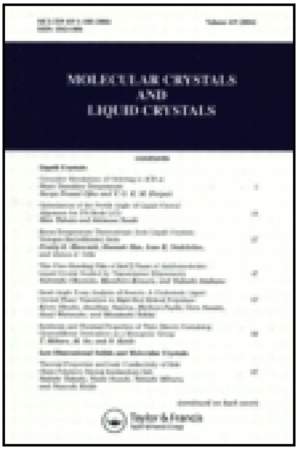

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A New Pseudophotochromic Benzothiazoles Doped PVC Films

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A NEW PSEUDOPHOTOCHROMIC BENZOTHIAZOLES DOPED PVC FILMS

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Abstract Under the influence of the UV light in 2-aryl substituted benzothiazoles doped PVC films take shapes. a new pseudophotochromic system. The coloured films were formed by two processes - the liberation of HCl during the photodegradation of PVC and an interaction between HCl and 2-arylsubstituted benzohiazoles (BT). They can return thermally to the colourless films and this process depends on the stability of the complexes $BTH^{+}.Cl^{-}$. Reversible photochromism was observed in the films on repeating irradiation with UV light. The experimental results, possible applications and future work on this pseudophotochromic system are also discussed.

INTRODUCTION

The phenomenon of photochromism has been investigated extensively by a large number of researchers over several decades[1]. Many substances have been found to exhibit this colouring and decolouring process. The most important groups of compounds are the spiropyrans, fulgides, pyrazoles, azobenzenes, triarylmethanes, polymethine dyes and substances that show. E-Z izomerization of double bonds[2]. In most of these systems the photochromic process proceeds by photochemically induced heterolytic bond fissure to a normally coloured zwiterionic structure followed by thermally induced reformation of this bond back to a colourless form of the molecule.

Our interest in the photoreactions of the BT is centred on the utilization of BT as photostabilizators of PVC[3]. The original notion was to generate a $BTH^+.Cl^-$ complex from BT and HCl - a product of the degradation of PVC. It is known that the protonation of 2-arylbenzothiazoles is associated with the higher basicity of the heterocyclic nitrogen atom in the benzothiazole ring[4]. The colour is altered dramatically on protonation of the BT with electron donating groups in the 2-aryl ring. In the unsubstituted 2-aryl benzothiazoles the same process accompanied by only a slight colour change.

EXPERIMENTAL

Materials

Commercial stabilizer free PVC powder was used and BT synthesized as described previously[5].

Film preparation

PVC films were obtained by casting of dichloroethane (20 cm^3 , Merck, spectroscopic grade) solutions of the polymer (1g) and the respective BT (0.25 wt%, based on PVC) on a glass plate. The solvent was removed at room temperature for 3-4 days and then under vacuum for 10 hours at 40°C. The typical film thickness was of about 30-50 μm.

Photoirradiation

The resulting film were irradiated at room temperature in air with filtered UV - light ($\lambda > 300$ nm) from a medium pressure Hg lamp at a distance of 20 cm for various periods of time through a thermal filter (H_2O).

Spectroscopic measurements

The pseudophotochromic process was followed by measuring at regular time intervals the UV spectra in the 300-600 nm range using Specord UV-VIS spectrophotometers.

RESULTS

Table 1 shows the photochromic characteristics of the PVC-BT films.

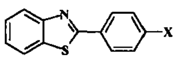
Figure 1 illustrates the changes which occur in the ultraviolet spectra of PVC-BT films irradiated in air (compound **10**). The absorption bands in the 370-500 nm region correspond to the formation of coloured species $BTH^+.Cl^-$ via the reaction:

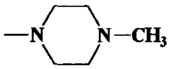
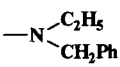
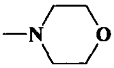
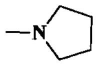
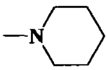
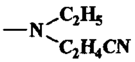
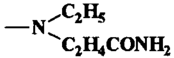
$$\mathrm{BT} + \mathrm{HCl\,(PVC)} \xrightarrow{h\nu} \mathrm{BT\overset{+}{H}.\overset{-}{Cl}}$$

The coloration / decoloration was reversible.

Fig. 2 illustrates the relationship between the absorbance at 300-400 nm (for BT) and 370-500 nm (for $BTH^+.Cl^-$) and the irradiation time τ of PVC-BT films.

TABLE I Photochromic characteristics of the PVC-BT films.

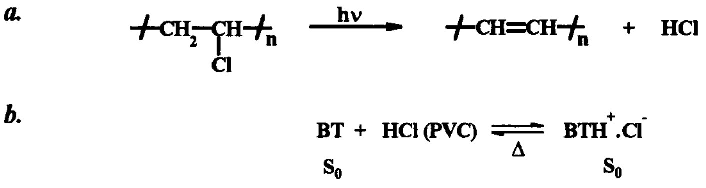
BT =


Compd. №	X	WT% BT/1g PVC	λ_{max} of unirradiated films (nm)	λ_{max} of irradiated films (nm)	$\Delta\lambda_{max} = \lambda_{BTH^+Cl^-} - \lambda_{BT}$
1	$-N(CH_3)_2$	0.25	365	438	73
2	$-N(C_2H_5)_2$	0.25	370	443	73
3		0.25	347	415	68
4	 $-N(C_2H_5)(CH_2Ph)$	0.25	360	425	65
5		0.25	352	425	73
6	$-NHCOCH_3$	0.25	332	372	40
7		0.25	370	450	80
8		0.25	365	443	75
9	 $-N(C_2H_5)(C_2H_4CN)$	0.25	358	425	67
10	 $-N(C_2H_5)(C_2H_4CONH_2)$	0.25	369	439	70

DISCUSSION

The development of new pseudophotochromic system which involve a PVC-BT is described. This system is in principle based on the photoinitiated dehydrochlorination of PVC and the interaction between HCl and BT. From our experimental results we conclude that there are at least two ways for description of the bimolecular photochromic systems:

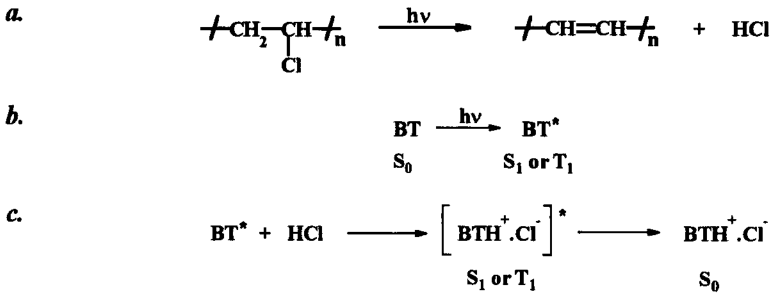
Scheme 1.



a. $+\!\left[CH_2-\underset{Cl}{CH}\right]_n \xrightarrow{h\nu} +\!\left[CH=CH\right]_n + HCl$

b. $\underset{S_0}{BT} + HCl\,(PVC) \underset{\Delta}{\rightleftharpoons} \underset{S_0}{BTH^+.Cl^-}$

Scheme 2.



a. $+\!\left[CH_2-\underset{Cl}{CH}\right]_n \xrightarrow{h\nu} +\!\left[CH=CH\right]_n + HCl$

b. $\underset{S_0}{BT} \xrightarrow{h\nu} \underset{S_1\,or\,T_1}{BT^*}$

c. $BT^* + HCl \longrightarrow \underset{S_1\,or\,T_1}{\left[BTH^+.Cl^-\right]^*} \longrightarrow \underset{S_0}{BTH^+.Cl^-}$

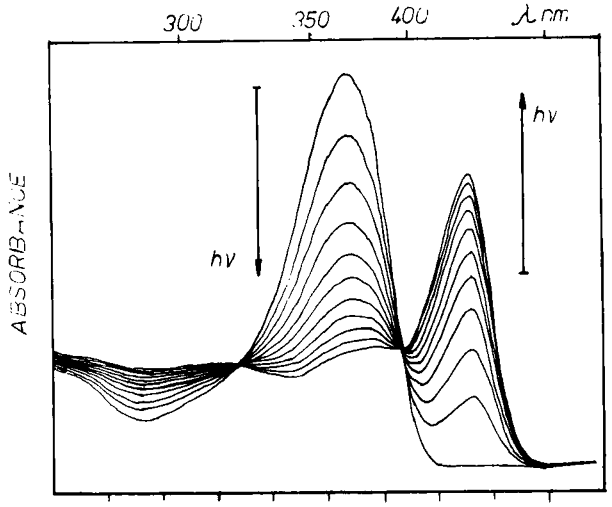


FIGURE 1 Typical reaction spectrum of BT-PVC films (compd. **10**)

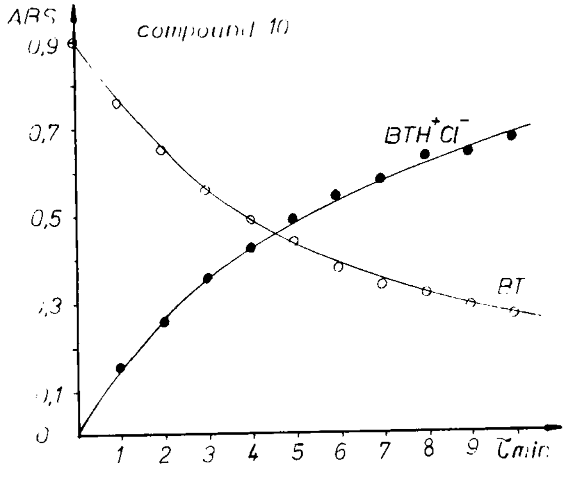
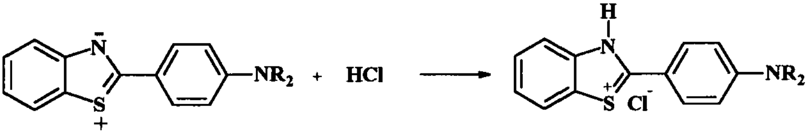
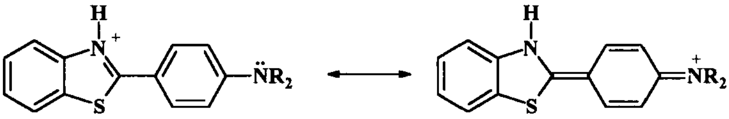


FIGURE 2 Relationship between the irradiation time (1 min) and the absorbance of BT to $BTH^+.Cl^-$ (compd. **10**)

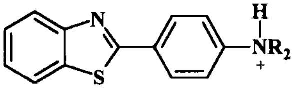
It is clear that in Scheme 1 the photochemical behaviour of the system can be represented by the photodegradation of PVC(a). The reaction between BT and HCl proceed in ground state (S_0) and the total conversion of BT into $BTH^+.Cl^-$ will depend on the quantity of the liberated HCl. As it is shown in Scheme 2, the second possibility includes a photoexcited process of BT. Then the interaction between BT* and HCl will have specific character and will depend on the excited state of state of BT. According to Palmer and Kennedy[6], 2-phenylbenzothiazole forms a long living readily detectable state as a triplet biradical or a charge-separated form, where the positive charge density is localized on the sulfur atom. It is clear that in such an excited triplet state of BT the protonation will be at heterocyclic nitrogen atom:



The substituted amino group in 2-phenyl ring acts as an electron donor and the heterocyclic nitrogen atom acts as a electron acceptor. As a result the maximum absorption of the compounds $BTH^{+}.Cl^{-}$ – (which has a nearly planar structure) are in the visible region. Such a structure have a delocalized π-molecular orbital over the molecule, which is more favourable for the formation and stabilization of the intramolecular charge separation state.

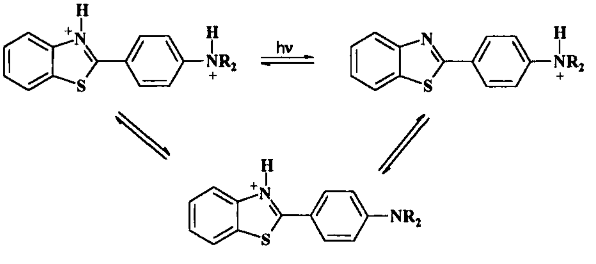


In contrast in the structure :



where *p*-aminophenyl group is protonation, its electron conjugative effect is lost. Then, its UV-spectra will be close to unsubstituted BT-λ_{max}~300-320 nm. These conclusions are in good agreement with the observation in the UV-spectra of the irradiated PVC-BT films two peaks-at 320 nm and 440 nm.

In the investigation PVC-BT films the basic centres are two - the amino groups and the tertiary nitrogen atom. Based on our results and pKa values and charge density data of Dogra at all[7,8], the first protonation occurs at the amino group and the second protonation at the heterocyclic nitrogen atom in the S_0 state. On excitation the basic strength of the *p*-aminophenyl group is strong reduced in contrast with the nitrogen atom in heterocyclic ring and the protonation is in the reverse order. Its very important to note that the presence of isosbestic points in a set of spectra, generated by changing the structure (PVC-BT to $BTH^{+}.Cl^{-}$) can be used under appropriate circumstances as evidence for the photochromic process. In this aspect, the changing of the absorbance with the irradiation time show that the photochromic conversion proceeds as a simple type photochemical reaction. It is noticeable that the concentration of $BTH^{+}.Cl^{-}$ does not increase so much. This fact, as and the reversion can be explained by two possibilities. One is connected with the low stability of the $BTH^{+}.Cl^{-}$ complexes. In the light of the results it seems safe to say that the second reason is connected with the existence of a biprotonic phototautomerization process in ground and excited state[8].



Several factors will influence of the equilibrium: pH range, the rate of deprotonation of the $-NHR_2^+$ group plus the rate of protonation of the tertiary nitrogen atom, the lifetimes of the species, the character of the irradiated PVC-BT films. Experiments in these directions are in progress.

REFERENCES

1. G. H. Brown, Photochromism Technique of Chemistry; Interscience; New York, ,vol. III. 1971
2. Photochromism Molecules and Systems, Edited by Heinz Duerr and Henri Bouas-Laurent, Elsevier 1990.
3. I. Petkov, T. Deligeorgiev, P. Markov, M. Evstatiev and St. Fakirov, Polymer Degradation and Stability , 33, 53 (1991).
4. A.I. Kiprianov, V.A.Shrubovitch, Zh. Ob. Chim., 29(2), 1290 (1959).
5. T.G.Deligeorgiev, Dyes & Pigm.,12, 243 (1990).
6. M. H. Palmer, S. M. F. Kennedy, J.Mol.Struct.,43, 203 (1978).
7. S.K.Dogra, Proc.Indian Acad. Sci., 104(6), 635 (1992).
8. J. K. Dey and S. K. Dogra, Bull. Chem.Soc. Japan, 64, 3142 (1991).