

Synthesis and Characterization of Main Chain Polyimides Containing Chalcone Derivatives for LC Alignment

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ABSTRACT: Two soluble polyimides containing chalcone derivatives in the main chains were successfully prepared using the Mitsunobu reaction at room temperature, reacting diols with diimides. With this reaction procedure the high temperature imidization step normally needed for the synthesis of polyimides is avoided and the polymers can be used for temperature sensitive applications. The main chain polyimides were characterized with FT-IR, NMR and DSC and the extent of the photoreaction was measured with FT-IR and UV-vis spectroscopy. Isobestic points were observed in the absorption spectral changes at the early stage of UV irradiation as a result of a single photochemical process. Further photoradiation is accompanied by deviation from the isobestic points, implying that another photochemical process has started. With FT-IR investigations it was concluded that photodimerization is the process occurring at low UV exposure doses and that *trans-cis* isomerization is starting simultaneously at higher doses. The optical anisotropic properties were investigated upon exposure of the polymers as thin films to linearly polarized UV (LPUV) light of different doses. Selected crosslinking in the parallel direction relative to the direction of the LPUV light and subsequent optical anisotropy in the film were achieved. [doi:10.1295/polymj.PJ2005218]

KEY WORDS Photoalignment / Chalcone / Polyimide / Photocrosslinking / Polymer Synthesis /

Thin polyimide films are commonly employed as alignment layers for liquid crystal displays (LCDs). Polyimides are thermally and chemically stable, have nice mechanical properties, are insoluble in and do not effect liquid crystals and polyimides provide high quality stable LC alignment with high anchoring energy.¹ In the production of LCDs, the alignment of liquid crystals is normally achieved by coating the substrate with soluble poly(amic acid) which is imidized at high temperature to polyimide² followed by rubbing with a cloth to enable alignment. However, this high temperature reaction obviates the use of temperature sensitive substrates such as flexible polymer films. Other drawbacks of this technology are the generation of electric charges and the risk of contamination, being a contact method. An alternative technique to rubbing is photoalignment, *i.e.*, exposing photosensitive polymers to linearly polarized UV (LPUV) light.^{3,4} Various methods of photoalignment have been reported based on photoinduced anisotropic [2+2] dimerization,⁵ isomerization,⁶ and decomposition⁷ reactions. Some types of photoactive polymers involve not only [2+2] dimerization but also *trans-cis* photoisomerization.⁸ Many different materials have been used for photoalignment, polyvinylcinnamates being one of the most common ones.⁹ A reason why these molecules align liquid crystals when exposed to LPUV light is that [2+2] cycloaddition causes anisotropic depletion of the photoactive group,⁵

another being that the *trans-cis* isomerization is responsible while dimerization enhances the thermal stability.¹⁰ Among many promising photosensitive groups, the chalcone group has been widely studied and affords high sensitivity to UV radiation.^{11,12} A polymer providing stable alignment with high photodimerization rate is expected by combining the nice properties of polyimide with the chalcone chromophore. Earlier investigations have mostly concerned polyimides bearing the chalcone moiety in the side chain.^{13,14} The thermal and optical stabilities are, however, not sufficiently high for these materials.¹⁵ When placing the photosensitive groups in the main chain the stability is expected to improve.¹⁷ Only a few investigations have been made concerning polyimides with chalcone chromophores in the main chain.^{16,17} These polyimides are synthesized in the common two-step procedure reacting dianhydride with diamine to provide poly(amic acid) precursor polymers, followed by a separate imidization process. In this work we found a new synthesis route to avoid the two-step procedure by using the Mitsunobu reaction¹⁸ at room temperature. The fully imidized polyimide is formed in one step and the poly(amic acid) intermediate is eliminated and thus curing at high temperature is avoided. The synthesized polymers are soluble in some common solvents for easy application to the substrate, but insoluble in the LC material. The synthesis of two soluble photoactive polyimides containing chalcone

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chromophores in the main chain are reported in this work, using Mitsunobu reaction conditions for the polycondensation of the monomers. The polyimides were characterized with FT-IR, NMR and DSC. The chemical photoreaction upon exposure to UV light was investigated with FT-IR and UV-vis spectroscopy both for solutions of the polyimides and for thin films. The optical anisotropic properties were investigated upon exposure of the polymers as thin films to LPUV light of different doses.

EXPERIMENTAL

Materials

The starting materials were obtained from Sigma-Aldrich. Anhydrous tetrahydrofuran (THF) and dimethylsulfoxide (DMSO) were obtained with high degree of purity. Triphenylphosphine was recrystallized from ethanol before use.

Monomer Synthesis

1-[4-(2-Hydroxy-ethoxy)-phenyl]-ethanone (II). Sodium hydroxide (4.8 g, 0.12 mol) was dissolved in 2-butanone (300 mL). 4-Hydroxyacetophenone (16.34 g, 0.12 mol), NaI (18.0 g, 0.12 mol) and chloroethanol (9.66 g, 0.12 mol) were added. The mixture was vigorously stirred for 3 days at 60 °C. The solvent was evaporated. The crude product was washed with aqueous NaOH (300 mL 0.4 M) to remove the formed salt. The product was extracted with diethyl ether and dried with MgSO₄. Yield: 32%. mp: 74 °C. IR (cm⁻¹): 3403 (OH), 1650 (C=O), 1595, 1571, 1512 (Ar C=C). ¹H NMR (CDCl₃): δ (ppm) = 7.92 (t, 2H, Ar-CH), 6.94 (t, 2H, Ar-CH), 4.14 (t, 2H, CH₂), 3.99 (d, 2H, CH₂), 2.55 (s, 3H, CH₃), 2.03 (s, 1H, OH).

4-(2-Hydroxy-ethoxy)-benzaldehyde (IV). Sodium hydroxide (4.8 g, 0.12 mol) was dissolved in 2-butanone (300 mL). 4-hydroxybenzaldehyde (14.65 g, 0.12 mol), 18.0 g (0.12 mol) NaI and 9.66 g (8.05 mL) (0.12 mol) chloroethanol were added. The mixture was vigorously stirred at 60 °C for 2 d. After removal of the solvent the crude product was washed with aqueous NaOH (300 mL 0.4 M) to remove the formed salt. The product was extracted with diethyl ether and dried with MgSO₄. Yield: 75%. IR (cm⁻¹): 3402 (OH), 1677 (aldehyde C=O), 1595, 1575, 1509 (Ar C=C). ¹H NMR (CDCl₃): δ (ppm) = 7.42 (t, 2H, Ar-CH), 6.86 (t, 2H, Ar-CH), 6.55 (s, 1H, CH=O), 4.11 (d, 2H, CH₂), 4.06 (s, 2H, CH₂), 2.85 (s, 1H, OH).

1,3-Bis-[4-(2-hydroxy-ethoxy)-phenyl]-propenone (V). **IV** (3.32 g, 20 mmol) was mixed with 10 mL methanol using magnetic stirring at room temperature. **II** (3.60 g, 20 mmol) was dissolved in 20 mL methanol and added to the reaction flask. Finally a 3% methanolic NaOH solution (20 mL) was added dropwise.

The mixture was left for 2 d with stirring and another 2 d without stirring. The solution was diluted with water and neutralized by dropwise addition of 50% HCl. The precipitate was filtered off and recrystallized from ethanol. Yield: 52%. mp: 148.5 °C. IR (cm⁻¹): 3384 (OH), 1653 (C=O), 1601 (chalcone C=C str, Ar C=C), 1569, 1507 (Ar C=C), 983 (chalcone C-H out of plane def). ¹H NMR (DMSO-*d*₆): δ (ppm) = 8.15 (d, 2H, Ar-CH), 7.84 (d, 2H, Ar-CH), 7.82 (d, 2H, C=OCH=CH), 7.68 (d, 2H, C=OCH=CH), 7.08 (d, 2H, Ar-CH), 7.02 (d, 2H, Ar-CH), 4.95 (t, 1H, OH), 4.93 (t, 1H, OH), 4.11 (t, 2H, CH₂), 4.06 (t, 2H, CH₂), 3.76 (t, 2H, CH₂), 3.73 (t, 2H, CH₂).

*Pyrrolo[3,4-*f*]isoindole-1,3,5,7-tetraone (Pyromellitic Diimide) (VII)*. Pyromellitic dianhydride (10.10 g, 46.3 mmol) and urea (4.24 g, 70.6 mmol) were mixed in a reaction flask. The temperature was raised to 200 °C for 2 h. After cooling to room temperature the resulting solid was ground into a fine powder and the reaction was continued at 200 °C for another hour. The crude product was washed with distilled water several times to remove unreacted urea. The product was dried and recrystallized from ethanol. Yield: 83%. mp: 453 °C. IR (cm⁻¹): 3200 (NH), 1772 (imide C=O asym str), 1692 (imide C=C sym str). ¹H NMR (DMSO-*d*₆): δ (ppm) = 8.1 (s, 2H, Ar-CH), 11.85 (s, 2H, NH).

4,4'-(Hexafluoroisopropylidene)diphthalimide (X). 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (4.98 g, 11.2 mmol) and urea (1.03 g, 17.2 mmol) were mixed in a reaction flask. The temperature was raised to 200 °C for 2 h. After cooling to room temperature the resulting solid was ground into a fine powder and the reaction was continued at 200 °C for another hour. The crude product was washed with distilled water several times to remove unreacted urea. The product was dried and recrystallized from ethanol. Yield: 83%. mp: 320 °C. IR (cm⁻¹): 3300 (NH), 1782 (imide C=O asym str), 1713 (imide C=C sym str). ¹H NMR (DMSO-*d*₆): δ (ppm) = 7.64 (s, 2H, Ar-CH), 7.82 (d, 2H, Ar-CH), 7.99 (d, 2H, Ar-CH), 11.70 (s, 2H, NH).

Polymer Synthesis

PIC-1 (VIII). Triphenylphosphine (4.88 g, 18.6 mmol) was mixed with anhydrous DMSO (15 mL) in a 100 mL schlenk flask. The reaction mixture was stirred and purged with nitrogen gas. **VII** (1.34013 g, 6.2 mmol) and **V** (2.03589 g, 6.2 mmol) were added. After dropwise addition of diisopropyl azodicarboxylate, DIAD (3.76 g, 18.6 mmol) in 2.5 mL anhydrous DMSO the reaction mixture was left to stir for 4 d at room temperature. The polymer was precipitated in 500 mL cold methanol, filtered off and dried in vacuum oven. Soxhlet extraction in methanol for 3 d was

made to purify the polymer. Yield: 94%. ^1H NMR (DMSO- d_6) δ (ppm): 8.0–8.3 (m, 4H, Ar–CH), 7.5–7.9 (m, 4H, Ar–CH, CH=CH), 6.9–7.1 (m, 4H, Ar–CH), 4.0–4.4 (m, 8H, CH₂–O, CH₂–N). ^{13}C NMR (DMSO- d_6) δ (ppm): 189 (chalcone C=O), 167 (imide C=O), 162 (Ar C–O), 159 (Ar C–O), 143 (CH=CH, carbon away from carbonyl), 137 (Ar C connected to chalcone carbonyl end), 131 (4C Ar), 130 (2C Ar), 128 (4C Ar), 127 (Ar C connected to chalcone), 121 (CH=CH, carbon close to carbonyl), 114 (4C Ar), 65 (O–CH₂), 37 (N–CH₂). IR (cm⁻¹): 1775 (imide C=O asym str), 1727 (imide C=O sym str), 1658 (chalcone C=O str), 1601 (chalcone C=C str, Ar C=C), 1572, 1509 (Ar C=C), 987 (chalcone C–H out of plane def). The glass transition temperature was 160 °C. $M_n = 6,500$ g/mol, NMR.

PIC-2 (XI). Triphenylphosphine (3.70 g, 14.1 mmol) was dissolved in anhydrous THF (14 mL) in a 100 mL schlenk flask. The reaction mixture was stirred and purged with nitrogen gas. **X** (2.07285 g, 4.7 mmol) and **V** (1.54339 g, 4.7 mmol) were added. After dropwise addition of diisopropyl azodicarboxylate, DIAD (2.85 g, 14.1 mmol) in 4 mL anhydrous THF the solution was left to stir for 4 d at room temperature. The polymer was precipitated in 500 mL cold methanol. To purify the polymer Soxhlet extraction in methanol for 3 d was made. Yield = 98%. ^1H NMR (DMSO- d_6): δ (ppm) = 8.1–7.6 (m, 16H, Ar–CH, CH=CH), 4.0–4.4 (m, 8H, CH₂–O, CH₂–N). ^{13}C NMR (DMSO- d_6) δ (ppm): 189 (chalcone C=O), 168 (imide C=O), 163 (Ar C–O), 159 (Ar C–O), 147 (2C Ar close to CF₃), 143 (CH=CH, carbon away from carbonyl), 137 (Ar C connected to chalcone carbonyl end), 131 (4C Ar), 130 (2C Ar), 128 (8C Ar), 127 (Ar C connected to chalcone), 122 (CF₃), 121 (CH=CH, carbon close to carbonyl), 114 (4C Ar), 65 (O–CH₂), 38 (C–(CF₃)₂), 37 (N–CH₂). IR (cm⁻¹): 1779 (imide C=O asym str), 1722 (imide C=O sym str), 1658 (chalcone C=O str), 1601 (chalcone C=C str, Ar C=C), 1573, 1509 (Ar C=C), 982 (chalcone C–H out of plane def). The glass transition temperature was 125 °C. $M_n = 7,400$ g/mol, NMR.

Characterization

Infrared spectra were measured on a Perkin Elmer One fourier transform spectrometer. ^1H NMR spectra were obtained with a JEOL 400 MHz spectrometer with the solvent proton signal as an internal standard. Thermal analysis was performed on a Perkin Elmer DSC Pyris Diamond at a heating rate of 10 °C min⁻¹. The second heating scan was used to determine the glass transition temperature (T_g). UV-vis spectra were recorded using a Perkin Elmer Lambda 900 photo-spectrometer. For the measurements in solution, the

polymers were dissolved in CH₂Cl₂ and illuminated with a 365 nm UV lamp. The concentrations of PIC-1 and PIC-2 were 0.02 g/L and 0.10 g/L respectively. Thin films of the polymers were prepared by spincoating (1500 rpm for 6 s and 3000 rpm for 60 s) a 2% cyclopentanone solution of the polymers onto quartz substrates. After evaporation of solvent in vacuum oven at 60 °C for 24 h they were exposed to LPUV light using an Ushio photoalignment lamp in nitrogen atmosphere. The thickness of the films were measured to 60 nm using a Veeco Dektak³ ST surface profile measuring system.

RESULTS AND DISCUSSION

Monomer Synthesis

The synthetic procedures are illustrated in Figure 1 and Figure 2.

Monomer **V** was prepared in 3 steps. First 4-hydroxyacetophenone was reacted with chloroethanol in the presence of sodium hydroxide and sodium iodide to give 1-[4-(2-hydroxy-ethoxy)-phenyl]-ethanone (**II**).¹⁹ The spacer was added in the same way to 4-hydroxybenzaldehyde to give 4-(2-hydroxy-ethoxy)-benzaldehyde (**IV**). The chalcone with spacers on both sides was prepared by reacting **II** and **IV** in a methanolic solution of sodium hydroxide at room temperature.²⁰ Monomer **VII** was prepared in a single step. Pyromellitic dianhydride was reacted with urea at 200 °C for a total of 3 h.²¹ Monomer **X** was prepared similar to monomer **VII**.

Polymer Synthesis

The two polymers, PIC-1 and PIC-2, were successfully synthesized by polycondensation under Mitsunobu conditions¹⁸ of two monomers on the basis of N-alkylation of the diimide. Both monomers were reacted under nitrogen with triphenylphosphine and diisopropyl azodicarboxylate, DIAD in anhydrous solvents.²¹ The polymerisation proceeds *via* an alcohol conversion to alkoxyphosphonium salt, which is a powerful alkyl donor group while the diimide anion acts as an alkyl group acceptor.

Polymer PIC-2 is more flexible than PIC-1 due to the hexafluoroisopropylidene linkage in between the stiff aromatic cores. This can be seen as a lower glass transition temperature for PIC-2, 125 °C, than for PIC-1, 160 °C. The fluorogroups in PIC-2 also contributes to increased transparency²² compared to PIC-1.

The molecular weight of both compounds was rather low using this method. This problem has been reported earlier^{21,23} and could in this case be due to the rigid nature of the diimides retarding the Mitsunobu reaction.

Synthesis of Polyimides Containing Chalcone Derivatives

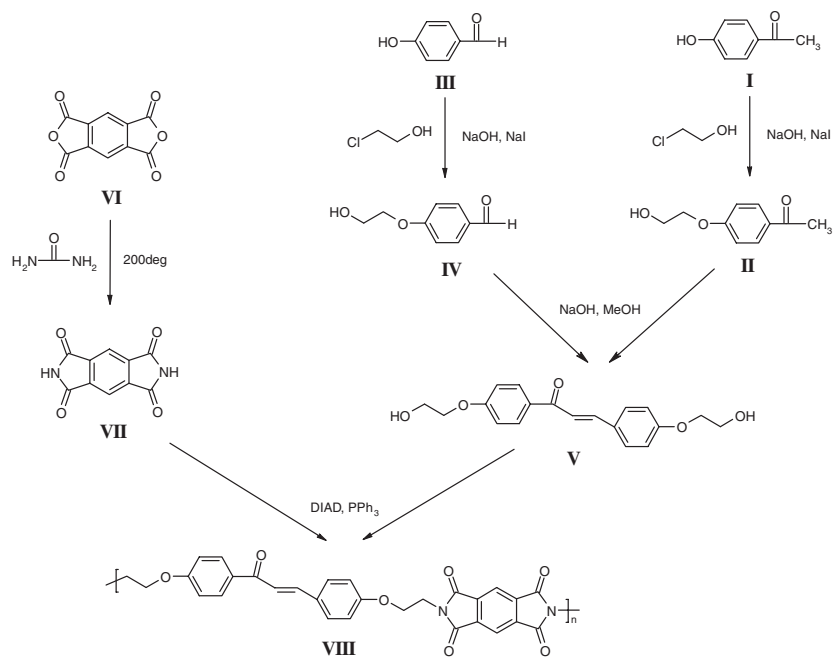


Figure 1. Synthetic procedure for PIC-1.

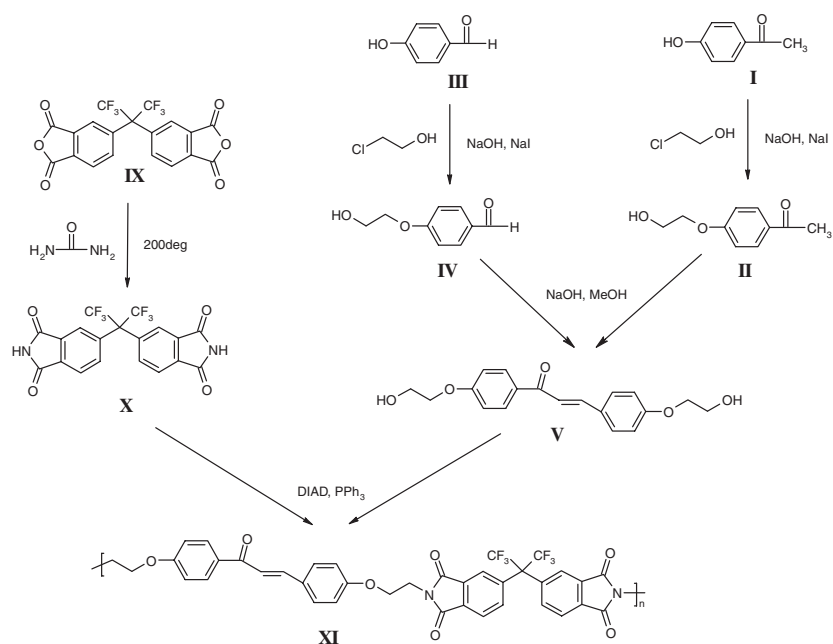


Figure 2. Synthetic procedure for PIC-2.

Photochemical Properties of PIC-1 and PIC-2

UV-vis spectra of the two polymers were recorded in CH_2Cl_2 solution before and after different periods of exposure to UV light. Both *trans-cis* isomerization and dimerization of chalcone are expected upon exposure of the polymers to UV irradiation as illustrated in Figure 3.

The unimolecular isomerization occurs through a rotation mechanism from the *trans*- to the *cis*-form when the UV light has excited the π -electrons of the carbon-carbon double bond. The dimerization, which

is a bimolecular reaction, results in a crosslinking of the polymer with formation of cyclobutane rings through a [2+2] cycloaddition of the carbon-carbon double bond. For the polymers in solution the chalcone moiety shows an absorption maximum at 336 nm for both PIC-1 (Figure 4) and PIC-2 (Figure 5) which is attributed to the π - π^* transitions through the chalcone system for the *trans*-isomer.

The intensity of this absorption decreases fast upon exposure to UV light which indicates the disturbance of conjugation, either due to dimerization or *trans-cis*

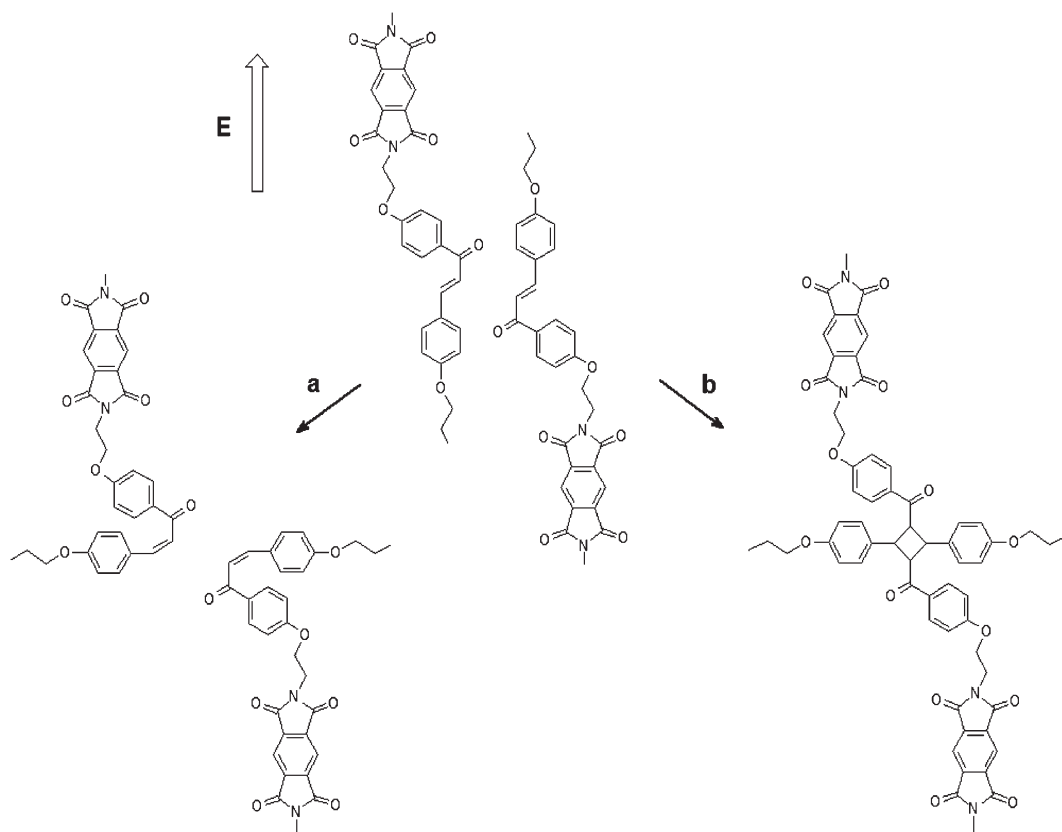


Figure 3. Photochemical reactions of PIC-1 upon exposure to UV light: (a) *trans-cis* isomerization and (b) [2+2] cycloaddition.

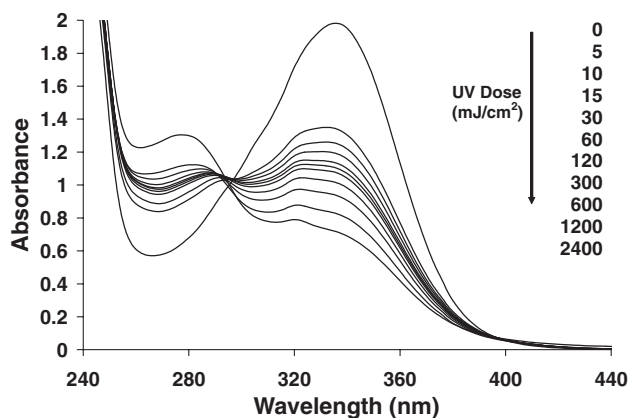


Figure 4. Absorption spectral changes of polymer PIC-1 in solution irradiated with unpolarized UV light.

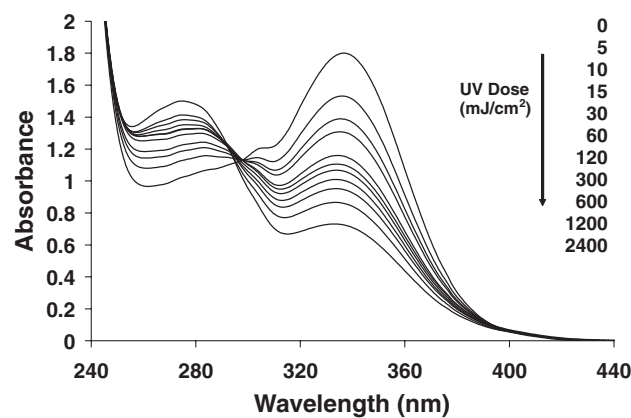


Figure 5. Absorption spectral changes of polymer PIC-2 in solution irradiated with unpolarized UV light.

isomerization. Simultaneously an increase of absorption is observed at 280 nm attributed to the photochemical product. For exposure doses less than 300 mJ/cm², there is an isosbestic point at 296 nm for both polymers which indicates an equilibrium between two species demonstrating that only one process occurs exclusively and only one photochemical product is formed. Further photoradiation results in deviations from the isosbestic points which reveal the formation of more than one product and the speed of conversion gradually slows down. The peaks of both photochemical products, the *cis*-isomer and the

dimer, are overlapping each other. After relaxation for a few hours there are no changes in the spectra which indicate that the products are stable. Thin films of the polymers were prepared by spincoating cyclopentanone solutions of the polymers onto quartz substrates. The absorption spectral changes of the two polymers PIC-1 (Figure 6) and PIC-2 (Figure 7) were studied upon exposure to linearly polarized UV light of different doses. A_{\parallel} and A_{\perp} denote absorbances parallel and perpendicular to the electric vector of the LPUV light.

The unexposed film shows an absorption spectra

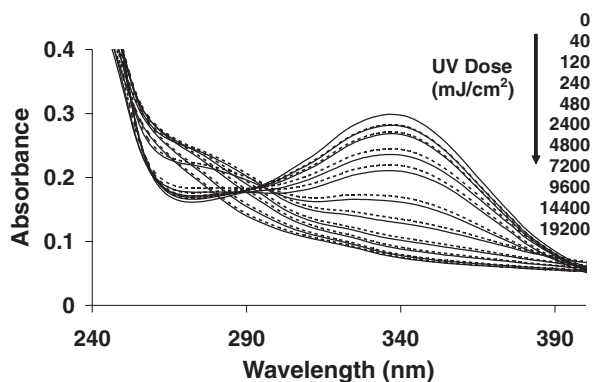


Figure 6. Absorption spectral changes of polymer PIC-1 as film irradiated with LPUV light.

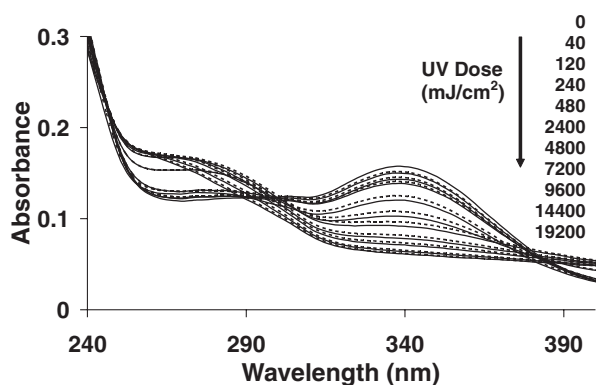


Figure 7. Absorption spectral changes of polymer PIC-2 as film irradiated with LPUV light.

profile similar to that in solution and with increasing exposure time there is a decrease of absorption at 336 nm (*trans*-isomer). For exposure doses up to 480 mJ/cm² an isobestic point is seen. After exposures of 7200 mJ/cm² both UV absorption peaks related to the *trans*-isomer and to the photochemical product, are decreasing and a decomposition of the polymer seem to be starting.

The perpendicular absorption at 336 nm was observed to be higher than the parallel absorption in the whole range of the irradiation time period. In Figure 8, the difference spectra of the absorbances perpendicular and parallel to the electric field of the LPUV light are shown. For PIC-1 the maximum was obtained after exposure of 480 mJ/cm², while for PIC-2 the maximum was reached after a longer exposure of 2400 mJ/cm². When crosslinking occurs it exerts an effect on the remaining part of the chains in different amounts. For polymer PIC-1 which is the more rigid of the two, crosslinking effects the chains more, while it takes longer time for the more flexible PIC-2 until the network has achieved such order that it appears as a difference in anisotropy. The following decrease in anisotropy for longer periods

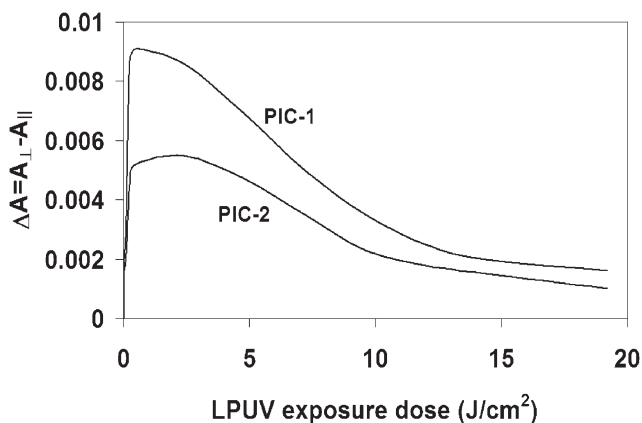


Figure 8. UV absorption difference spectra of the two polymer films PIC-1 and PIC-2 irradiated with UV light.

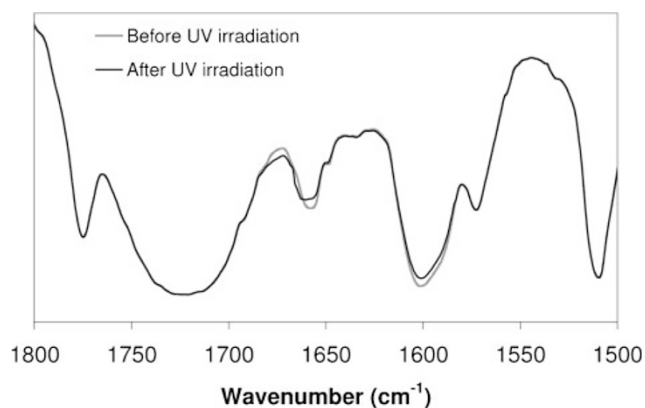


Figure 9. Infrared spectra of PIC-1 before and after UV irradiation.

of UV exposure is explained by a higher extent of crosslinking in any direction from the polarization direction of the UV light.

Comparison of UV-vis and Infrared Spectroscopic Study

UV-vis absorption spectral changes show any conversion of the *trans*-isomer with the dimer and the *cis*-isomer as possible products. To be able to distinguish between the two products FT-IR measurements were made before and after different UV light exposure doses, see Figure 9.

Studies of the absorption at 1601 cm⁻¹ which is related to the stretching vibrations of the olefinic carbon-carbon double bond in the chalcone moieties, show gradual decrease of the intensity with increasing UV light dose. The reason for the reduction of these absorptions is that the conjugated system of the chalcone is disrupted due to breaking of the double bond. In addition the intensity of the C=O unsaturated ketone carbonyl stretching band at 1658 cm⁻¹ is shifted and broadened with UV exposure time and a new absorption band, attributed to a saturated ketone car-

bonyl stretching vibration, at 1672 cm^{-1} appears in the spectra of the two polymers after UV irradiation. The problem with the absorption spectral band at 1601 cm^{-1} is that it is normally superposed with the absorption bands of the double bonds in the benzene ring, but the benzene ring is not effected by UV light and the other two absorptions of the double bonds in the ring are not changed, thus any change in the absorption at 1601 cm^{-1} is due to a breaking of the double bond in chalcone.^{13,16,24} By monitoring the behaviour of the 1601 cm^{-1} absorption the extent of photocrosslinking can be investigated but *trans-cis* isomerization can not be followed.

The conversion of the *trans*-isomer was determined by the rate of disappearance of the carbon-carbon double bond using the following expression:

$$\text{Conversion (\%)} = (A_0 - A_t)/A_0 \times 100$$

where A_0 is the absorption intensity before irradiation and A_t is the absorption intensity after different irradiation times. The result is presented in Figure 10 for PIC-1. The results for PIC-2 are similar.

Comparing the conversion of *trans*-isomer in the UV-vis spectra for solution and film it is obvious that the initial rate of conversion is much higher in solution than in film because the polymer chains have higher mobility in solution and the polymer in solution also reaches a higher total conversion than the film at the highest exposure dose. When the films are exposed to higher intensities than shown in Figure 10 the conversion seem to increase further, but in this case, as is seen in Figure 6, there is no continuing increase of product but instead a decomposition of the material is beginning. When comparing the IR curve and the UV-vis curve for the film in Figure 10 it is seen that initially the IR curve follows the UV-vis curve. This confirms that at low exposures, as long as the isosbestic point is seen in the UV-vis spectra, a single photochemical process is taking place. This process is photocrosslinking since the results from

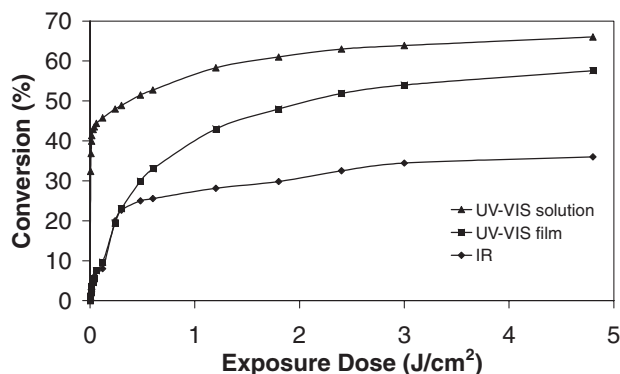


Figure 10. Conversion of PIC-1 as a function of exposure dose from UV-vis and IR spectroscopy.

FT-IR represent only the change in the concentration of carbon-carbon double bond due to breaking of the double bond. At larger UV exposure doses than 300 mJ/cm^2 the rate of conversion of the double bond is drastically decreased for the IR curve and it deviates from the UV-vis curve. This is in good agreement with the energy where the isosbestic point is no longer seen in the UV vis absorption spectra. The deviation of the two curves happens because the competing *trans-cis* isomerization is starting and two products are formed simultaneously. With further photoirradiation the energy is enough for the rotation mechanism to take place and convert the *trans*-isomer to the *cis*-form. This process can be followed with the UV-vis absorptions but not with the FT-IR absorptions. The isomerization and dimerization takes place simultaneously above 300 mJ/cm^2 , but the crosslinking to a much smaller extent. Combining the results of the UV-vis and FT-IR measurements we find that for UV exposure doses of less than 300 mJ/cm^2 the polymers undergo photodimerization. At larger UV doses *trans-cis* isomerization is occurring as well but the degree of crosslinking is slowing down.

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