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Photoinduced Crosslinking of Distyrylbenzene Containing Blockcopolymers for Manufacture of New Photoalignment Layers

by

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13. ABSTRACT *(Maximum 200 words)*

- Photooriented polymer films have received increased interest for the alignment of liquid crystals [1,2]
- Photoalignment layers obtained by photochemical reactions reduce the disadvantages, i.e. dust formation and static electricity build up during the rubbing process, of commercially used rubbed polyimide films.
- Particularly surface effects are crucial for the alignment of liquid crystals controlled by photoactive polymeric films.
- Azobenzene, coumarin and cinnamate containing polymers have been already investigated in detail
- In the case of azobenzene chromophore containing polymers *trans-cis* photoisomerization is significant for photoorientation
- Crosslinked polymer films oriented by irradiation of main chain polymers with linearly polarized light possess an increased stability in comparison with non-crosslinked polymer films
- The polymers investigated in this work are main chain polymers, which contain the distyrylbenzene chromophore and a flexible aliphatic chain
- *Trans-cis* photoisomerization and [2+2] photocycloaddition can competitively occur during irradiation of the photochromic main chain polymers even in the glassy state
- The new fluorine containing photoactive polymers 1 and 2, which contain the distyrylbenzene chromophore within the main chain, have been investigated in comparison with the photoactive polymer 3, which possesses a similar chemical structure
- The capability of the photoalignment layer in order to align a liquid crystal was investigated as a function of both surface topography and photoinduced dichroism of the photoalignment layer

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Photoinduced Crosslinking of Distyrylbenzene Containing Blockcopolymers for Manufacture of New Photoalignment Layers

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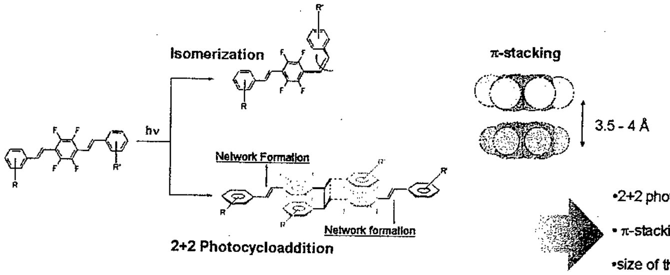
Introduction

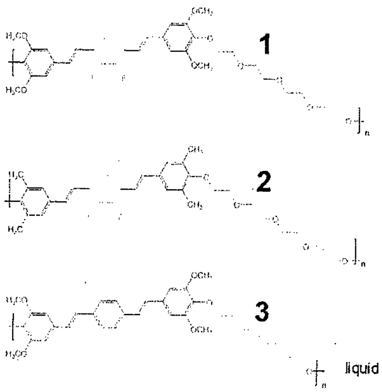
- Photooriented polymer films have received increased interest for the alignment of liquid crystals [1,2]
- Photoalignment layers obtained by photochemical reactions reduce the disadvantages, i.e. dust formation and static electricity build up during the rubbing process, of commercially used rubbed polyimide films.
- Particularly surface effects are crucial for the alignment of liquid crystals controlled by photoactive polymeric films.
- Azobenzene, coumarin and cinnamate containing polymers have been already investigated in detail
- In the case of azobenzene chromophore containing polymers *trans-cis* photoisomerization is significant for photoorientation
- Crosslinked polymer films oriented by irradiation of main chain polymers with linearly polarized light possess an increased stability in comparison with non-crosslinked polymer films
- The polymers investigated in this work are main chain polymers, which contain the distyrylbenzene chromophore and a flexible aliphatic chain
- *Trans-cis* photoisomerization and [2+2] photocycloaddition can competitively occur during irradiation of the photochromic main chain polymers even in the glassy state
- The new fluorine containing photoactive polymers **1** and **2**, which contain the distyrylbenzene chromophore within the main chain, have been investigated in comparison with the photoactive polymer **3**, which possesses a similar chemical structure
- The capability of the photoalignment layer in order to align a liquid crystal was investigated as a function of both surface topography and photoinduced dichroism of the photoalignment layer

Photochemical Pathways [5]



- 2+2 photocycloaddition and *trans-cis* photoisomerization competitively occur
- π-stacking between fluorinated and non-fluorine containing aromatic groups prealigns the chromophore for 2+2 photocycloaddition
- size of the quadrupolar moment controls the strength of π-stacking

Materials [3,4]



liquid crystal **ZLI 2293** (donated by MERCK)

Methods

Linearly polarized light (mercury lamp, 365 nm Interference filter) was used for irradiation experiments

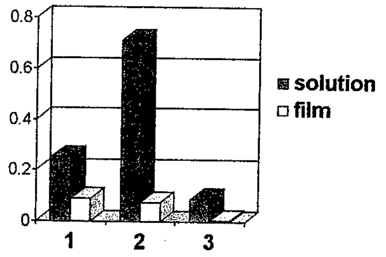
UV spectra: Perkin Elmer λ2 and a diode-array spectrometer (Polytec XDAP V2.3)

The latter was taken for anisotropy measurements (dichroism=$(E_{||}-E_{\perp})/(E_{||}+E_{\perp})$)

AFM-technique (AUTOPROBE CP, Park Scientific) was employed for characterization of film surfaces

Polarized FTIR measurements were carried out for determination of the dichroism of the liquid crystal (CN stretching vibration at 2225 cm^{-1})

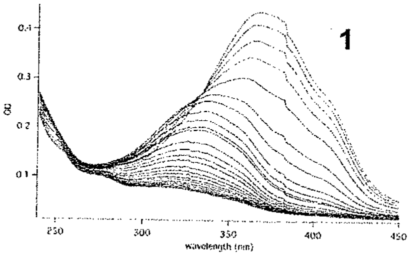
Quantum Yields for Photoreaction



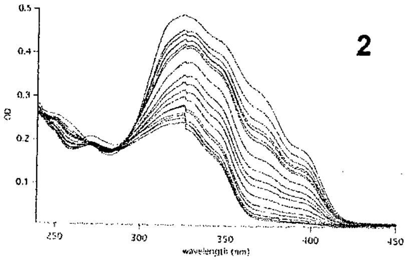
- fluorine containing polymers possess a higher photoreactivity
- polymer **3**, which does not contain any fluorine, shows a minor tendency for photoreaction in both solution and film
- lower quantum yields in the films are caused by the decreased mobility in the matrix
- lower quantum yields in solution of polymer **1** in comparison with polymer **2** can be discussed by formation of ICT (solvent dependent emission) as a competitive process

Irradiation of the Films with Linearly Polarized Light

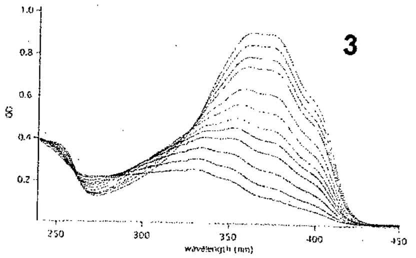
(λ_{irr} = 365 nm, P_{irr} = 4-5 mW/cm^2)



- Spectral changes of polymer **1** show hypsochromic shift of the maximum due to the formation of a photoproduct
- Spectra go through an isosbestic point
- *trans-cis* Photoisomerization can be discussed as the main reaction occurring at the beginning of the irradiation process
- At longer irradiation times, the spectra no longer went through an isosbestic point
- Photobleaching is observed at prolonged irradiation times
- The absorption maximum remains constant in the case of [2+2] photocycloaddition and only the absorption reduces

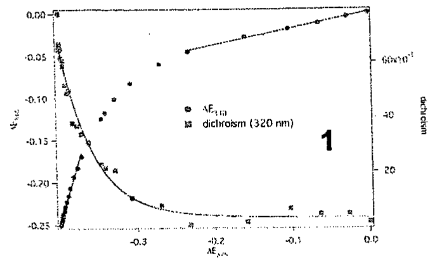


- Spectral changes of polymer **2** show no hypsochromic shift of the maximum due to photobleaching
- Spectra do not go through an isosbestic point
- [2+2] photocycloaddition can be discussed as the main reaction occurring during the entire irradiation process
- The absorption maximum remains constant and only the absorption reduces during the entire irradiation process



- In analogy to polymer **1**, the spectral changes of polymer **3** show hypsochromic shift of the maximum
- Spectra go through an isosbestic point (red colored spectra)
- As discussed in case of polymer **1**, *trans-cis* photoisomerization´ is the main reaction occurring at the beginning of the irradiation process
- At longer irradiation times, the spectra no longer went through an isosbestic point as similarly shown for polymer **1**
- Photobleaching (blue colored spectra) is observed at prolonged irradiation times

Extinction Differences (ED) Diagramms and Photoinduced Dichroism in Dependence on ED

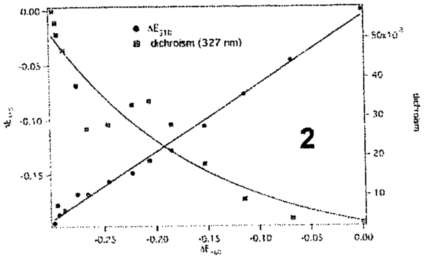


The extinction differences diagram of polymer **1** shows two main photoprocesses

We assign the first reaction to photoisomerization and the latter to photobleaching

No dichroism is obtained if the *trans-cis* isomerization reaction occurs

Significant increase in dichroism and the formation of a crosslinked anisotropic film is observed if photobleaching occurs as the main photoreaction



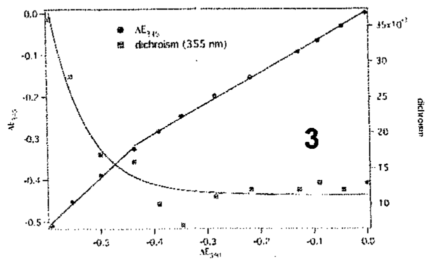
Only photobleaching occurs during irradiation of polymer **2**

The extinction differences indicate the occurance of a single photoprocess

The dichroism continuously increases with prolonged irradiation

This result clearly indicates the importance of photobleaching reactions for manufacturing of an anisotropic polymer network

[2+2] photocycloaddition mainly contributes to dichroism after irradiation



The extinction differences diagram of polymer **3** shows two main photoprocesses similarly to polymer **1**

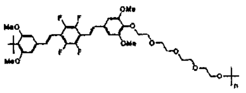
Increase in dichroism is lower in comparison with polymer **1**

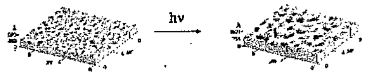
[2+2] Photocycloaddition contributes to dichroism after irradiation

trans-cis Photoisomerization is of minor importance in case of the main chain polymers **1-3** although that photoreaction dominates for azobenzenes

Surface Topography

Surface Roughness ($RMS_{10\mu m}$) Change of Polymer 1



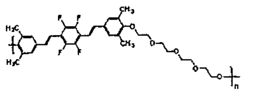


$RMS_{10\mu m}$ = 6 nm

$RMS_{10\mu m}$ = 11 nm

irradiation with linearly polarized light results in a significant increase of surface roughness

Surface Roughness ($RMS_{10\mu m}$) Change of Polymer 2

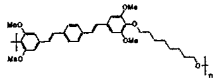


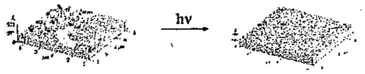
$RMS_{10\mu m}$ = 3,5 nm

$RMS_{10\mu m}$ = 18 nm

irradiation with linearly polarized light results in a tremendous increase of surface roughness

Surface Roughness ($RMS_{10\mu m}$) Change of Polymer 3





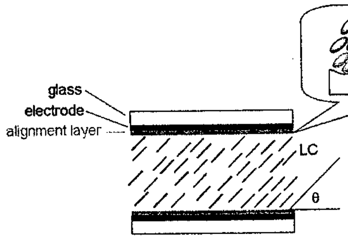
$RMS_{10\mu m}$ = 2,5 nm

$RMS_{10\mu m}$ = 1,5 nm

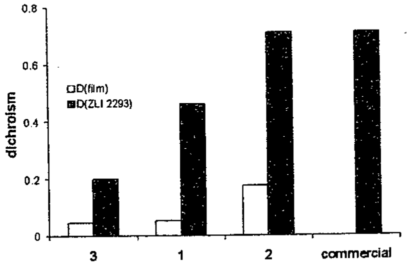
-the nonirradiated film contains an adsorbate layer
-irradiation with linearly polarized light does not increase surface roughness

Alignment of a Liquid Crystal by Using the Photoalignment Layers Based on the Polymers 1-3

LC Device



polarizer position: 90°(●) 180°(▨)



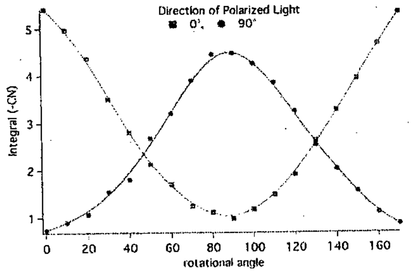
The dichroism of the oriented liquid crystal is considerably higher in comparison with the photoalignment layer used for its orientation

The largest dichroism was found for the anisotropic polymer network based on polymer **2**

The dichroism of the liquid crystal, which was aligned by the anisotropic polymer network based on polymer **2**, is comparable with that of a commercial cell made of a rubbed polyimide film

Anisotropic networks based on both fluorine containing polymers **1** and **2** result in a higher dichroism of the liquid crystal in comparison with the anisotropic network based on polymer **3** that contains no fluorine

A system with [2+2] photocycloaddition (polymer **2**) possesses the best capability to orient the liquid crystal



The integral of the CN-stretching vibration plotted as a function of the rotation angle shows a minimum at 90° rotation angle for the sample irradiated with 0° polarizer position during irradiation with linearly polarized light

A maximum for the integral of the CN-stretching vibration was obtained at the same rotation angle if a perpendicular polarizer position (90°) was taken for the irradiation process

Advantages of Our Photoalignment Layers

[2+2] photocycloaddition results in an insoluble crosslinked material that does not loose its dichroism upon heating at elevated temperatures

Absorption hypsochromically shifts into the ultraviolet spectral region

Nearly colorless irradiated materials were obtained after irradiation

Satisfied thermostability of the anisotropic network structure

Satisfied adhesion of the anisotropic polymer networks on modified glass substrates

Increased photoreactivity because of fluorine substitution

Use of polymer **2** for photoalignment layer manufacture results in an alignment of the LC, which is comparable with that of a commercial cell made of a rubbed polyimide film

Easy manufacture of the polymer films by spin coating

No dust problems

Acknowledgement

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