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Photochemical Surface Modification of Polyethylene Films by New Azidobenzenesulfonamides

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New azidobenzenesulfonamides are synthesized. Their photophysical and photochemical properties have been investigated. The photophysical properties of these compounds were investigated by ^1H NMR, IR, and UV spectroscopy. The surface photomodification of polyethylene (PE) films by using new azidobenzenesulfonamides is carried out. The wetting angles for three liquids of different polarities (water, formamide, and diiodomethane) have been studied to estimate the surface modification performed. The obtained wetting angles are used for the determination of the surface free energy γ_S (γ), as well as its polar γ_s^p, dispersive Owens–Wendt γ_s^d, Lifshits–van der Waals γ^{LW}, and acid-base γ^{AB} components, by applying the Lifshits–van der Waals/acid-base methods.

Keywords: sulfonamides; surface energy; surface photomodification

1. INTRODUCTION

The development of modern technologies enables one to create polymer materials with a number of properties which would be impossible to realize in a single polymer. A polymer can acquire special properties either in the course of interchain 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 the data of the use of organic azides for a modification of polymer materials [5–7]. The ability of azides to

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the photochemical decomposition which results in forming an active nitrene biradical can be used for a modification of the polymer surface [8]. The 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 a modified surface by various biologically active groups is one of the issues of current importance in the modern 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].

The intense interest in sulfonamides can be explained by the fact that they have been well-known in medicine for a long time by their high bactericidal activity and are used due to active chemotherapeutical properties [15–17]. Sulfonamides are also used in photography, fungicidal and insecticidal mixtures and as detergents [18]. Therefore, a perspective direction is to obtain polymers containing sulfonamide fragments with several non-conjugated π-electron systems in their basic or side chains. The directed energy transfer between two non-conjugated π-electron systems is perspective for obtaining azides with a certain photoactivity. First, we have synthesized new azidobenzenesulfonamidesand investigated their photochemical properties. The high photochemical activity of the obtained azidobenzenesulfonamides allows one to use them as modifiers of polymer materials.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

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

2.2. Characterization Techniques

^{1}H NMR (400 MHz) spectra were recorded on a "Mercury-400" spectrometer using DMSO-d_6 as a solvent. Chemical shifts are in ppm from

the internal standard tetramethylsilane (TMS). UV-VIS measurements were performed at room temperature in solutions in a quartz cuvette ($C = 10^{-5}$ mole/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 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 the results were averaged.

2.3. Synthesis of Sulfonamides Derivatives

N-(3-acetylphenyl)-4-aminobenzenesulfonamide (sl)

23.35 g (0.1 mole) of *N*-acetylsulfanilyl chloride was added to a flask containing 13.5 g (0.1 mole) of 3-aminoacetophenone in dry pyridine (100 ml). After the addition, the reaction mixture was heated at 75°C and stirred for 4 h, and the reaction was monitored by thin-layer chromatography (TLC). The solution was acidified with hydrochloric acid and stirred for 1 h at 50°C. After cooling, precipitates were collected by filtration and washed with an aqueous solution. The acetyl derivative was hydrolyzed by the boiling of 31 g with 5 g of sodium hydroxide and 150 ml of water for 2 h. 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, 2*H*), 7.37 (d, Ar, 2*H*), 5.74 (s, NH_2, 2*H*), 9.95 (s, SO_2 NH, 1*H*).

N-(1-naphthalenyl)-4-aminobenzenesulfonamide (sl)

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

^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 7.30 (d, Ar, 2*H*), 7.42 (d, Ar, 2*H*), 5.72 (s, NH_2, 2*H*), 9.61 (s, SO_2NH, 1*H*).

N-(3-acetylphenyl)-4-azidobenzenesulfonamide (al)

The mixture of concentrated hydrochloric acid (2 ml) and water (10 ml) was added to a solution of 0.95 g (0.00327 mole) 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 mole) of $NaNO_2$ in 5 mL of water was added dropwise to the solution, keeping the temperature of the reaction mixture at −10°C

for 5 h. The reaction mixture was stirred for 30 min at −5°C. The reaction mixture was added dropwise to a cooled solution of 0.6376 g (0.00981 mole) 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, 2*H*), 7.76 (d, Ar, 2*H*), 3.84 (s, CH_3, 3*H*), 10.44 (s, SO_2NH, 1*H*). 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. 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, 2*H*), 7.40 (d, Ar, 2*H*), 10.08 (s, SO_2NH, 1*H*), 7.14–8.04 (m, 7*H*). UV-VIS (ethanol) λ_{max}: 264 nm. IR (KBr, cm^{-1}): 2080, 1580, 1270.

4-azidobenzenesulfonamide (aIII)

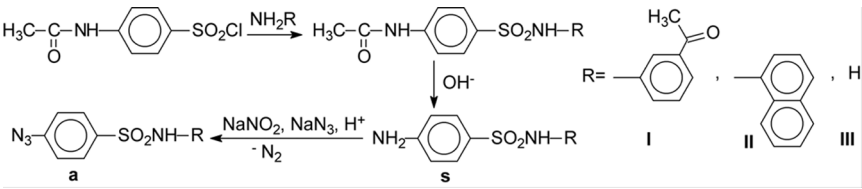
This compound was obtained according to the method described for **aI**, m.p. 145°C (white crystals), yield 63%. The product was recrystallized from ethanol.

^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 7.18 (d, Ar, 2*H*), 7.83 (d, Ar, 2*H*), 7.21 (s, SO_2NH_2, 1*H*). UV-VIS (ethanol) λ_{max}: 260 nm. IR (KBr, cm^{-1}): 2100, 1600.

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

2.4. Photochemical Properties of Azidobenzenesulfonamides

Phenyl azides are known to undergo the photoreaction under UV irradiation. The reaction of photolysis with the formation of active nitrenes (either singlet or triplet) has been observed [19]. Singlet



SCHEME 1 Synthesis of azidobenzenesulfonamides.

phenylnitrene is a 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 spectroscopies in matrices and in solutions of the 3*H*-azepine derivative, respectively [20,21]. Nitrenes possess a high reaction ability and take part in photoreactions.

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 is shown in Figure 1. A strong decrease of the absorption in the regions of 245–290 (**aI**), 250–300 (**aII**), and 238–292 nm (**aIII**) and their increase in the regions of 295–400 (**aI**), 220–235 (**aIII**), 230–250, and 308–385 nm (**aII**) are observed. Their spectral characteristics are presented in Table 1.

In order to investigate the photoactive abilities of new azidobenzenesulfonamides, the photolysis quantum yields were determined.

High photochemical activity of azidobenzenesulfonamides was confirmed by the obtained results. In the case of **aII**, a lower photolysis quantum yield was explained by the existence of effective singlet-triplet and triplet-triplet conversion of the excitation energy on the naphthalene π-electron system. This was described in details previously [22].

2.5. Modification of PE Films

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

The Owens–Wendt [23] and Lifshits-van der Waals/acid-base [24] approaches were used to estimate the surface free energy $\gamma_S(\mathrm{mJ/m^2})$ and its components–polar γ_s^p and dispersive γ_s^d ones of the polyethylene surfaces. The data of three test liquids used to determine the surface free energy of PE are shown in Table 2. All liquids were supplied in the analytical-reagent quality. Approximately 70 contact angles were determined for each drop.

FT-IR-ATR (PE films after irradiation): The important bands in examining the degradation mechanisms include the broad υ (C=C) between 1585 and 1600 $\mathrm{cm^{-1}}$, δ (C–H) at 1000 $\mathrm{cm^{-1}}$, δ (SO_2N) at 1360 and 1280 $\mathrm{cm^{-1}}$, υ (C=O) at 1676 $\mathrm{cm^{-1}}$ and δ (C–H) at 840 $\mathrm{cm^{-1}}$.

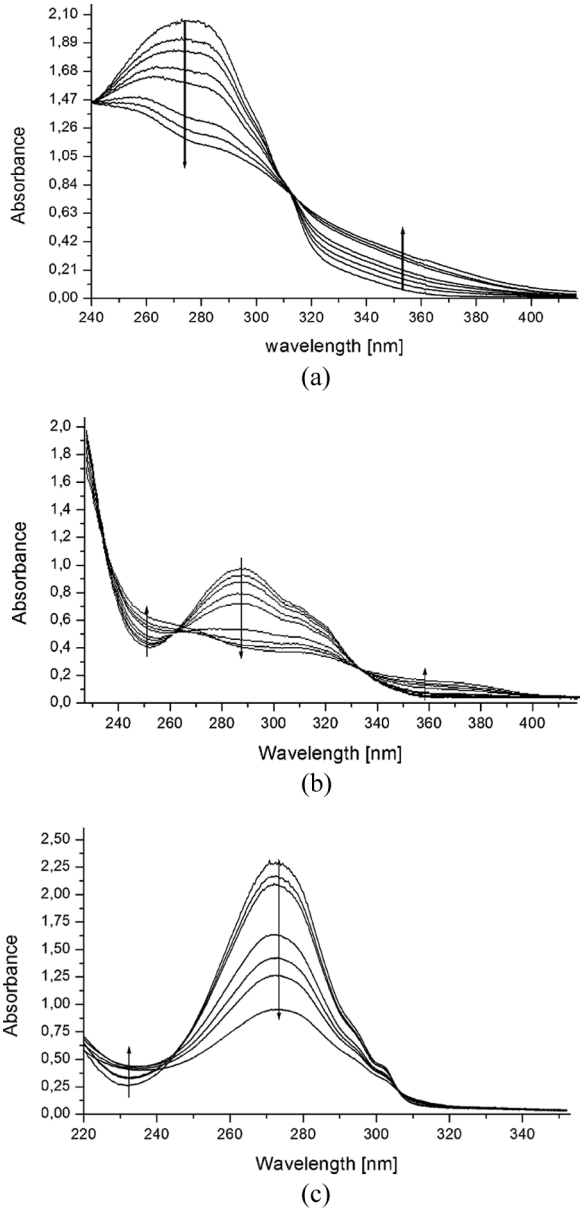


FIGURE 1 Changes of the absorption spectrum of **aI** (a), **aII** (b), and **aIII** (c) in ethanol (C = 10–5 mole/l) during UV-irradiation (313 nm).

TABLE 1 Spectral Characteristics of Azidobenzenesulfonamides in Ethanol: The Absorption Maximum and Quantum Yield of Photolysis

Compound	λ_{max}	φ
aI	265	0.48
aII	264	0.14
aIII	260	0.51

3. RESULTS AND DISCUSSION

The syntheses have proceeded in two stages: the preparation of sulfonamides and azides based on them. New azidobenzenesulfonamides were synthesized by the diazotization of the corresponding amines and the treatment of diazonium salt with an aqueous solution of sodium azide [25]. The additional procedure of surface photomodification of PE was used.

The Young equation

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

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 (Fig. 2) [26]. The quantities γ_S and γ_{SL} cannot be determined indirectly through experiments, and 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, the Owens–Wendt theoretical approach describing the interfacial tension γ_{SL}, being a function of γ_S and γ_L, has been used. In correspondence to the Berthelot hypothesis, the surface tension on the solid–liquid interface may be examined in the first approximation as the average value over the interaction in every state.

Owens and Wendt set up that the surface free energy possesses two components, polar and dispersive ones: $\gamma_S = \gamma_S^d + \gamma_S^p$. They satisfy the

TABLE 2 Values of Surface Tension and Their Constituents γ_L^d and γ_L^p (mJ/m^2) for a Testing Liquid (at 20°C)

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

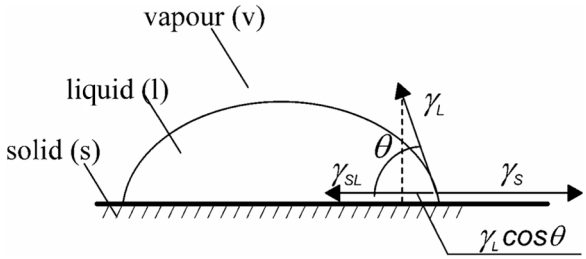


FIGURE 2 Description of a wetting state by Young; θ – contact angle, γ_S – surface tension of the solid; γ_L – surface tension of the liquid; and γ_{SL} – interfacial tension solid/liquid.

equation

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

where γ_S – surface free energy of the polymer surface in vacuum, γ_L – surface free energy of a testing liquid, γ_L^d and γ_L^p are, respectively, the dispersive and polar components of the surface free energy of the testing liquid, and γ_S^d and γ_S^p are, respectively, the dispersive and polar components of the surface free energy of the polymer surface.

The Young equation yields the following formula:

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

To determine γ_S from relation (3), it is necessary to measure the angle θ at least for two different liquids with the known values of γ_L^d and γ_L^p and then to solve the system of equations. Let one of these liquids be characterized by a high value of γ_L^d and a low value of γ_L^p, and let the corresponding values for the second liquid be in the inverse relationship. The most often, water and diiodomethane were used as the pair of testing liquids.

The values of the surface free energy and its components for testing liquids used in contact angle measurements are collected in Table 2.

The values of contact angle θ for the experimental samples of PE are presented in Figure 3.

We observed the significant changes of contact angles for all samples after the photochemical modification. The surface free energy γ_S was calculated as the sum of its dispersive and polar components (Fig. 4).

The PE films after the modification by **aI** have a low surface energy 29.01 mJ/m^2 with a negligible polar component. At the modification by

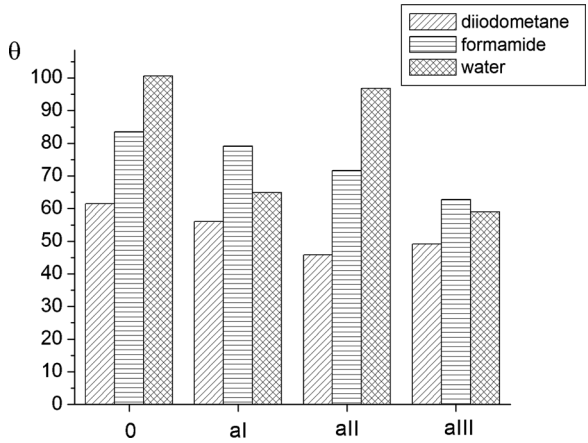


FIGURE 3 Contact angles for polyethylene – liquid: 0 – unmodified film; **aI**, **aII**, **aIII** – photomodified samples by azidobenzenesulfonamides.

aII, γ_S considerably increases to 35.49 mJ/m^2. A PE film which was modified by **aIII** possessed a higher surface energy of 42.94 mJ/m^2 with the large polar component equal to 15.55 mJ/m^2 (Fig. 4). The surfaces become more hydrophilic with increasing the polar component, 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 favorable for the surface wetting.

The calculations according to the basic-acid Van Oss–Good theory were realized to check the surface polarity. The surface free energy can be presented as a sum of two components:

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB}.$$

The quantity γ_i^{LW} is related to all long-range interactions such as the dispersive, polar, and inductive ones, and γ_i^{AB} results from acid-basic interactions. Index i can take values from the set of natural number, 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 of the Lewis base or Lewis acid) and apolar (the properties of neither Lewis base nor Lewis acid).

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

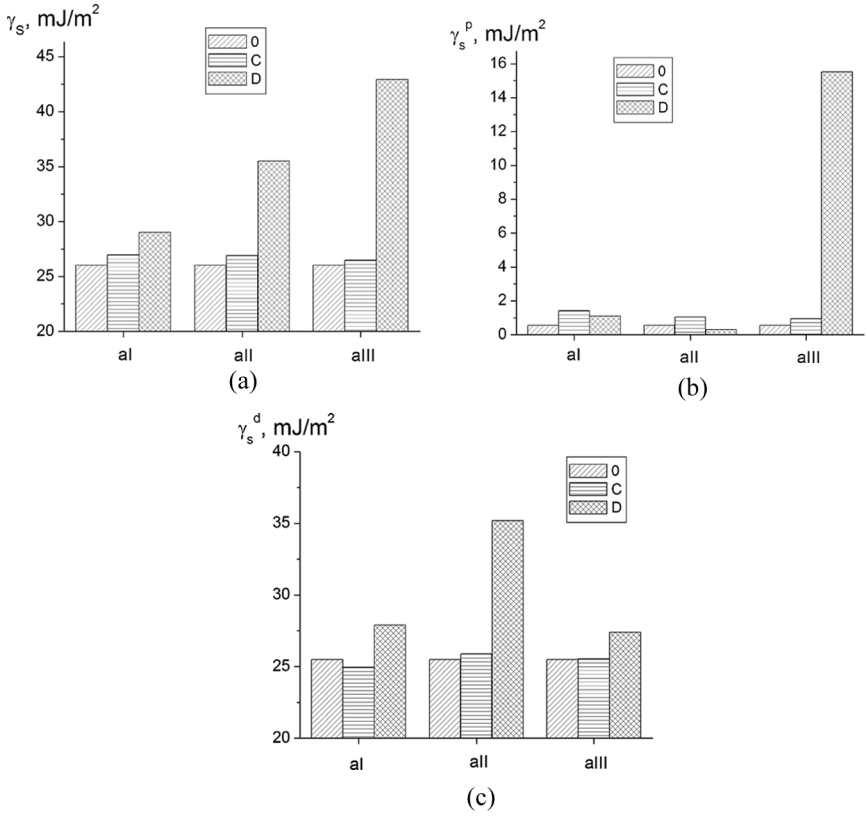


FIGURE 4 Surface free energy (a) of PE films calculated by the Owens – Wendt approach and its: (b) – polar (γ_S^p); (c) – dispersive (γ_S^d) components; 0 – unmodified film, C – unirradiated, D – photomodified samples by azidobenzene-sulfonamides **aI**, **aII**, and **aIII**.

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

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

The calculation results for tested surfaces are presented in Table 3.

TABLE 3 Values of Surface Free Energy γ (mJ/m^2) of PE Films Calculated by the Acid-Base Approach and its Constituents γ^{LW} and γ^{AB} (0 – Unmodified film, C – non-irradiated, D – Photomodified Samples by Azidobenzenesulfonamides **aI**, **aII**, and **aIII**)

	γ^{LW}		γ^{AB}		γ^{+}		γ^{-}		γ	
Sample	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 obtained values of the surface free energy γ, as well as its components Lifshits–van der Waals γ^{LW} and acid-base γ^{AB} by the Lifshits–van der Waals/Van Oss–Good (acid-base method), are in good accordance with the Owens–Wendt approach (Table 3).

High polarity of the polyethylene surface modified by azide **aIII** was confirmed by the values of surface free energy determined by the Van Oss–Good method and by results obtained by the Owens–Wendt method. The electronodonor character of the surface was proved by a high share of the γ^{-} component corresponding to the Lewis base. At the same time, it is worth noting the high contribution of the γ^{LW} component to the surface free energy related to all long-range interactions.

4. CONCLUSIONS

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

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