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DEVELOPMENT OF A PHOTOCHROMIC POLYMER COMPOSITION

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The possibility of enhancing the photochromic effect for creating polymer compositions with improved photochromic characteristics (photostability, high photosensitivity, expanded operative wavelength range, and increased darkening intensity) is investigated, and its prospects are discussed.

The attention of researchers working in the field of chemistry and physics of polymeric materials is focused on controlling the design and synthesis at the molecular and supramolecular levels via the influence of temperature, mechanical action, exposure to light of different wavelengths, application of magnetic and electric fields, etc. The output of publications related to the development of compositions with the photochromic effect – the process of reversible color change under exposure to light of certain wavelengths – is continuously growing [1-4].

Polymeric optical materials are widely used in various fields of science and technology. One of the important polymer properties is the ability to easily combine with substances that have valuable optical properties but cannot be used by themselves due to a complex of physico-mechanical properties [1]. Introduction into a polymer of photochromic organic polymeric additives results in production of photochromic materials whose transparency varies under the influence of light.

Photochromic polymeric materials can be prepared simply by mixing the polymer and the photochromic additive, or by chemically incorporating photochromic groups into the polymer [2]. Physical or chemical photochromism is at the heart of reversible photo-transformations accompanied by a change in absorption spectra in the visible region [3].

Physical photochromism is due to the transition of atoms and molecules, upon absorption of light, for a finite amount of time (lifetime) into electronically excited states characterized by new absorption spectra.

Chemical photochromism is associated with deep intramolecular rearrangements of the compound under the influence of light, which lead to the temporary formation of new thermodynamically unstable chemical compounds [4].

Upon the irradiation of polymers with light of a certain wavelength other photochemical transformations can be observed that can be used to modify the polymer films. For example, the transition of the *trans*-configuration of the polymer into the *cis*-configuration under irradiation with light (photoisomerization) may be accompanied by a significant change in the absorption spectra. Such photochromic polymers capable of reversibly changing their color upon being illuminated with light of a specific wavelength are used as optical filters, photosensitive lenses, and negative photographic materials [5].

The most effective photochromic systems are derived based on pigments: spiro- and naphthopyrans [6-11]. Naphthopyran possesses the valuable ability to preserve its photochromic properties in various polymer matrices, while the polymer matrix has a significant impact on the characteristics of photochromic transformations. By changing its properties it is possible to control the speed of photochromic transitions of naphthopyrans and the lifetime of the metastable state. To create photochromic polymeric compositions with improved properties, variation of the structure of naphthopyrans as well as polymer matrices is necessary [12].

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Table 1. Hansen Solubility Parameters for Polystyrene and Solvents.

Object of investigation	dD	dP	dH
Polystyrene	17.5	6.1	4.1
Solvents			
Benzene	18.42	1.02	2.86
Toluene	17.99	1.43	2.04
Hexane	14.77	0	0
Acetone	15.46	10.4	6.9
Methyl ethyl ketone (MEK)	15.85	9	5.1
Diethyl ether	14.38	2.9	5.1
Ethyl acetate	15.18	5.3	9.2
Butyl acetate	15.65	3.7	6.3
Chloroform	17.64	3	4.24
Carbon tetrachloride (CTC)	17.64	0	0
Solvent mixtures			
Acetone/CTC	16.55	5.2	3.45
Toluene/MEK	16.92	5.215	3.57
Hexane/ethyl acetate	14.975	2.65	4.6
MEK/chloroform	16.745	6	4.67
Benzene/butyl acetate	17.035	2.36	4.58

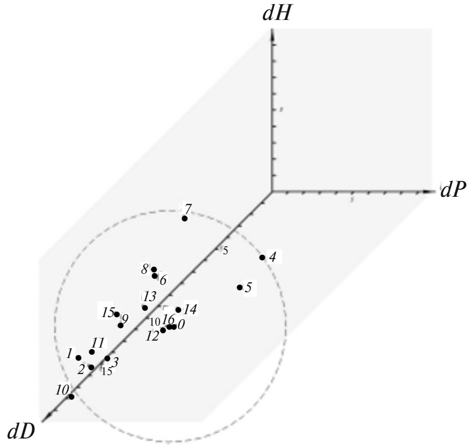

Fig. 1 Solvent strength of the polystyrene solvents

The purpose of this research is to develop methods to enhance the photochromic effect for creating polymer compositions with improved photochromic characteristics: photostability, high photosensitivity, expanded operative wavelength range, and more intense color.

The polymeric matrices should have satisfactory physical and mechanical parameters, high transparency, and compatibility with photochromic pigments [13]. In this work, polystyrene (PS), a polymer having a high optical transparency, was used as the polymer matrix. Polystyrene is a rigid amorphous polymer with a low mechanical tensile and bending strength. Its physico-chemical properties are determined by the presence of phenolic groups, which prevent an orderly arrangement of macromolecules and the formation of crystalline formations. The chemical properties of polystyrene are due to the high reactivity of the vinyl side group. Polystyrene belongs to a group of rather inert plastics. It is resistant to alkalis and hydrohalic acids; it is unstable to the action of concentrated nitric acid and glacial acetic acid. Thermal degradation of polystyrene proceeds at an appreciable rate at temperatures above 200 °C. The main product of decomposition is a styrene monomer.

In the paper the basic physical and chemical properties of polystyrene are investigated. The density of PS was measured by the pycnometric method and found to be 1.1 g/cm^3. Its molecular weight (M) was determined by the

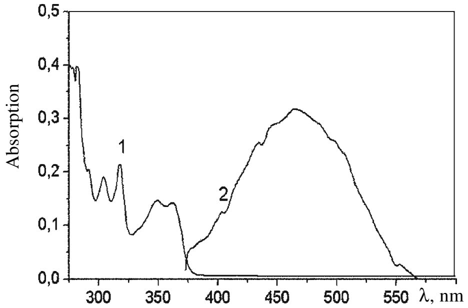

Fig. 2.

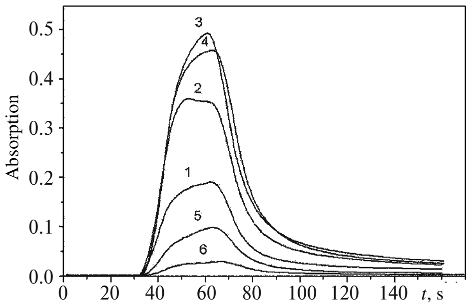

Fig. 3.

Fig. 2. Absorption (*1*) and additional absorption (*2*) spectra of yellow naphthopyran under UV irradiation of the film No. 1.

Fig. 3. Kinetics of increase and relaxation of additional absorption in the UV-irradiated film No. 1 (yellow) at different wavelengths of the probe radiation (λ, nm): *1* – 400; *2* – 425; *3* – 450; *4* – 500; *5* – 550; *6* – 575.

Table 2. Optical Transmission of Films at Maximum Darkening under UV Irradiation.

Pigment	Transmittance of films, *T*	Measurement wavelength λ, nm	Solvent
Yellow	0.145	500	Acetone + CTC
Blue	0.730	600	Acetone + CTC
Yellow + blue	0.100	500	Acetone + CTC
	Influence of solvent		
Yellow	0.080	500	Toluene
Yellow	0.070	500	o-Xylene

viscometric method using toluene as a solvent and was found to be 57600. PS is easily deformed at a relatively low temperature of 80 °C, and its glass transition temperature is 93 °C. The application of PS requires a maximum reduction of residual monomer concentration in its content [14]. The volatility of polystyrene used in this work is 0.48% at 100 °C.

The solvent power of polystyrene solvents was determined by the Hansen method [15]. There are many solubility theories: MOSCED, UNIFAC, Jouyban-Acree, Yalkowsy, MOD (Mobile Order and Disorder), and Hildebrand. The Hildebrand solubility parameter notes the radius vector of a substance of a known wavelength, but does not show the direction, while the Hansen solubility parameter gives the end coordinates of the vector, therefore, indicating its direction. Each substance has three solubility parameters: the dispersion interaction component *dD*, the polar interaction component *dP*, and the hydrogen bonds interaction component *dH*. The values of *dD*, *dP*, and *dH* are reference values [16].

There is a mathematical relationship between the Hansen and Hildebrand solubility parameters, from which the length of the radius vector can be calculated: $HSP^2 = dD^2 + dP^2 + dH^2$. The Hansen solubility parameter (HSP) can be found from this equation. The *HSP* parameter includes the Hildebrand solubility parameter. *HSP* is valid for multi-component systems. Moreover, even if a mixture of solvents is difficult to study using other solubility theories, in *HSP* the solvent mixture is considered by simply adding the radius vectors. Table 1 shows the Hansen solubility parameters calculated for polystyrene.

A three-dimensional graph of the solvent power of the solvents of polystyrene was constructed according to the data in Table 1 (Fig. 1).

Films were obtained by the influx method from the solutions of PS and light-sensitive pigments – yellow (sample No. 1) and blue (sample No. 2). The resulting films 100 microns thick were transparent, durable, and without visible defects. The optimal conditions for obtaining the polymer film were determined: the dissolution temperature is 80 °C, the concentration of the PS solution is 12%, and pigment concentration is 5%.

To measure the photochromic properties of the film, a spherical ultra-high pressure mercury lamp of the type DRSh-250 was used as the radiation source, which is a powerful source of ultraviolet (UV) radiation. The absorption

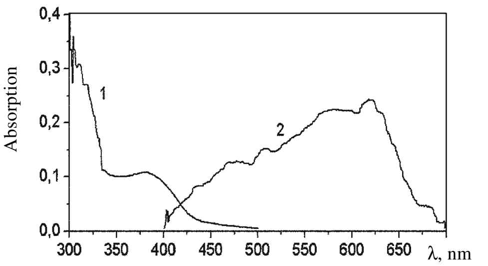

Fig. 4.

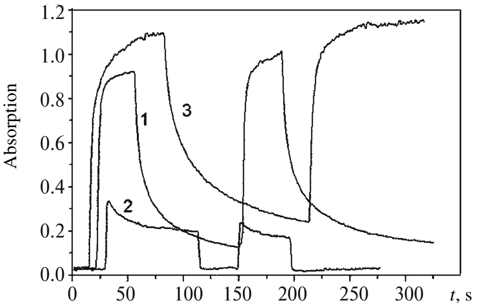

Fig. 5.

Fig. 4. The absorption spectrum (*1*) and additional absorption spectrum (*2*) of (blue) naphthopyran under UV irradiation of the film No. 2.

Fig. 5. Kinetics of increase and relaxation of additional absorption in the UV-irradiated films No. 1 (*1*), No. 2 (*2*), and No. 3 with a mixture of yellow and blue naphthopyran (*3*): *1*, *3* – $\lambda = 500$ nm; *2* – $\lambda = 600$ nm.

spectra of the pigments dissolved in PS were measured using a standard spectrophotometer "Specord M40." The kinetics of changes in additional absorption was studied using a spectral computing complex at different wavelengths (λ) under UV radiation. The additional absorption spectra of the films were also measured under UV radiation.

From Table 1 and Fig. 1 it can be seen that polystyrene readily dissolves in its own monomer, in aromatic and chlorinated hydrocarbons, in esters, but is not soluble in lower alcohols, aliphatic hydrocarbons, phenols, and ethers.

This study shows the advantages of using mixtures of solvents. High solvency of mixtures with respect to polystyrene has been determined. In particular, the rate of the dissolution process in a mixture of acetone with carbon tetrachloride (CTC) is 15 times higher as compared with the individual solvents.

Table 2 shows the results of calculating the transmittance coefficient T at the corresponding wavelength of probe radiation for samples No. 1 and No. 2 and their mixtures – sample No. 3 ($T = I/I_0$, where I is the intensity of the beam transmitted through the film, and I_0 is the intensity of the incident beam).

As can be seen from Table 2, the maximum photochromic effect (minimum T) in a mixture of solvents corresponds to naphthopyran yellow with blue – 0.100. When considering the individual solvents, the maximum photochromic effect is observed in *o*-xylene for naphthopyran yellow.

Figs. 2-5 show experimental data on the optical properties of the films.

Figs. 2 and 3 show the absorption spectra of naphthopyran yellow (curve *1*), the spectrum of additional absorption of the film under UV irradiation (curve *2*), and the kinetics of change in additional absorption of the film No. 1 with yellow naphthopyran under UV irradiation for different wavelengths of the probe radiation (Fig. 3, curves *1*-*6*).

Fig. 2 shows that the maximum of intrinsic absorption by yellow naphthopyran is in the ultraviolet region of the spectrum and begins at 375 nm. Upon UV irradiation of the film No. 1 (with yellow naphthopyran) there is additional absorption in the visible region of the spectrum with a maximum at 470 nm.

From Fig. 3 it follows that under UV irradiation the shape of the curve of the kinetics of growth and relaxation of additional absorption of the film No. 1 is weakly dependent on the wavelength of the probe radiation. The only difference is in the magnitude of the maximum darkening, which is 0.5 at 450 nm (curve *3*).

Fig. 4 shows the spectrum of intrinsic absorption of blue naphthopyran, which is located in the ultraviolet region of the spectrum and begins at 425 nm. Under UV irradiation of the film No. 2 (with blue naphthopyran) a wide band of additional absorption arises in the visible region of the spectrum with a maximum at 620 nm.

Fig. 5 shows the comparative data on the kinetics of growth and relaxation of additional absorption under UV-irradiation of films No. 1 (curve *1*), No. 2 (curve *2*), and No. 3 with a mixture of yellow and blue naphthopyrans (curve *3*). The greatest darkening effect was observed in the mixture of naphthopyrans (curve *3*). As for the darkening time, for the blue naphthopyran it is 5 s, while for the yellow and for the mixture of naphthopyrans it is 15 s. The darkening relaxation time after turning off UV radiation is on the order of tens of seconds for both naphthopyrans.

Analysis of the dependences shown in Figs. 2-5 shows that sample No. 2 (blue, Fig. 5) has the highest darkening speed. High absorption of sunlight UV radiation is another important advantage of this pigment (Fig. 4). However, the maximum darkening effect is achieved in the sample No. 3 (mixture of yellow and blue pigments), which is three times greater than that for sample No. 2 with the blue pigment (Fig. 5).

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