Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A Study on the Photosensitivity of Chlorine-containing Polymers

Qiu Jiabai [a], Zhou Xiaomin [a], Wang Zhiping [a], Chen Luisheng [a] & Wang Yanqiao [a]

[a] Institute of Chemistry, Academia Sinica, Beijing, China

Version of record first published: 04 Oct 2006.

To cite this article: Qiu Jiabai, Zhou Xiaomin, Wang Zhiping, Chen Luisheng & Wang Yanqiao (1992): A Study on the Photosensitivity of Chlorine-containing Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 218:1, 129-134

To link to this article: http://dx.doi.org/10.1080/10587259208047028

Mol. Cryst. Liq. Cryst. 1992, Vol. 218, pp. 129–134
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

A Study on the Photosensitivity of Chlorine-containing Polymers

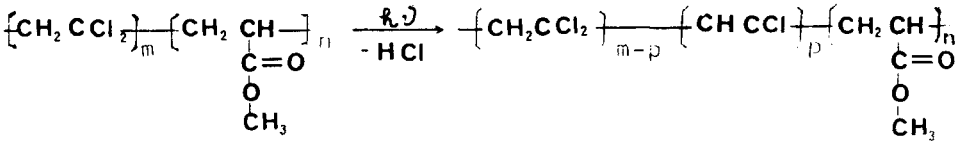
Qiu Jiabai, Zhou Xiaomin, Wang Zhiping,
Chen Luisheng, Wang Yanqiao
(Institute of Chemistry, Academia Sinica, Beijing, China)

It is reported that vinylidene-chloride-methyl acrylate copolymer is used as image recording material in terms of photochemical process[1]. It is interesting to broaden its utilization of photosensitive materials. In this paper a series of chlorine-containing polymers or copolymers, such as vinylidene chloride-acrylonitrile copolymer(1),vinylidene chloride-methyl acrylate copolymer(2), vinylchloride-vinylidene chloride copolymer(3), chlorinated rubber(4), vinyl-chloride-vinyl acetate copolymer(5) and polyvinyl-chloride (6), are selected. For these materials the mechanism of image-formation is discussed and their photosensitivities are compared.

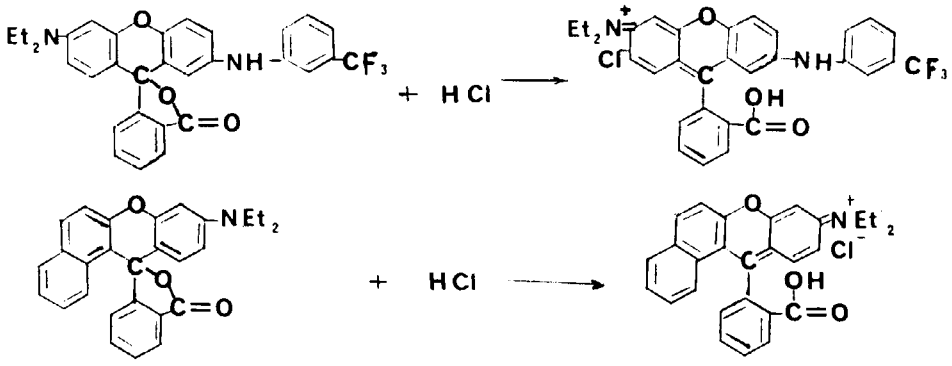
A. The Mechanism of Image Formation

In order to investigate the mechanism of image formation in chlorine-containing materials the vinylidene chloride-methyl acrylate copolymer (2) is chosen as representative. The photosensitive system is composed of (2) and Leuco-base dye (fluoranes FT-2 and F-4). The mechanism is supposed as follows:

Firstly the copolymer undergoes photolysis to release HCL by UV exposure.



Then the released HCL reacts with Leuco base to form dye.



The absorption spectra of formed dyes, measured by HP-8451A UV-Vis spectrophotometer are shown in Fig.1 and Fig.2.

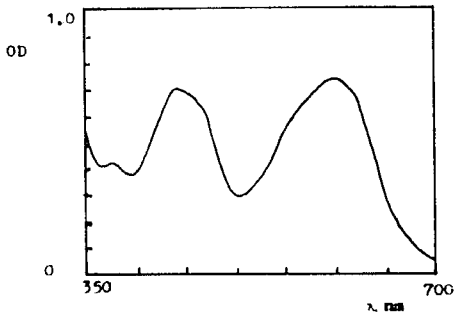


Fig.1 The UV-Vis absorption spectrum of fluorane dye(FT-2)

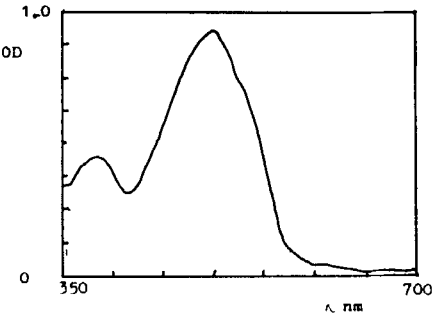


Fig.2 The UV-Vis absorption spectrum of fluorane dye F-4

In exposed area the color is changed from colorless to red or black while in unexposed area the color is not changed, still colorless. Thus a negative image is obtained by different color.

For evidence of this mechanism following experiments have been made.

1. Forming dye in reaction(2) or (3) is direct evidence for photolysis of copolymer (2) in reaction(1). Reaction(2) or (3) could not take place, if there would be no HCL released in reaction(1).

2. Detection of CL^- with $AgNO_3$ solution. The copolymer(2) after UV exposure with a 8W low pressure mercury lamp during 3 hr, and 11cm apart was immersed in water for 24hr. Then

the $AgNO_3$ solution was added to the water after filtrating the copolymer. In this way the precipitate AgCl is found. A parallel vacant experiment was made but no precipitate was formed. This result shows that Cl^- actually released from (2) during UV-exposure.

3. Determination of spectral characteristics. The spectral characteristics of (2) before and after UV-exposure are given in curve A and B in Fig.3 respectively.

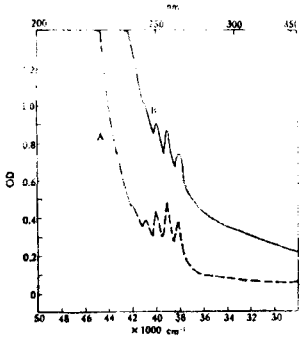


Fig.3 The spectral characteristics of (2).
A: before exposure
B: after exposure.

It can be seen that the absorption range shifts to the longer wavelength region after exposure. It signifies the appearance of conjugated ethylenic hydrocarbon, corresponding to the reaction (1).

4. ESCA measurement[2]. ESCA spectra of copolymer(2) in different exposure time are shown in Fig.4.

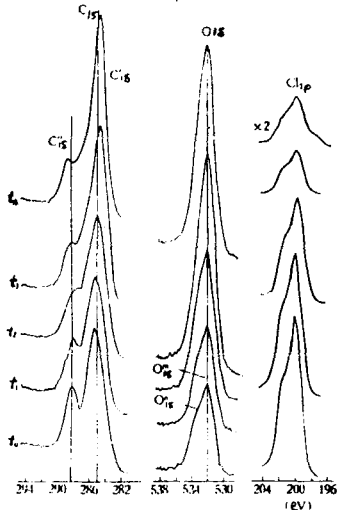
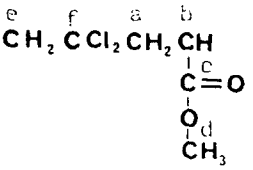


Fig.4 ESCA spectra of copolymer (2) in different exposure time. t_0=0, t_1=5, t_2=15, t_3=30, t_4=60 (min).

The structural formula of (2) is signalized as follows:



There are two peaks in ESCA spectra. Peak C'_{1s} is composed of peaks C^{a}_{1s}, C^{b}_{1s}, C^{d}_{1s} and C^{e}_{1s}. Peak C''_{1s} is composed of peaks C^{f}_{1s} and C^{c}_{1s}. It is found that peaks C''_{1s} and CL_{2p} decrease with increase of exposure time and at the same time peak C'_{1s} increases. These results show that chlorine content in copolymer (2) decreases due to HCL release.

All above results proved that the copolymer (2) upon UV light exposure undergoes photolysis as represented in reaction (1).

B. Photosensitivity of the different chlorine-containing polymers and copolymers.

In order to compare the photosensitivity of different Cl-containing materials the photosensitive films are prepared by following procedure: coating solutions are composed of Cl-containing polymer, Leuco Base dye and solvent in the weight ratio of 5:1:25. These solution are coated on the base film and dried. The thickness of the photosensitive layer is about 4-5μm. The compositions of these films are listed in table 1.

Table 1. Compositions of photosensitive films

No.	Cl-content in material %	Leuco base dye
1	48.27	FT-2
2	57.14	FT-2
3	63.87	FT-2
4	65.13	FT-2
5	48.55	FT-2
6	56.59	FT-2
7	48.27	F-4
8	57.14	F-4
9	63.87	F-4
10	65.13	F-4
11	48.55	F-4
12	56.59	F-4

These films are exposed with a 8W low mercury lamp. The light intensity on the film is about 1.45mW/cm^2. The optical density which is measurement of photosensitivity is determined by Sakura PDA-65 Densitometer. The results are shown in Fig.5 and Fig.6.

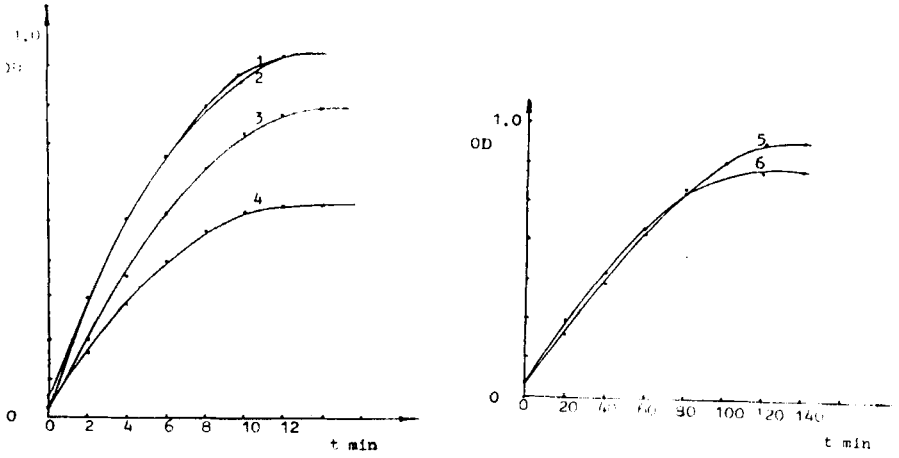


Fig.5 Photosensitivities of films of Cl-containing polymers and FT-2.

1: vinylidene chloride-acrylonitrile copolymer
2: vinylidene chloride-methyl acrylate copolymer
3: vinylchloride-vinylidene chloride copolymer
4: chlorinated rubber
5: vinylchloride-vinyl acetate copolymer
6: polyvinyl-chloride

It can be concluded that the photosensitivity of these materials is arranged in following sequence:

(1) > (2) > (3) > (4) > (5) > (6). From these results it can be seen that the photosensitivity is undependent on the chlorine content in materials, but dependent on the enviroment conditions of Cl-containing chain in polymer or copolymer, such as interaction of neighbouring groups in macromolecules in materials, crystalinity and others[3]. For example, activation energy for dehydrochloride in polyvinylidene is reduced in 4-7 Kcal/mol., When vinylidene is co-

polymerized with styrene or methyl methacrylate.

The conclusion give a guide for choice of Cl-containing polymer or copolymer in making acid sensitive film, as organic information recording materials.

REFERENCES

(1) Qin Jiabai, Wang Yanqiao, J.Photopolymer Sci. & Techn., 1 (2), 295-302 (1988).

(2) Chen Liushen, Shi Ruguang, Polymer Communications, No.6, 428-433 (1982).

(3) Burnett,G.M., Holdon,R.A., Europ Polymer J, 3 449(1967).
Burnett,G.M., Holdon,R.A., Hay,J.N., Europ Polymer J, 4 83(1968).
Holdon,R.A., Hay,J.N., Polymer Sci., A-1, 6 951(1968).

Acknowldgement: Thanks to Prof. Bai Fenglian for discussing this paper.