na]^+$

9-AA	$CDCl_3$, 6.22 (d, 1H, J = 10.2 Hz), 6.65 (dd, 1H, J = 10.8 and 17.2 Hz) and 6.87 (d, 1H, J = 17.2 Hz) for vinyl protons, 7.47 and 7.49 (dd, 4H, J = 8.4 and 8.8 Hz, H_2, H_3, H_6 and H_7), 7.94 (d, 2H, J =- 8.8 Hz) and 8.02 (d, 2H, J = 8.4 Hz) for H_1, H_4, H_5 and H_8, 8.38 (s, 1H, H_{10}).	730, 780, 840 and 880 (γC-H, 9-substituted anthryl ring) γC-H, 1490 and 1660 (CO-NH), 1620 (υC=C) and 3230 (υNH).	256, 332, 348, 366, 386	270.16 $[M+Na]^+$
9-AM	$CDCl_3$, 2.25 (s, 3H, -CH_3), 5.65 (s, 1H) and 6.14 (s, 1H) for vinyl protons, 7.47 and 7.53 (dd, 4H, J = 8.4 and 8.8 Hz, H_2, H_3, H_6 and H_7), 8.03 (d, 4H, J = 8.8 Hz, H_1, H_4, H_5 and H_8), 8.46 (s, 1H, H_{10}).	730, 778, 835 and 882 (γC-H, 9-substituted anthryl ring), 1485 and 1645 (CO-NH), 1610 (υC=C) and 3240 (υNH).	258, 350, 368, 386	284.17 $[M+Na]^+$


8.5 8.0 7.5 7.0 6.5 6.0 5.5
1-AA (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5
2.5 2.0
1-AM (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0
2-AA (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5
2.0 1.5
2-AM (ppm)

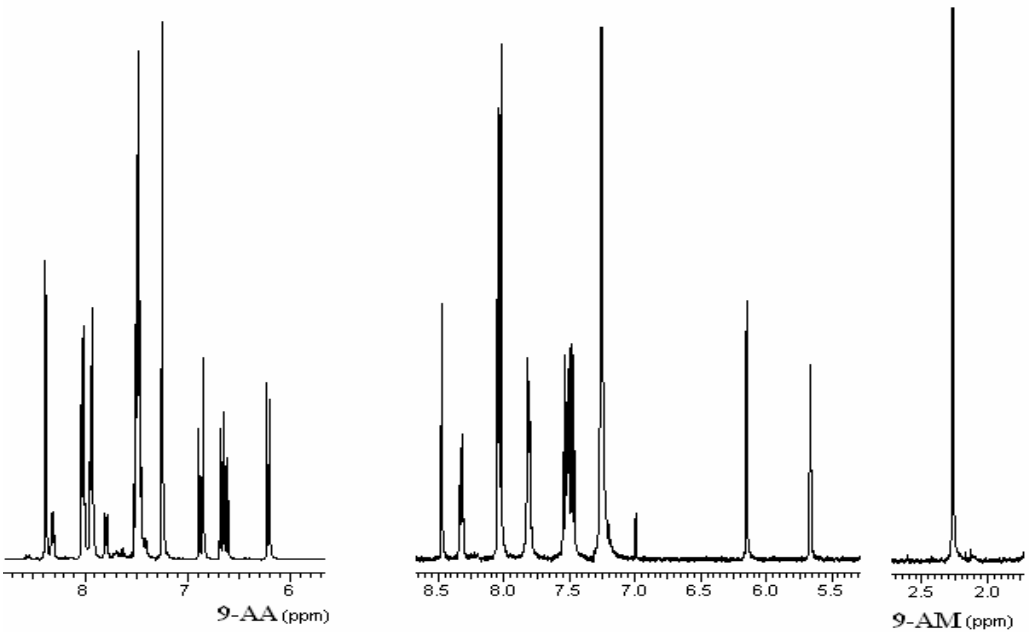


Figure 1. ^{1}H-NMR spectra (in $CDCl_3$ or DMSO-d_6) of acrylamides and methacrylamides.

UV-Vis Studies

The UV-Vis spectra of monomers are shown in Figure 2. The absorption spectra of anthracene derivatives show two absorptions bands assigned to the π-π* absorption in anthracene ring. The strong band positioned at low wavelength (250-280 nm) is due to horizontal polarization of the substituent (transition $^{1}B_b$-1A according to the Platt's nomenclature [11]). The band placed at higher wavelength has a hyperfine structure and is assigned to the vertical polarization of anthracene ring. The substitution of anthracene at position 2 (i.e., 2-AA and 2-AM) is reflected in UV by a clear bathocromic shifting of the first band (280 nm) as compared with 1- or 9-substitution (256-258 nm).

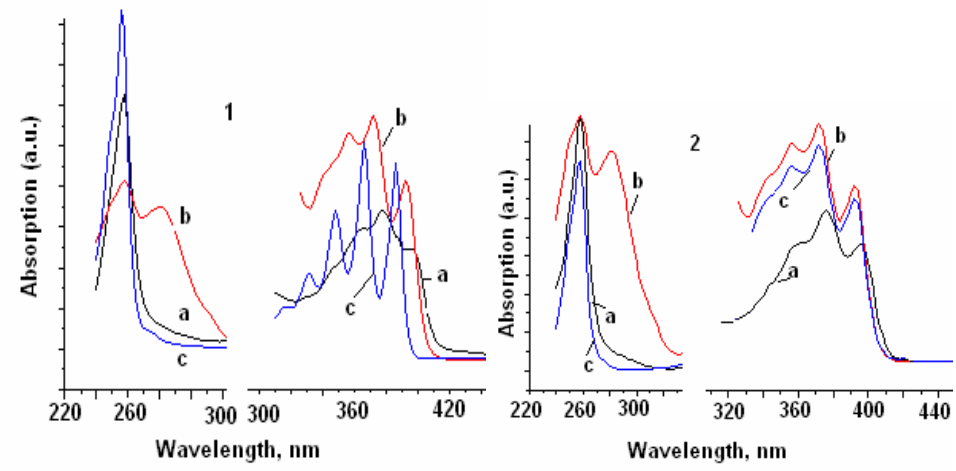


Figure 2. UV spectra ($CHCl_3$) of: (1) acrylamides; a) 1-AA, b) 2-AA, c) 9-AA, and (2) methacrylamide monomers; a) 1-AM, b) 2-AM, c) 9-AM.

In a preliminary experiment, acrylamide was radical copolymerized with 1-anthryl acrylamide (2 % mole). The labeled polyacrylamide, soluble in water, containing 1% anthryl group showing UV absorption in the same region as the anthracene comonomer was obtained. (Figure 3).

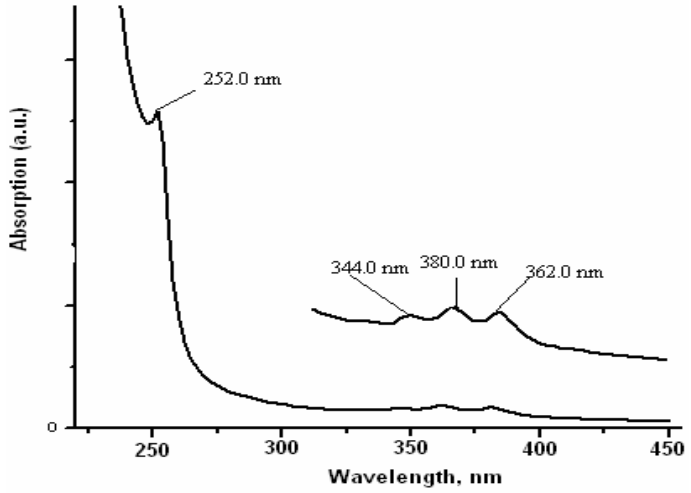


Figure 3. UV-vis spectrum of polyacrylamide labeled with 1% anthracene monomer.

Experimental

Anthracene, 1-aminoanthraquinone, 2-aminoanthraquinone, acryloyl chloride, methacryloyl chloride, triethylamine (all from Aldrich) are used as received. All solvents; toluene, N.N'-dimethylformamide (DMF), tetrahydrofuran (THF), chloroform, methanol, are commercial products and were used as recieved or dried by usual methods.

Characterization Techniques

FT-IR spectra were recorded on KBr pellets using a DIGILAB-FTS 2000 spectrometer. The UV-Vis spectra were measured using **an UV-Vis SPECORD 200 Analytik Jena spectrometer in $CHCl_3$ as solvent.** ^{1}H-NMR spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer (400 MHz) as solutions in $CDCl_3$ or DMSO-d_6 and chemical shifts were reported in ppm. The supposed chemical structure of products was confirmed by elemental analysis and NMR spectra using both types of signals, arising from vinyl and aromatic protons. Signals assignment is given in Table 2. The ESI mass spectra were obtained on a Agilent 6520 Accurate Mass LC ESI Q-ToF MS.

Synthesis of Monomers

(Meth)acrylamide monomers were synthesized by coupling reaction between corresponding anthryl amines and acryloyl or methacryloyl chloride. The 1- and 2-anthryl amines were prepared in our laboratory by reduction of 1- and 2-aminoanthraquinone with Zn/NaOH, according to the reported method [9]. 9-Anthrylamine was synthesized by a two steps method, starting from anthracene, that was first nitrated to 9-nitroanthracene, followed by reducing of 9-nitroanthracene with $SnCl_2$ [10]. Scheme 1 shows the reaction paths and structures of the functionalized

monomers. A general procedure for synthesis of monomers is presented for 1-anthryl acrylamide.

1-Anthryl acrylamide: In a three-neck round bottom flask equipped with a dropping funnel, condenser, nitrogen inlet-outlet and magnetic stirrer, 4 g 1-anthrylamine (0.02 mol) in 60 mL dried toluene and 2 mL (0.02 mol) triethylamine were introduced. The solution was cooled at 5^{o}C and 1.855 g (0.02 mol) acryloyl chloride in 10 mL toluene was dropped during a period of 15min. The mixture was stirred for 2 h at 5^{o}C and for 5 h at room temperature. Triethylamine chlorhydrate was filtrated and toluene solution was washed with diluted Na_2CO_3 solution, water and dried on $CaCl_2$. The solvent was removed and the solid product was twice recrystallized from acetone. The other monomers were synthesized in a similar manner.

Copolymerization of acrylamide with 1-AA was carried out in a Schlenk tube equipped with magnetic stirrer, nitrogen inlet and condenser. A solution obtained from 0.1289 g (0.493 mmol) 1-AA, 0.6820 g (9.594 mmol) acrylamide and 1.8 mg AIBN in 5 mL dioxane was maintained at 65^{o}C for 24 h. The copolymer was precipitated in cold methanol as a white product. Yield = 58 %. The content of the anthracene monomer in polyacrylamide was estimated by ^{1}H-NMR (from aromatic/aliphatic signals ratio) as 1% mol. The presence of the anthracene groups in polyacrylamide is clearly evidenced in the UV spectrum (Figure 3).

Conclusions

We have synthesized six novel monomers starting from three anthracene amines by reaction with acryloyl- and methacryloyl chloride, in presence of triethylamine. The structure of all monomers has proved by elemental analysis and ESI-MS. The FTIR, ^{1}H-NMR and UV data were also

presented. Preliminary attempts to obtain anthryl (metha)acrylamide polymers by radical polymerization have failed due to the known inhibiting role of the anthracene substituent. The anthracene monomers could be used to label usual polymers by copolymerization.

References

1. Scaffer, R. M., *IBM J. Res. Dev.*, **15**, 1 (1971).
2. Mukoh, A., Mori, Y., Sakashita, K., Nozaki, S., Hagitani A., *Org. Phot. Mater.*, USA patent **3**, 764590 (1973).
3. Rameshbabu, K., Kim, Y., Kwon, T., Yoo, J., Kim, E., *Tetrahedron Lett.*, **48**, 27 (2007).
4. Chen, H. Y., Chen, C. T., Chen, C. T., *Macromolecules*, **43**, 8, (2010); Sun, J., Chen, J., Zou, J., Ren, S., Zhong, H., Zeng, D., Du, J., Xu, E., Fang, Q., *Polymer*, **49**, 9 (2008); Park, J.W., Kang, P., Park, H., Oh, H. Y., Yang, J. H., Kim, Y. H., Kwon, S. K., *Dyes Pigments*, **85**, 3 (2010); Park, J. Y., Jung, S. Y., Lee, J. Y., Baek, Y. G., *Thin Solid Films*, **516**, 10 (2008); Lee, J. Y., Choi, M. H., Moon, D. K., Haw, J. R., *J. Ind. Eng. Chem.*, **16**, 3 (2010); Valentini, L., Bagnis, D., Marrocchi, A., Scri, M., Taticchi, A., Kenny, J. M., *Chem. Mater.*, **20**, 1 (2008).
5. Park, J. H., Chung, D. S., Park, J. W., Ahn, T., Kong, H., Jung, Y. K., Lee, J., Yi, M. H., Park, C. E., Kwon, S. K., Shim, H. K., *Org. Lett.*, **9**, 13 *(2007).*
6. Hargreaves, J. S., Webber, S. E., *Macromolecules*, **16**, 6 (1993).
7. Stolka, M., *Macromolecules*, **8**, 1 (1975); Stolka, M., Yanus, J. F., Pearson, J. M., *Macromolecules*, **9**, 2 (1976); Simionescu, C. I., Grigoras, M., Barboiu, V., *J. Polym. Sci.: Polym. Chem. Ed.*, **23**, 8

(1985); Pearson, J. M., *J. Macromol. Sci. – Chem.*, A, **9**, 6 (1975); Simionescu, C. I., Grigoras, M. *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 10 (1989); Simionescu, C. I., Onofrei, G., Grigoras, M. *Makromol. Chem.*, **188**, 505 (1987).

8. Hargreaves, J. H., *J. Polym. Sci.: Part A: Polym. Chem.*, **27**, 1 (1989).
9. Kaplan, F., Conroy, H., *J. Org. Chem.*, **28**, 6 (1963).
10. Braun, C. E., Cook C. D., *Organic Syntheses*, Coll. **IV**, 59 (1963).
11. Platt J. R., *J. Chem. Phys.*, **17**, 5 (1949).