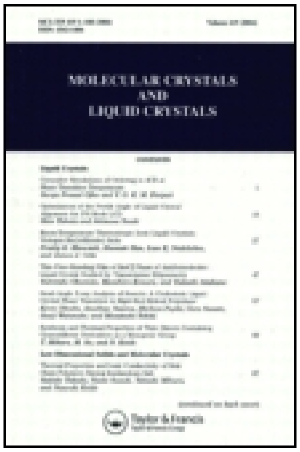

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Absorption Studies of Optically Nonlinear Side-Chain Polymer and Polymer-Dye Films Oriented by Corona Poling

Armin Wedel [a] , Rudi Danz [a] , Wolfgang Künstler [a] [b] & Klaus Tauer [a] [c]

[a] Fraunhofer-Institute of Applied Polymer Science, Kantstrasse 55, O-1530, Teltow-Seehof, F. R. G.

[b] University of Potsdam, Kantstrasse 55, O-1530, Teltow-Seehof, F. R. G.

[c] Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Kantstrasse 55, O-1530, Teltow-Seehof, F. R. G.

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ABSORPTION STUDIES OF OPTICALLY NONLINEAR SIDE-CHAIN POLYMER AND POLYMER-DYE FILMS ORIENTED BY CORONA POLING

ARMIN WEDEL, RUDI DANZ, WOLFGANG KÜNSTLER[‡] and KLAUS TAUER[†]
Fraunhofer-Institute of Applied Polymer Science,
Kantstrasse 55, O-1530 Teltow-Seehof, F.R.G.

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Abstract Spectroscopic absorption measurements in the wavelength range from 700 to 300 nm are used to study the orientation of optically nonlinear side-chain groups in an acrylic polymer and dye guest molecules in a polymer matrix by corona poling process. The time stability and the annealing behaviour of these films are measured. The poling process produces efficient orientational order at room temperature of the acrylic side-chain polymers. With stepwise annealing up to poling conditions the orientation order was measured. The guest-host systems show a different behaviour.

INTRODUCTION

The copolymerization of optically nonlinear polymers and the incorporation of optically active dopants into polymer films induce new useful electrical and optical properties of these materials. Polymer glasses doped with optically nonlinear organic dye molecules and nonlinear optical polymers posses reasonably large second order nonlinear optical susceptibilities.[1] This concept involves electric field poling in the near of the glass transition temperature (T_g) of the sample resulting in an alignment of the dipolar dye molecules or side chains and yielding a non-centrosymmetric structure.

Corona poling is a well situated method for charging of polymers and has been used to pole electrets or polyvinylidene fluoride (PVDF) films, for example. Corona poling by discharge in an inhomogeneous electric field, usually at atmospheric pressure, can be performed at room temperature, but poling at elevated temperature has several advantages for polymers. For example, poling of polymer guest-host systems in the near of T_g increases the molecular mobility of the guest molecules and allows rotation to occur during poling. Lowering the temperature well below T_g during applied field, the guest molecules can be frozen into their new orientation.

EXPERIMENTAL

Copolymer synthesis

The side-chain copolymers were synthesized by a special dispersion polymerization technique with a surface active azo-initiator. The polymerization was carried out in the following manner: 90 g of water as dispersing agent, 0.8 g ($2.008 \cdot 10^{-3}$ moles) of the azo-comonomer (Figure 1), 10 g (0.1 moles) of methylmethacrylat (MMA) and 0.25 g of surface active initiator were well mixed at 80 °C in a polymerization flask equipped with stirrer, condenser and nitrogen injection.[2] The polymerization was stopped after a polymerization time of 390 minutes and the final copolymer dispersion was coagulated in methanol/HCL mixture.

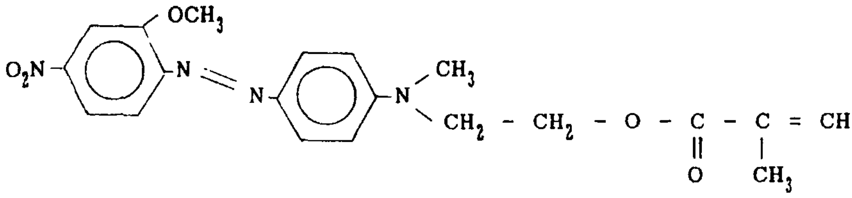


FIGURE 1 Azo-comonomer of the side-chain polymer.

The polymerization conversion was above 95%. The copolymers were washed with methanol and purified by two-fold precipitation from a toluene solution with methanol/HCL. The purified coplymer was characterized by viscosity and elemental composition which gave an intrinsic viscosity number [η] of 1.57 dl/g (25 °C, benzene as solvent, Ubbelohde viscometer) and a dye content of 4.9 % w/w related to MMA units. T_g was measured via DSC (Perkin Elmer DSC 7) as ca. 115 °C. Dispersion polymerization leads to much higher polymerization rates and molecular weights compared to solution polymerization.

Sample preparation

The side-chain polymer was dissolved in ethyl-acetoacetate. For preparation of polymer-dye composite films 10% w/w of azoviolet dye (Fluka 73020) and azo-comonomer were dissolved with polymethylmethacrylate (PMMA, $T_g \approx 120$ °C) in ethylacetoacetate, respectively. The azoviolet dye was also dissolved with polystyrene (PS, $T_g \approx 100$ °C) in xylene, and with polycarbonate (PC, $T_g \approx 145$ °C) in chloroform. All polymer solutions were mixed well, filtered through a glass frit filter and spin coated onto indium-tin-oxide (ITO) glass. Spun films were dried in an oven at 60 °C for 1 hour to reduce the content of solvents. The thickness of dried films ranged from 1.5 to 2.5 µm.

Corona poling

A cross sectional view of the poling arrangement is given in Figure 2. The corona discharge was generated by a

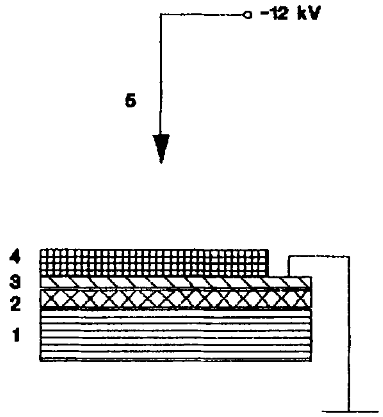


FIGURE 2 Poling arrangement. (1) glass substrate, (2) SiO_2, d = 70 nm, (3) indium-tin-oxide layer, d = 30 nm, (4) polymer layer, (5) needle electrode

needle electrode biased with -12 kV across a 22 mm air gap normal to a grounded planar electrode. The temperature could be raised by a heating plate positioned under the planar electrode or lowered by air flow. The temperature was measured with thermocouple on the top of this electrode. The substrates were placed film side up onto planar electrode. Reaching the poling temperature (T_p) in the near of T_g the poling field was applied and held constant, while after 5 min the temperature of the film was lowered to room temperature (RT). The poling field was applied for approximately 15 min across all films.

Absorbance measurements

The absorption spectra were measured with the UV/VIS/NIR spectrometer Lambda 19 from Perkin Elmer.

We have compared the optical absorbance of thermopoled and unpoled samples. Changes in absorbance generated by the alignment of the dipolar dye molecules or side chains in the electric field were used as an indicator of frozen ordering in the polymer films.[3] To ensure that the absorbance changes did not arise from electrochemical or thermal degradation, samples were reheated to poling temperature.

RESULTS

The absorption spectra of the azo-copolymer and PMMA with azo-comonomer are given in Figure 3 and Figure 4.

After poling a decrease in absorbance produced by the alignment of the dipolar dye molecules as well as a shift to longer wavelengths for the azo-copolymer and to shorter wavelengths for the PMMA/azo-comonomer composite were observed. The absorbance was measured after 1, 2, 4 and 24 hours to resolve the time dependence of the absorption behaviour at RT. The short-time behaviour of the absorbance shows a slight increase for both the azo-copolymer and the PMMA/azo-comonomer. This increase in absorbance is attributed to a slight relaxation of oriented dye molecules. After annealing at poling temperature T_P the absorbance increased back to the unpoled value for the copolymer and to about 50% of the unpoled value for the PMMA/comonomer composite (Figure 5).

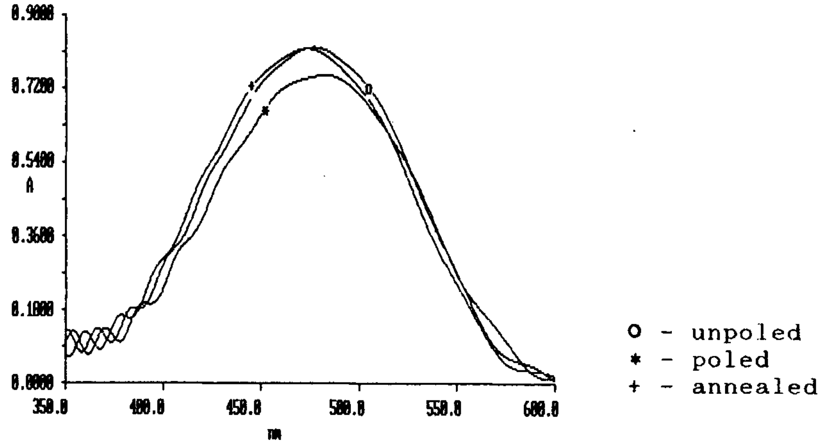


FIGURE 3 Spectra of the side chain polymer.

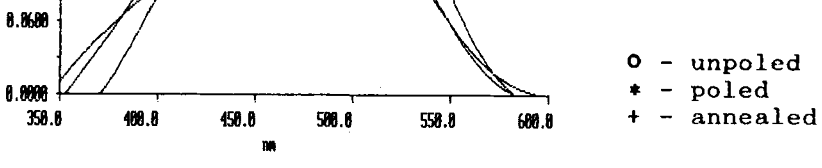


FIGURE 4 Spectra of the PMMA/comonomer composite.

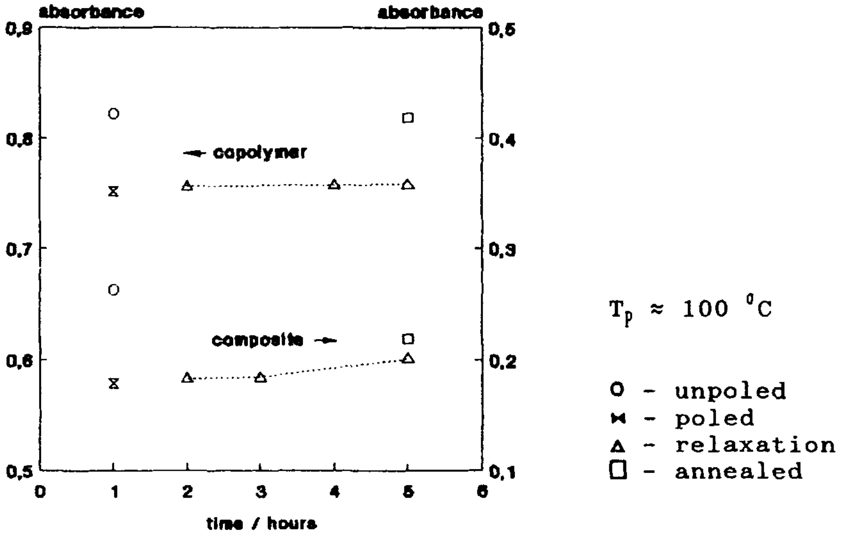


FIGURE 5 Short-time absorption behaviour for the azo-copolymer and the PMMA/comonomer composite.

The same behaviour was observed for PMMA/azoviolet dye composites (Figure 6).

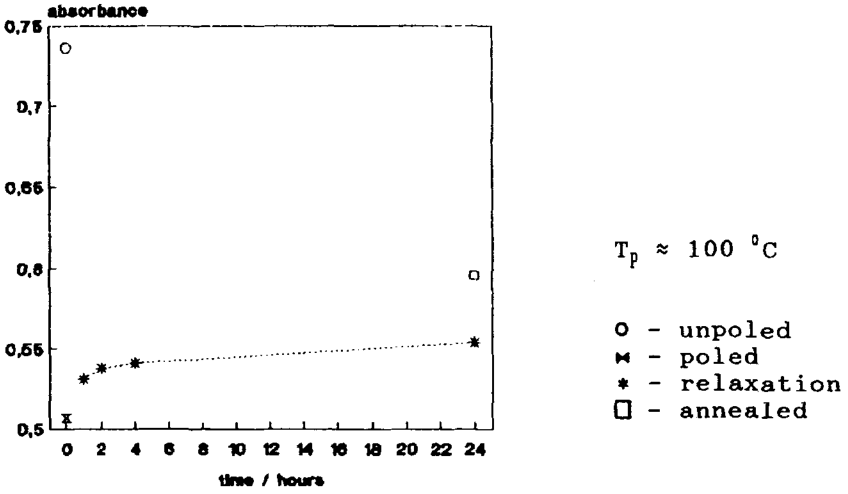
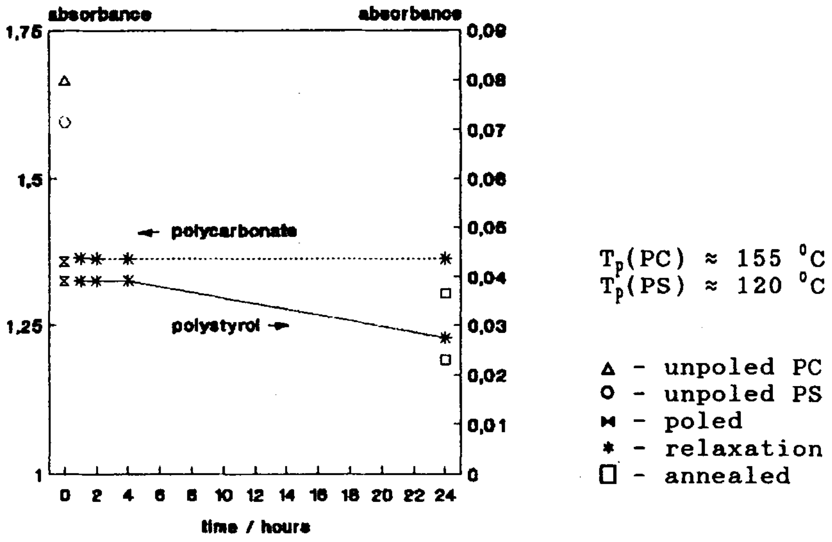


FIGURE 6 Absorption studies of a PMMA/azoviolet dye composite.

For the other polymer/dye composites the short-time behaviour is the same but the annealing behaviour differs from that of PMMA composites: After annealing a decrease in the absorbance was observed (Figure 7).



$T_p(PC) \approx 155\ ^0C$
$T_p(PS) \approx 120\ ^0C$

FIGURE 7 Absorption studies of PC/azoviolet and PS/azoviolet dye composite.

CONCLUSIONS

Corona poling induces an alignment of optically nonlinear dye molecules in an azo-copolymer and in polymer/dye composites. The dipolar orientation after poling remains stable for these materials at RT in comparison to the results of Hampsch et al. [4], which show a strong relaxation of dipolar orientation by SHG measurements. This orientational order can be described by an order parameter Φ, which is directly proportional to an induced birefringence due to the interaction between dipoles and the internal electric field.[5]

The results of this study indicate that the azo-copolymer has a lower order parameter ($\Phi = 0.1$) in comparison to polymer/dye composites ($\Phi = 0.3$).

After annealing the azo-copolymer shows a reversible behaviour, what differs from that of composites.

The annealing behaviour of PS- and PC-composites is very significant. It is possible that by annealing at poling temperatures the internal electric field could increase the order of the dye because of the higher mobility near T_g.

The behaviour of the same dye in different hosts is caused by different host-structures and depends on the glass transition behaviour of these materials.

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[*] Present address, University of Potsdam, Kantstrasse 55, O-1530 Teltow-Seehof, F.R.G.

[†] Present address, Max-Planck-Institut für Kolloid- und Grenzflächenforschung,
Kantstrasse 55, O-1530 Teltow-Seehof, F.R.G.

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