Photoresponsive polymers: 1. Preparation and properties of a polymer containing 2-phenyl-1,3-indandione as chromophore

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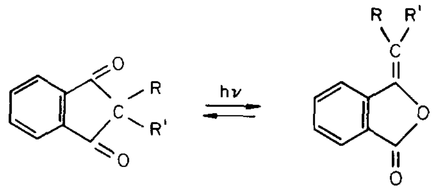
A polymer containing photochromic moieties is obtained by means of the transesterification of poly(vinyl acetate) with 2-phenyl-5-carboxy-1,3-indandione. Upon u.v. irradiation of a solution and film of this polymer a transition to its benzalphthalide form is observed. It is assumed that the photochemical isomerization of 2-phenyl-1,3-indandione can also start from its enol form.

(Keywords: photoresponsive polymers; photochromism; 2-phenyl-1,3-indandione)

INTRODUCTION

Over the last 30 years numerous studies have been carried out on various photoresponsive polymers. One of the possible routes to prepare such polymers is to attach photochromic compounds to the polymer chains. Photochromism is a phenomenon that was discovered towards the end of the last century, although the term 'photochromism' was introduced much later. Photochromism is defined as a reversible transition of some chemical compounds between two states of different absorption spectra. As a mandatory condition, at least in one direction, this change should be introduced by light[1].

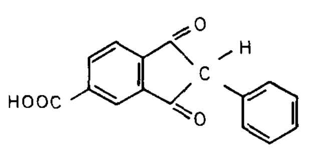
A group of interesting compounds with photochromic properties is the 2-substituted 1,3-indandiones[2], which convert on irradiation into alkylidenephthalides:



(1)

This isomerization is almost 100%. Despite their good photochromic properties, the above compounds have not been attached to any polymer chain.

The purpose of this study was to prepare and investigate a polymer containing photochromic groups based on 2-phenyl-1,3-indandione. 2-Phenyl-5-carboxy-1,3-indandione (**1**) was used.



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The photochromic properties of **1** are combined with the presence of a reactive carboxylic group. We prepared **1** by isomerization of 6-carboxy-3-benzylidenephthalide, obtained according to a procedure similar to that described previously[3]. Poly(vinyl acetate) (PVAc) was chosen as a polymer carrier. It has a low glass transition temperature (T_g) which facilitates the photochromic change in the solid phase.

EXPERIMENTAL

Materials

The materials used were commercially obtained: PVAc ($M_w = 45\,000$, BDH, UK), pyridine (freshly distilled, $n_D^{20} = 1.5009$; POCh Glivice, Poland) and tetrabutyl titanate (Fluka).

Synthesis of 2-phenyl-5-carboxy-1,3-indandione (1)

A mixture of trimellitic anhydride (9.6 g, 0.05 mol), phenylacetic acid (10.2 g, 0.075 mol) and sodium acetate (94.5 g, 0.055 mol) was heated for 10 h at 190°C. After cooling the solid was ground, washed with hot water, dried and then recrystallized from methanol [m.p. 280°C; yield 11. 1 g (83.45%)].

Analysis $C_{16}H_{10}O_4$ (226.26), calculated: C 72.18, H 3.79; found: C 71.95, H 4.12%. Then, 2.66 g (0.01 mol) of the product was suspended in methanol (4 ml) and a 6% solution of sodium methylate (1 ml) was added. The mixture was refluxed for 1 h. The red–brown solution was diluted with water (10 ml) and the precipitate formed was acidified with dilute hydrochloric acid to pH 2. The precipitate formed was filtered, dried and recrystallized from glacial acetic acid [m.p. 289°C; yield 2.4 g (90%)].

Preparation of the i-propyl ester of 1

Compound **1** (0.22 g) and thionyl chloride (5 ml) were refluxed for 1 h. Excess thionyl chloride was then removed and i-propanol (2 ml) was added to the residue. The clear solution was refluxed for 1 h and then evaporated to dryness. The i-propyl ester **2** was recrystallized from

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a chloroform–cyclohexane mixture [m.p. 120°C; yield 0.19 g (54%)].

Analysis $C_{19}H_{16}O_4$ (308.34), calculated: C 74.01, H 5.23; found: C 73.63, H 5.38%.

Transesterification of PVAc

In a round-bottom flask PVAc (1 g) and pyridine (12 ml) were stirred until the PVAc dissolved. Then, **1** (0.24 g) and tetrabutyl titanate (0.035 g) were added and the solution was heated under reflux for 1 h, and then pyridine was distilled. The first distillate, a mixture of pyridine and acetic acid, had a n_D^{20} value of 1.4894. Further portions of pyridine were added and the distillation was continued until the refractive index of pure pyridine was recorded and then the solution was distilled to dryness. The dry residue was treated with benzene and the solution obtained was filtered and precipitated in ligroin. The polymer was dried to constant weight (yield 0.95 g) and was soluble in chloroform, acetone and dimethylformamide (DMF).

Analysis, found: C 59.52, H 7.28%. The calculated values for PVAc and for the completely transesterified polymer with type **1** units are C 55.81, H 7.03% and C 73.97, H 4.14%, respectively. An interpolation based on the analysis found showed that 23% of the acetate groups are substituted by type **1** residues.

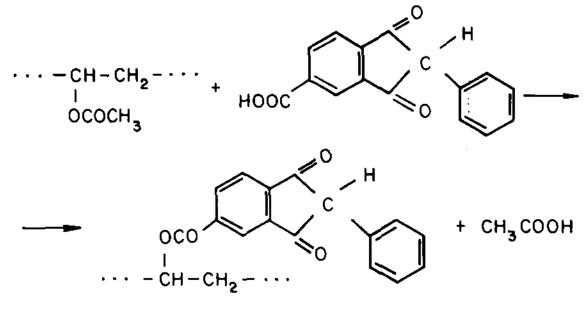
Spectral and photochemical investigations

U.v. spectra were obtained using a u.v.-vis. Specord spectrophotometer (Carl Zeiss, Jena, Germany).

Irradiation was carried out with a high pressure mercury lamp (maximum intensity at 365 nm) and a glass filter on a solution of copolymer **3** in a quartz vessel and on a film. The film (40–50 μm thick) was prepared by evaporating a 4% solution of **3** in chloroform on a quartz plate.

RESULTS AND DISCUSSION

Attaching the chromophore-containing compound **1** to the PVAc chain was carried out by transesterification with tetrabutyl titanate as catalyst in pyridine solution:



(2)

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After isolation and reprecipitation the polymer obtained is red. This colour is not due to impurities of **1** (which is also red), since the polymer was extracted from the reaction mixture with benzene which does not dissolve **1**. This is indirect evidence that transesterification has occurred. Further proof is the change of the refractive index of the pyridine distillates due to the acetic acid evolved [reaction (2)]. Elemental analysis showed ~23% chromophoric moieties in the transesterification product. Thus, the latter can be regarded as a copolymer containing vinyl acetate basic units and structural repeating units of the vinyl ester of **1** in a ratio of ~3:1.

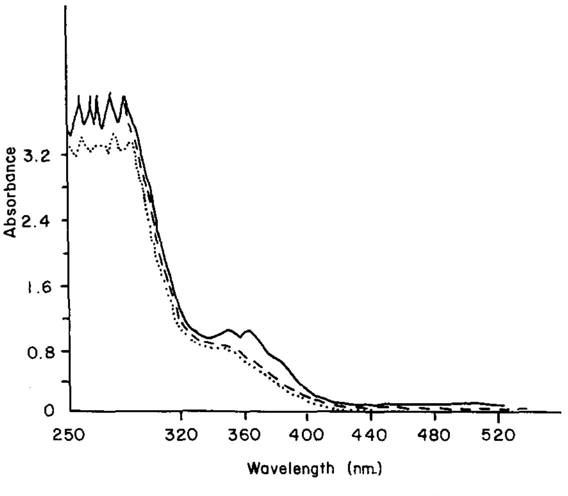
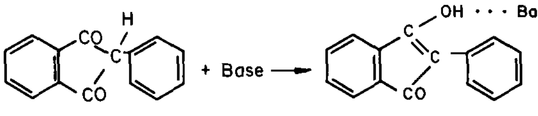


Figure 1 Electronic spectra of **2** in DMF (2.5 g l^{-1}, ——), and of **3** in DMF (10 g l^{-1}, ···) and in chloroform (10 g l^{-1}, – – –)

The electronic spectra of **3** and of the i-propyl ester of **1** (**2**) (which is a model compound of the phenylindandione moieties in **3**) are similar (*Figure 1*). This could be considered as proof for the polymer structure. The spectra of **3**, taken in chloroform and in DMF, are nearly identical. This is on first consideration bewildering, since according to reference 4 2-phenyl-1,3-indandione (**4**) converts into its enol form in the presence of aprotic bases (DMF in our case):



(3)

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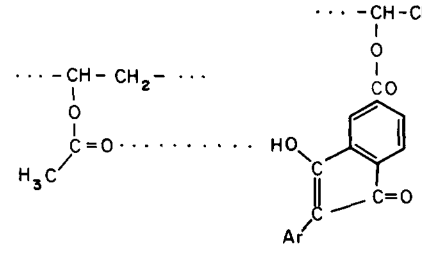
In chloroform the equilibrium is expected to be drawn strongly to the left and phenylindandione should exist only in its keto form without absorption above 400 nm. However, according to Pipkin and Stella[4], formation of the enol isomer is facilitated by interactions via hydrogen bridges. In our case, the formation of hydrogen bonds between the enol hydroxyl group and the PVAc carboxyl group is also possible:



(4)

As already stated, on u.v. irradiation **4** isomerizes to benzalphthalide [reaction (1), R′ = H; *Figure 2*]. On irradiation of copolymer **3** we observed effects corresponding to the photochromic character of the phenylindandione substituents in the polymer chain. Electronic spectra of **3** in chloroform before and after 10 min irradiation are shown in *Figure 3*. The spectrum before irradiation shows that some of the phenylindandione moieties in the copolymer are in the enol form (absorption above 400 nm is present). Unfortunately, we cannot obtain the spectrum of the copolymer with phenylindandione moieties only in the keto form, since **1** is insoluble in non-polar solvents (cyclohexane, benzene,

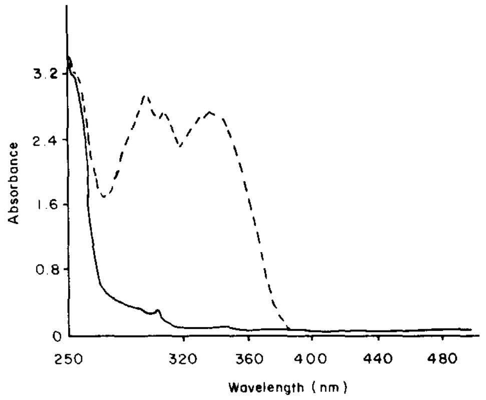


Figure 2 Electronic spectra of **4** ($3.6\times10^{-4}\,\text{m}\,\text{l}^{-1}$) in chloroform before (——) and after (– – –) 10 min of irradiation

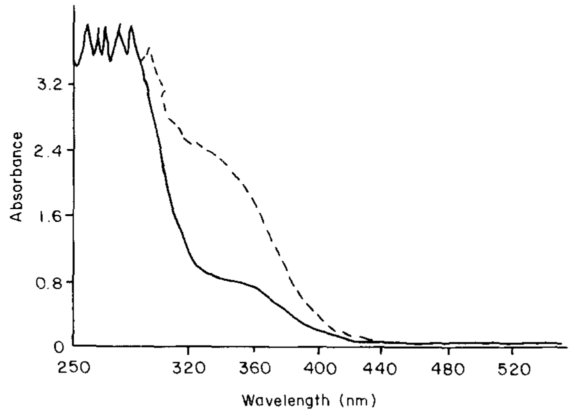


Figure 3 Electronic spectra of **3** in chloroform ($10\,\text{g}\,\text{l}^{-1}$) before (——) and after (– – –) 10 min of irradiation

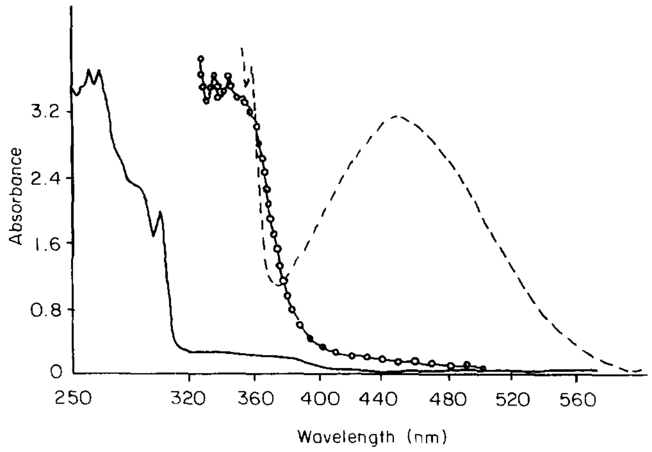


Figure 4 Electronic spectra of **4** ($2.7\times10^{-3}\,\text{m}\,\text{l}^{-1}$) (——) and **4** and triethylamine ($5.5\times10^{-2}\,\text{m}\,\text{l}^{-1}$) before (– – –) and after (···) 10 min of irradiation (solvent: chloroform)

chloroform) and the synthesis cannot be carried out starting from this form. Moreover, the acetate groups of PVAc will always be a premise for the keto–enol equilibrium to be drawn towards the enol. The strong absorption which appears in the 280–300 nm region proves that the phenylindandione residues have been transformed into benzalphthalide ones.

Of special interest is the isomerization mechanism studied earlier[5] starting from the keto form. In the case of **3** in solution the keto and enol forms of the phenylindandione groups coexist, and this allows two possible isomerization routes. According to the first route only the keto form isomerizes. To maintain the keto–enol equilibrium, the enol converts into a diketone until all the indandione moieties have transformed into benzalphthalide ones. The other possibility is that both the keto and enol forms isomerize directly.

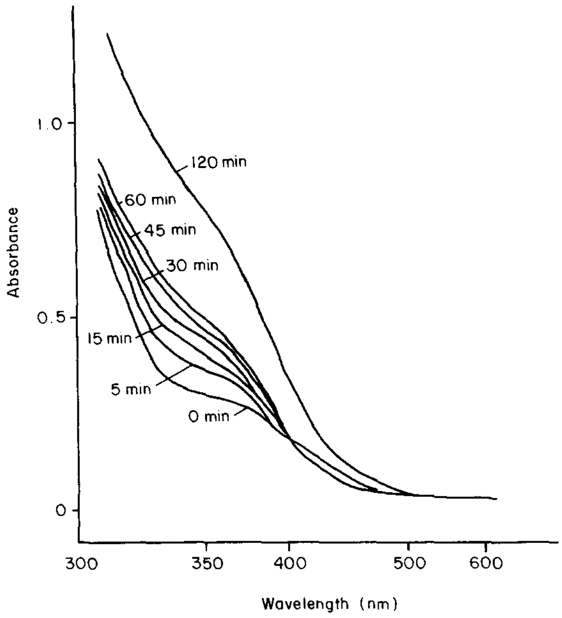


Figure 5 Electronic spectra of **3** (film) at 35°C with varying irradiation time

The first route is in accordance with the isomerization mechanism of phenylindandione[5]. The second possibility assumes direct isomerization from the enol form which has not been reported in the literature so far. To test the second assumption we carried out an experiment, and the results are presented in *Figure 4*. The u.v. spectra of **4** in chloroform and triethylamine before and after irradiation are shown. The equimolar ratio of **4** and triethylamine (strong base) results in an immediate enolization of **4** in spite of the non-polar chloroform. After irradiation, the spectrum obtained is typical for benzalphthalide. We regard this result as supporting the assumption that **4** and its polymer derivative **3** can also isomerize to benzalphthalide from the enol form.

The copolymer also preserves its photochromic character in the solid state. The studies were carried out at room temperature and above the T_g of **3**, set at ~30°C by means of d.s.c. Irradiation of the copolymer at room temperature (below 30°C) has no isomerization effect. Only above the T_g, when the mobility of the segments in the polymer chain increases, does isomerization proceed. *Figure 5* shows u.v. spectra of irradiated copolymer film at 35°C. It shows that irradiation leads to increased absorption in the 320–370 nm range due to the transition of phenylindandione moieties into benzalphthalide ones. The degree of transition depends on time: the longer the irradiation time, the stronger is the new absorption.

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