ANOMALOUS STABILITY OF “COLORED” FORM OF SPIROXAZINE PHOTOCHROMS TRAPPED IN POLYCARBONATE MATRIX AFTER SUPERCRITICAL FLUID IMPREGNATION

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Various thermoplastic polymers (polyethylene, polypropylene, PMMA, polycarbonate) were impregnated with spiroxazine photochrom (-1',3',3'-threemethylspyro (indoline-2,3-3H- antrazeno- [2,1-b] [1,4] oxazin) (SAO) dissolved in supercritical CO₂ SAO molecules have usually stable unexcited form (A) that transfers to unstable “colored” form (B) under the action of UV light. It was found that, unlike other polymers under study, the supercritical fluid (SCF) impregnation of polycarbonate (PC) with SAO causes the anomalous stabilization of its colored form B. The bleaching time of SAO in PC after its photoexcitation (900 s) is two orders of magnitude higher than that in polypropylene. Moreover, after supercritical fluid impregnation of PC up to 20% of SAO is originally formed in colored form, which is not bleachable for 250 days (the whole period of observation), i.e. is extremely stable. The temperature and pressure effects on SAO concentration in different polymer matrixes were measured. At least some part of SAO incorporated into the polymeric matrix forms nanocrystals of ~10-20 nm size. Possible mechanisms of the observed effect of the anomalous stability of colored SAO form trapped in the polycarbonate matrix after its SCF are discussed.

INTRODUCTION

Supercritical fluids became increasingly important for functionalization of different polymeric materials [1-4]. In this work (focused on the development of new optical materials) various thermoplastic polymers (polyethylene, polypropylene, polymethylacrylate, polycarbonate) were impregnated with spiroxazine photochrom molecules dissolved in supercritical CO₂ (scCO₂). Indoline spiroxazines are widely used present as photochroms to develop novel photochromic materials. Interest to spiroxazine photochroms is caused by relatively easy synthesis of these compounds, significant frequency shift of photo-induced absorption band with respect to that of unexcited state (that is important for applications), high efficiency of photo-transformation, and high coefficient of extinction of photo-induced form. Photochromism of spiroxazine compounds is quite sensitive to their molecular structure which allows wide variation of photochromic parameters [5]. Besides, spiroxazine compounds are quite photo-stable. The use of scCO₂ (which can easily be removed from polymer by depressurization) as a solvent for incorporation of spiroxazine compounds into polymer matrix, allows to avoid undesirable effects of solvent residuals to photochromism of polymer - spiroxazine system.

It is shown in this work that the concentration of spiroxazine molecules incorporated into polymer by scCO₂ and the kinetics of bleaching of their colored form, is controlled by the type of polymer matrix. It was also revealed that impregnation of polycarbonate with one SAO (indoline-2',3'-3H- antrazeno-[2,1-b] [1,4] oxazin) causes the substantial stabilization of “colored” form, as distinguished from other polymer-photochrom pairs. Moreover, some part of SAO molecules in polycarbonate matrix remains excited (“colored”) for a long time (maximal observation time of unrelaxed (B) form is 250 days). Our electron microscopic studies show that some part of SAO molecules in polymer matrix forms nanoclusters 10-20 nm in size. We discuss possible mechanisms of the observed effect of anomalous stability of colored SAO form trapped in the polycarbonate matrix after its impregnation in scCO₂.

EXPERIMENTAL

Various thermoplastic polymer samples in the form of films (120-1000 µm in thickness) were used in our experiments: polymethylacrylate (PMMA) Mₐ ≈ 5.10⁵; low density polyethylene (LDPE), Mₐ = 4.10⁵; polypropylene (PP), Mₐ = 5.10⁵; polycarbonate (-O-C₆H₄-C(CH₃)₂-C₆H₄-OCO)-n (PK), Mₐ ≈ 3-5.10⁵. SAO molecule (Fig.1) transforms from initial (“uncolored”) form (A) to excited (“colored”) form (B) under the action of UV light [6]. Form A has the absorption band in UV range, while form B
absorbs light in $\lambda_{\text{max}} = 607$-$631$ nm spectral range (depending on the properties of matrix and solvent.) that gives intense blue coloring of sample. Photochromism of SAO is conditioned by photodissociation of $A$ form by $C$-$O$ spirobond with subsequent cis-trans-isomerization and formation of $B$ form, which is characterized by coplanar structure and conjunction of $\pi$-electrons of indoline and oxazine groups. The reverse process (dark bleaching) $B \rightarrow A$ trans-cis-isomerization and locking of oxazine cycle (Fig.1) has a typical time $< 1$s.

To incorporate SAO molecules into polymer matrix we have used the technique of SCF impregnation. ScCO$_2$ was used as a solvent for SAO molecules. Our setup for SCF impregnation of polymers was described in [4]. Polymer samples and about 20 mg of SAO were placed into the high pressure chamber. The chamber was heated up to 80-90°C and pressured with CO$_2$ up to 150-220 atm. Typical SCF processing interval was 30min. The amount of SAO incorporated into polymer sample was measured from the intensity of absorption band of $A$ form at $\lambda = 403$ nm measured with Genesys-2 spectrophotometer.

Nanoparticles of SAO fabricated in the polymer matrix after SCF impregnation, were monitored with TEM technique (LEO 912 AB OMEGA).

RESULTS

Concentration of incorporated photochrom

Fig. 3 shows SAO concentration in different polymer samples incorporated by scCO$_2$ as a function of temperature. The rise of temperature results in significant increase of SAO concentration for all polymer samples. We believe that difference in incorporated SAO concentration for different polymers is caused mainly by the difference in their crystallinity, since the effect of impregnation takes place predominantly in amorphous parts of polymer. Also, SAO concentration increases with CO$_2$ pressure (Fig. 4), which is controls the density and solubility of SAO in scCO$_2$. 
Effect of anomalous stabilization of colored form of SAO trapped in PK

Molecules of SAO incorporated into polymers by sc-CO₂ have been excited with UV lamp into colored (B) form. It was found that for PP, LDPE and PMMA transforms quite quickly from colored form to initial (A) form (Table 1). At the same time, the temporal stability of B form of SAO incorporated into PK is 200 times higher than that for PP samples, and dark bleaching time is about 900s.

Table 1. Bleaching times of colored form of SAO τ in different polymers.

<table>
<thead>
<tr>
<th>№</th>
<th>Polymer</th>
<th>[SAO], % mass.</th>
<th>τ, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PP</td>
<td>0.4</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>LDPE</td>
<td>1.2</td>
<td>&lt;5</td>
</tr>
<tr>
<td>3</td>
<td>PK</td>
<td>0.9</td>
<td>900</td>
</tr>
<tr>
<td>4</td>
<td>PPMA</td>
<td>0.2</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Notice, that SAO molecules incorporated into PP, LDPE and PMMA samples, are localized in matrices of these polymer in uncolored form only. All these samples are uncolored after impregnation with SAO. At the same time, in the case of PP samples some part of incorporated SAO molecules are formed in state B even without any photo-excitation. This follows, for example, from Fig. 2. Besides, this is supported by the fact that PK samples after SCF impregnation with SAO have blue color typical for B form.

Total amount of SAO in B form just after SCF impregnation of PK samples depends on temperature and can reach 10% of overall SAO amount in PK sample. Moreover, the post-treatment rise of SAO amount in B form during 10-20 hours takes place (Fig. 6).
Total amount of SAO in B form in 10-20 hours after the completion of PK samples impregnation, depends on temperature and can reach 15-20% of overall SAO amount in PK sample.

It is of importance that PK samples SCF impregnated with SAO do not change the intensity of their blue color (and intensity of B form absorption band at 600nm) during more than 250 days after completion of SCF impregnation of PK sample with SAO.

**Formation of nanoparticles**

Fig. 7 shows electron microphotographs of PK and PMMA samples which are SCF impregnated with SAO (pressure - 180atm, temperature - 80°C, impregnation period - 30 min), where one can see the crystalline nanoparticles of SAO. The crystallinity of SAO nanoparticles is confirmed by diffractogramm, shown at right upper angle of Fig.7a. The circular rings obtained for PK sample (Fig.7a) gives the evidence of large amount of small (~ 2-5nm) crystallites. Some separate reflexes here correspond to larger (10 -20 nm) nanoparticles. At the same time, for PMMA samples we have managed to observe just separate regions, composing small amount of SAO nanoparticles 2 -7nm in size.

**Discussion**

Photochromism of SAO molecules is conditioned by their photo-induced transition from initial (uncolored, “closed”) state A to photo-induced (colored, “open”) state B [5]. SAO molecule in A state is composed of two coplanar fragments – indoline and spiroxazine, which have orthogonal mutual orientations [5]. Orthogonality of indoline and spiroxazine parts of SAO means, that π-electron systems are not interacted. This is why the absorption spectrum of SAO in A form has the series of bands in 200-400nm range. Oxazine fragment is responsible for bands in λ > 300 nm range, while indoline fragment – for bands with λ < 300nm. According to [5], UV irradiation causes the brake of C=N–O bond and mutual rotation of orthogonal fragments up to coplanar state (Fig. 8).
Fig.8. Chemical structure of uncolored (A) and colored (B) forms of indoline spiroxazine molecules.

Me-methyl, X – benzyl or naphthal.

Coplanar (B) state of SAO molecule has intense absorption at \( \lambda \approx 610 \text{nm} \). The time of B→A transition in SAO incorporated into elastic matrices (LDPE, PP), is quite fast, \( \tau_{0.5} < 1-5 \text{s} \) (Table 1). However in glasslike polymers the rate of such transition can be much lower, that follows from our experiments with SAO incorporation into polycarbonate matrix, where the observed \( \tau_{0.5} \) value was quite large – 900 s (Table 1).

The most important observation of this work is the observation of anomalously stable colored form of SAO in polycarbonate after its SCF impregnation in the absence of any photo-excitation. Thus, the coplanar conformation of SAO in PC matrix was formed in SCF reactor after SCF impregnation of PC with SAO and subsequent release of CO2 pressure. It should be noted that according to our experiments formation of colored state of SAO has been also observed during post-impregnation period (for 10-20hours). As it follows from Figs.6, the post-impregnation out-diffusion of CO2 from PC sample is accompanied by the rise of \( \lambda = 610 \text{nm} \) absorption band and, hence, by the amount of SAO molecules in B form.

The use of SCF impregnation to incorporate SAO into PC matrix is most likely principal to fabricate anomalously stable colored state of SAO. When SAO molecules are incorporated into polymers (even by SCF technique) without polyphenylene fragments, the colored form of SAO is not stabilized. We believe that stabilization of coplanar conformation B of SAO molecule, which has aromatic fragments with the system of conjunctive \( \pi \)-bonds, is caused by formation of intramolecular charge transfer complexes between such coplanar fragments and bis-phenol fragments of PK. Electron density in such complexes is likely to be shifted from carbonyl oxygen atom of B form of SAO to carbonyl carbon atom of polycarbonate with subsequent redistribution over the whole charge transfer complex, that benefits stabilization of coplanar structure of B form of SAO. These assumptions are supported by the fact, that dissolution of colored PK samples in chloroform causes transition of SAO from B to A form. Release of CO2 pressure after SCF impregnation, causes the decrease of polymer free volume, that plagues SAO transition from coplanar to orthogonal form A and contributes to stabilization of B form.

Effect of nanoparticles formation in polymer matrix after SCF impregnation, observed by TEM, represents an interest in itself. However, the fact that nanoparticles were observed both in PC and in PMMA (where B form of SAO was not stabilized) matrixes, means that the effect of anomalous stabilization of colored form of SAO in PC is hardly connected with nanoparticles formation.

Conclusions
Molecules of spiroxazine photochroms have usually stable unexcited form (A) that transfers to unstable “colored” form (B) under the action of UV light. In this work (focused on the development of new optical materials) various thermoplastic polymers (polyethylene, polypropylene, polymethylmetacrylate, polycarbonate) have been impregnated with spiroxazine photochrom (indoline-2,3-3H-antrazeno-[2,1-b][1,4]oxazin) (SAO) dissolved in scCO2. It was revealed that polymer type affects significantly on rate of SCF impregnation and, also, on the kinetics of bleaching of “colored” form of SAO incorporated in polymer matrix by scCO2. Impregnation of polycarbonate with SAO causes the substantial stabilization of “colored” form, as distinguished from other polymer-SA0 pairs. Bleaching time of photoexcited SAO molecules in polycarbonate (900s) is two orders of magnitude higher than that for SAO in polypropylene. Moreover, some part of SAO molecules in polycarbonate matrix (up to 20%) remains excited (“colored”) for a long time (maximal observation time of unrelaxed (B) form is 250 days). Our electron microscopic studies show that some part of spiroxazines in polymer matrix forms nano-clusters 10-20 nm in size. We believe, that effect of anomalous stability of “colored” form of spiroxazine photochroms (SAO) in polycarbonate matrix after supercritical fluid impregnation is caused by trapping of some part of SAO
molecules in its \textbf{B} form (which has coplanar geometry, by contrast to unexcited (\textbf{A}) form) in polycarbonate. Effect of scCO$_2$ impregnation causes swelling of PC matrix that allows easy formation of π−π complex of aromatic fragments of SAO and PC. Squeezing of matrix after release of CO$_2$ promotes trapping of plane π−π complex in polymer matrix and stabilization of colored form of SAO.

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REFERENCES