STUDY OF THE SURFACE MODIFICATION OF POLYETHYLENE FILMS VIA PHOTOCHEMICAL REACTION WITH AZIDOSULFONAMIDES

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New azidobenzenesulfonamides were synthesized. Their photophysical and photochemical properties have been investigated. Surface photomodification of polyethylene (PE) films by using new azidobenzenesulfonamides was carried out. The wetting angles for three liquids of different polarity (water, formamide and diiodomethane) have been studied to estimate the surface modification performed. The received values of wetting angles for determining the surface free energy γ_S (γ) by the Owens-Wendt and Lifshitz-van der Waals γ^{LW}, acid-base γ^{AB} by the Lifshitz-van der Waals/acid-base methods.

1. Introduction

A polymer can acquire special properties either in the course of inter-chain polymer alloying by adding certain monomer units to the basic monomer being polymerized [1] or by modifying the ready-made sample [2-4].

Scientific resources abound in data concerning the use of organic azides for modification of polymer materials [5-7]. The ability of azides for photochemical decomposition which results in forming an active nitren biradical can be used for modification of polymer surface [8]. Surface modification is a convenient and sometimes the only way of polymer materials' acquiring necessary properties since it does not change the polymer structure in mass.

Designing the structure of modified surface by various biologically active groups is one of the issues of current importance in present day polymer chemistry. Previously there have been investigated the ways of introducing biologically active preparations into a polymer chain which results in obtaining pharmacologically active polymers [9-11]. Polyethylene (PE) is one of the more widespread polymers used for industrial and biomedical applications due to its special properties which include low density, flexibility and high chemical resistance [12-14].

First we have synthesized new azidobenzenesulfonamides and investigated their photochemical properties. High photochemical activity of obtained azidobenzenesulfonamides has given possibility to use them as modifiers of polymer materials.

2. Experimental part

Materials. 1-naphthylamine, purchased from Aldrich, was purified by a double recrystallization from an absolute methanol solution. *N*-acetylsulfanilyl chloride, 3-aminoacetophenone, 4-aminobenzenesulfonamide (Aldrich) were used without further purification. Pyridine, ethanol were of analytical grade, dried and purified before use. Diiodomethane, formamide (Fluka) are spectroscopic grade and used as received.

N-(3-acetylphenyl)-4-aminobenzenesulfonamide (sI). *N*-acetylsulfanilyl chloride 23.35 g (0.1 mol) was added to a flask containing 3-aminoacetophenone 13.5 g (0.1 mol) in dry pyridine (100 mL). After

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addition, the reaction mixture was heated at 75°C and stirred for 4 hours and the reaction was monitored by thin-layer chromatography TLC. The solution was acidified with hydrochloric acid and stirred for 1 hour at 50°C. After cooling, precipitates were collected by filtration, washed with aqueous solution. The acetyl derivative was hydrolyzed by boiling of 31 g with 5 g of sodium hydroxide and 150 mL of water for two hours. The excess sodium hydroxide was neutralized, activated charcoal was added, and the hot mixture clarified, giving a colorless solution. The product was recrystallized from ethanol, m.p.: 183°C, yield: 81 %.

^{1}H NMR (400 MHz, DMSO-d$_6$), % (ppm): 6.52 (d, Ar, 2H), 7.37 (d, Ar, 2H), 5.74 (s, NH$_2$, 2H), 9.95 (s, SO$_2$ NH, 1H).

N-(1-naphthalenyl)-4-aminobenzenesulfonamide (sII). A solution of 1-naphthylamine and *N*-acetylsulfanilyl chloride was heated at 75°C and stirred for 4 hours and treated in a manner similar to the procedure described above to afford colorless leaflets in 88% yield, m.p.: 205°C.

^{1}H NMR (400 MHz, DMSO-d$_6$), % (ppm): 7.30 (d, Ar, 2H), 7.42 (d, Ar, 2H), 5.72 (s, NH$_2$, 2H), 9.61 (s, SO$_2$ NH, 1H).

N-(3-acetylphenyl)-4-azidobenzenesulfonamide (aI). The mixture of concentrated hydrochloric acid (2 mL) and water (10 mL) was added to a solution of 0.95 g (0.00327 mol) of *N*-(3-acetylphenyl)-4-aminobenzenesulfonamide in 5 mL of ethanol. The reaction mixture was stirred for 15 min at 0°C and a solution of 0.225 g (0.00327 mol) of NaNO$_2$ in 5 mL of water was added dropwise to the solution, keeping the temperature of the reaction mixture -5 ÷ -10°C. The reaction mixture was stirred for 30 min at -5 °C. The reaction mixture was added dropwise to the cooled solution of 0.6376 g (0.00981 mol) of NaN$_3$ in 3 mL of water. After this, the reaction mixture was stirred for 1 h at room temperature. The organic material was extracted. The product was recrystallized from ethanol, m.p. 135°C (white crystals), yield 53%.

^{1}H NMR (400 MHz, DMSO-d$_6$), % (ppm): 7.18 (d, Ar, 2H), 7.76 (d, Ar, 2H), 3.84 (s, CH$_3$, 3H), 10.44 (s, SO$_2$ NH, 1H). UV- VIS (ethanol) λ_{max}: 265 nm. IR (KBr, cm^{-1}): 2100, 1630, 1580, 1500, 740.
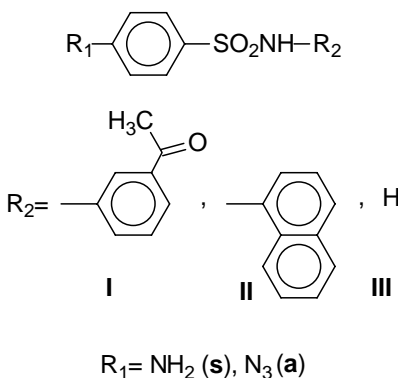
N-(1-naphthalenyl)-4-azidobenzenesulfonamide (aII). aII was prepared by the route of **aI** preparation. The light yellow crystals were collected by filtration and recrystallized from ethanol. Yield 48%, m.p. 138°C.

^{1}H NMR (400 MHz, DMSO-d$_6$), % (ppm): 7.15 (d, Ar, 2H), 7.40 (d, Ar, 2H), 10.08 (s, SO$_2$ NH, 1H), 7.14 – 8.04 (m, 7H). UV- VIS (ethanol) λ_{max}: 264 nm. IR (KBr, cm^{-1}): 2080, 1580, 1270.

4-azidobenzenesulfonamide (aIII). This compound was obtained according to the method described for **aI**, m.p. 145°C (white crystals), yield 63%. The product was recrystallized from ethanol.

^{1}H NMR (400 MHz, DMSO-d$_6$), % (ppm): 7.18 (d, Ar, 2H), 7.83 (d, Ar, 2H), 7.21 (s, SO$_2$ NH$_2$, 1H). UV- VIS (ethanol) λ_{max}: 260 nm. IR (KBr, cm^{-1}): 2100, 1600.

The chemical structures of synthesized compounds are shown in Scheme 1.

Scheme 1. Chemical structures of benzenesulfonamide derivatives.

Physical Measurements. ^{1}H NMR (400 MHz) spectra were recorded on a "Mercury-400" spectrometer using DMSO-d$_6$ as solvent. Chemical shifts are in ppm from the internal standard tetramethylsilane (TMS). UV-VIS measurements were performed at room temperature in solutions in quartz cuvette (C=10^{-5} mol/L) with a "Specord UV VIS" spectrometer. The IR spectra were obtained on a UR-20 spectrometer in KBr. FT-IR-ATR spectroscopy was done over a range of 4000-800 cm^{-1} at room temperature. All measurements of contact angles are advancing angles and were performed with a KRUSS G 10 contact

angle measuring instrument. On each sample at least four different locations were measured and results were averaged.

Modification of PE Films. The possibilities of surface photo-modification of PE films LDPE (GGNX 18 D003) by new azides containing biological active sulfonamide group **aI-aIII** have been studied. PE films (size 4×7 cm) were prepared. Polymer films were sheeted by 1% azidobenzenesulfonamide using acetone as solvent and dry samples were irradiated by UV lamp DRT-1000 during 30 minutes at 20°C. The properties of modified polymer surface were established by IR- spectroscopy and direct contact angle measurement for standard liquids: diiodomethane, formamide and water, using Kruss G-10 instrument.

The Owens-Wendt [15] and Lifshitz-van der Waals/acid-base [16] approaches were used to estimate values of surface free energy γ_S (mJ/m^2) and its components – polar γ_s^p and dispersive γ_s^d of the polyethylene surfaces. The data of three test liquids used to determine the surface free energy of PE are shown in Table 1. All liquids were provided in an analytical-reagent quality. Approximately 70 contact angles were determined for each drop.

FT-IR-ATR (PE films after irradiation): The important bands in examining degradation mechanisms include the broad v (C=C) between 1585 and 1600 cm^{-1}, δ (C-H) at 1000 cm^{-1}, δ (SO$_2$N) at 1360 and 1280 cm^{-1}, v (C=O) at 1676 cm^{-1}, δ (C-H) at 840 cm^{-1}.

3. Results and discussion

Synthesis of Azidobenzenesulfonamides. The syntheses have proceeded in two stages: preparation of the sulfonamides and azides based on them. New azidobenzenesulfonamides were synthesized by diazotization of corresponding amines and treatment by diazonium salt with aqueous solution of sodium azide [17].

Photochemistry of Azidobenzenesulfonamides. Phenyl azides are known to undergo the photo-reaction under UV irradiation. The reaction of photolysis with formation active nitrenes (either singlet or triplet) has been observed [18]. Singlet phenylnitrene is primary reactive intermediate formed upon the photolysis of phenyl azide. Although triplet phenylnitrene, as well as didehydroazepine, has been directly observed by means of IR and UV spectroscopy in matrices and in solutions and the 3*H*-azepine derivative, respectively [19, 20]. Nitrenes possess high reaction ability and take part in photoreactions.
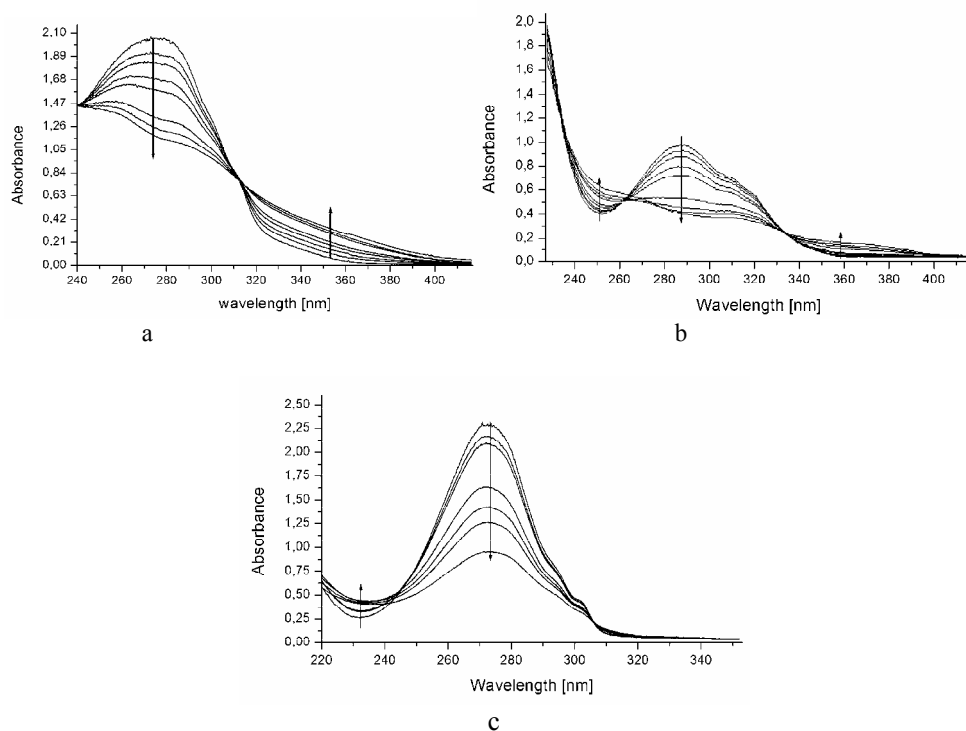

Fig. 1. Changes of the absorption spectrum of **aI** (a), **aII** (b) and **aIII** (c) in ethanol (C = 10^{-5} mol/L) during UV- irradiation (313 nm).

The photolysis process with strong spectral changes which took place during UV irradiation (313 nm) of the solution of **aI**, **aII** and **aIII** in ethanol was shown in Fig. 1. A strong decrease of the absorption in the region in 245-290 nm (**aI**), 250-300 (**aII**), 238-292 (**aIII**) and their increase in the region 295-400 nm (**aI**), 220-235 nm (**aIII**), 230-250 nm, 308-385 nm (**aII**) were observed. The quantum yields of photolysis of azidobenzenesulfonamides were determined to be $\varphi_{aI} \approx 0.48$, $\varphi_{aII} \approx 0.14$, $\varphi_{aIII} \approx 0.51$.

High photochemical activity of azidobenzenesulfonamides was confirmed by the received results. In the case of **aII** more low value of photolysis quantum yield was explained by existence of effective singlet-triplet and triplet-triplet conversion of the excitation energy on the naphthalene π-electron system. This was described with details previously [21].

Theoretical bases of contact wetting and measurement results. The additional procedure of surface photo-modification of PE was used. Young's equation (1) allows a calculation of the stationary wetting angle of contact and describes the equilibrium of forces between the surface tensions at the 3-phase boundary [22].

$$\gamma_S = \gamma_{SL} + \gamma_L \times \cos\theta \tag{1}$$

γ_S and γ_{SL} cannot be determined indirectly through experiments either, γ_S is not a clearly defined physical parameter. In order to determine the surface energy of solids through a measurement of the contact angle, Owens-Wendt theoretical statement describing the interfacial tension γ_{SL} have been used. γ_{SL} is known in function of γ_S and γ_L. In correspondence to Berthelot hypothesis surface tension in the frontier phase division solid – liquid in first approximation may be examine as average value of each states interaction.

Owens and Wendt set up that surface free energy possessed two components: polar and dispersive $\gamma_S = \gamma_S^d + \gamma_S^p$ and the following equation was proposed:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_L^d \times \gamma_S^d} - 2\sqrt{\gamma_L^p \times \gamma_S^p} \tag{2}$$

where γ_S - surface free energy of polymer surface in vacuum, γ_L - surface free energy of testing liquid, γ_L^d - dispersive component of surface free energy of testing liquid, γ_L^p -polar component of surface free energy of testing liquid, γ_S^d - dispersive component of surface free energy of polymer surface, γ_S^p -polar component of surface free energy of polymer surface.

Including Young equation such formula can be taken out:

$$\gamma_L \frac{1 + \cos\theta}{2} = \sqrt{\gamma_S^d \times \gamma_L^d} + \sqrt{\gamma_S^p \times \gamma_L^p} \tag{3}$$

For γ_S determination from equation (3) it is necessary to measure angle θ at least for two various liquids with known values of γ_L^d and γ_L^p, and then to solve the system of equations. One of this liquids should be characterized by high value of γ_L^d and low value of γ_L^p and the second liquid - inversely. The most often, water and diiodomethane were used as the pair of testing liquids.

The values of surface free energy and its components for testing liquids used in contact angle measurements are collected in Table 1.

Table 1. The values of surface tension and their constituent γ_L^d, γ_L^p (mJ/m^2) for testing liquid (at 20°C).

Liquid	γ_L	γ_L^d	γ_L^p
Diiodomethan	50.8	50.8	0
Formamide	58.0	39.0	19.0
Water	72.8	21.8	51.0

The values of contact angle θ for experimental samples PE are presented in Fig. 2:
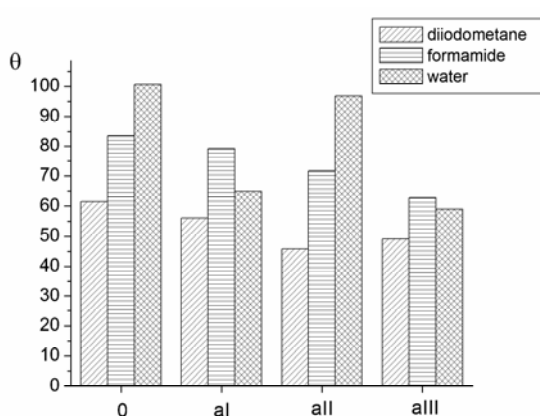

*Fig. 2. Contact angles for polyethylene- liquid: 0 - unmodified film; **aI**, **aII**, **aIII** - photo- modified samples by azidobenzenesulfonamides.*

The significant changes of contact angles for all samples after photochemical modification were observed. The surface free energy γ_S was calculated as the sum of its dispersive and polar components (Fig. 3).
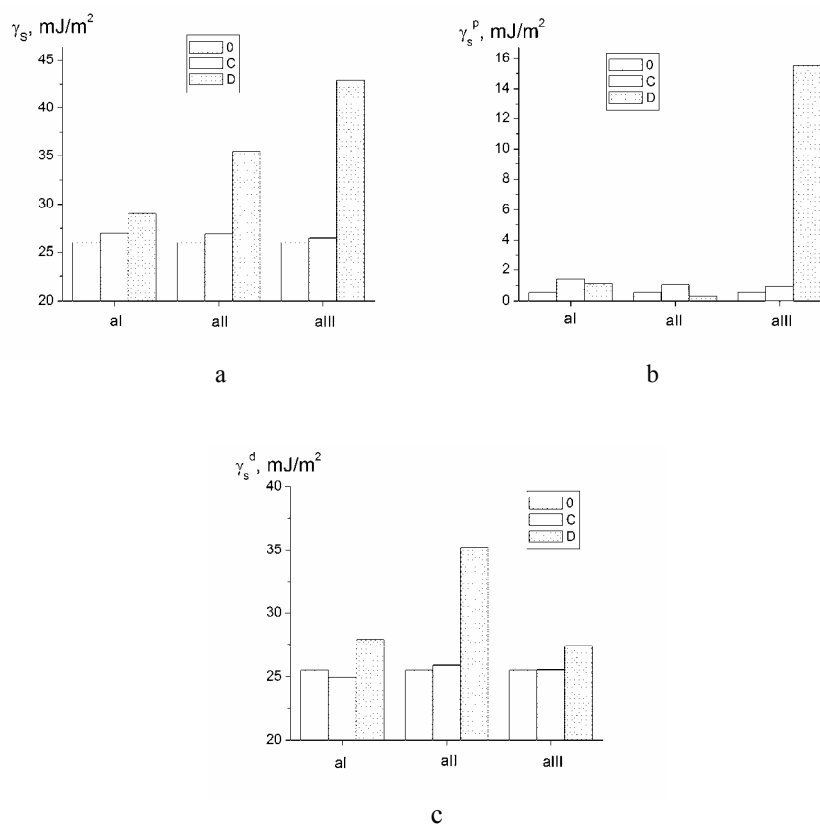

*Fig. 3. Surface free energy **a**) of PE films calculated by Owens-Wendt approach and its: **b**) – polar (γ_S^p); **c**) – dispersive (γ_S^d) shares; 0 - unmodified film, C- unirradiated, D - photo-modified samples by azidobenzenesulfonamides **aI**, **aII**, **aIII**.*

PE films after modification by **aI** have a low surface energy 29.01 mJ/m^2 with a negligible polar component, by **aII** γ_S considerably increase 35.49 mJ/m^2. PE film which was modified by **aIII** possessed a higher surface energy 42.94 mJ/m^2 with large polar component 15.55 mJ/m^2 (Fig. 3). The surfaces become more hydrophilic with increasing polar shares, i.e. the contact angle of water drops falls due to the better wetting. The effects can be explained as a consequence of the photochemical modification of the surface. High energy values are favourable for surface wetting.

The calculations according to basic-acid Van Oss-Good theory were realized to check surface polarity. Surface free energy can be presented as sum of two components: $\gamma_i = \gamma_i^{LW} + \gamma_i^{AB}$.

γ_i^{LW} is connected with all long range interactions such as dispersive, polar and inductive interactions. γ_i^{AB} results from acid-basic interactions. Index i can take values from natural number set and the following surface or testing liquids are signed by it.

According to this theory chemical substances can be divided into: bipolar (with properties suitable both for Lewis bases and for Lewis acids), monopolar (with properties characteristic either for Lewis base or Lewis acid) and apolar (neither Lewis base nor Lewis acid properties).

For bipolar substances $\gamma_i^{AB} = 2(\gamma_i^+ \times \gamma_i^-)^{1/2}$, where γ^+ signed γ^{AB} component corresponding to Lewis acid surface free energy and γ^- signed γ^{AB} component corresponding to Lewis base.

For mono- and apolar substances $\gamma^{AB} = 0$. Three components: γ_S^{LW}, γ_S^+ and γ_S^- should be known to calculate surface free energy γ_S of tested material. These components can be determined from the results of contact angle examinations. Tested surface should be wetted by three various liquids (these values γ_{Li}^{LW}, γ_{Li}^+ and γ_{Li}^- should be find). Then, γ_S can be calculated from system of three equations:

$$\sqrt{\gamma_S^{LW} \times \gamma_{Li}^{LW}} + \sqrt{\gamma_{Li}^+ \times \gamma_{Li}^-} + \sqrt{\gamma_S^+ \times \gamma_S^-} = \gamma_{Li} \frac{1 + \cos\theta}{2} \tag{4}$$

The calculation results for tested surfaces are presented in Table 2.

*Table 2. The values of surface free energy γ (mJ /m^2) of PE films calculated by acid-base approach and its constituent γ^{LW} and γ^{AB} (0- unmodified film, C- unirradiated, D- photo-modified samples by azidobenzenesulfonamides **aI, aII, aIII**).*

Sample	γ^{LW}		γ^{AB}		γ^+		γ^-		γ	
	C	D	C	D	C	D	C	D	C	D
0	27.72		1.32		0.20		2.15		29.05	
aI	28.09	30.83	2.50	1.97	0.32	0.25	4.86	3.83	30.59	32.81
aII	27.83	36.56	0.72	0.31	0.05	0.03	2.70	0.81	28.55	36.88
aIII	28.83	34.74	2.88	7.21	0.50	0.35	4.15	36.87	31.71	41.95

The received values of the surface free energy γ, as well as its components Lifshitz-van der Waals γ^{LW}, acid-base γ^{AB} by the Lifshitz-van der Waals/Van Oss-Good (acid-base method) are in a good accordance with Owens-Wendt approach (Table 2).

High polarity of polyethylene surface modified by azide **aIII** was confirmed by the values of surface free energy determined by Van Oss-Good method and also by results received by Owens-Wendt method. The electronodonor character of surface was proved by high part of γ^- component, corresponding to Lewis base. At the same time, high part of γ^{LW} component in surface free energy, connected with all long range interactions should be underlined.

4. Conclusions

In the present work, surface photo-modification of PE films by new azidobenzenesulfonamides was carried out. The ability of azidobenzenesulfonamides for polymer surface modification was shown. The

hydrophilic character of surface was received by using azidobenzenesulfonamides as modifier. During photo-modification process only surface properties of modified product, not polymer structure in mass, was changed. In all cases PE films modified with azides were characterized by increased values of γ_S. The achieved results provide for photochemical modification of polymer material surfaces by azides based on benzenesulfonamides which enables to use them as perspective materials, for example as biostabilizers for plastic masses.

Acknowledgement

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