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Optical properties of a nonlinear *p*-phenylenevinylene oligomer side chain polymer in films and fiber preforms.

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ABSTRACT

Linear and nonlinear optical properties of a new soluble polymer bearing distyrylbenzene chromophore, the alkoxy-sulphono-substituted *p*-phenylenevinylene oligomer (MTPV-ORSO) attached as a side-chain to the methyl methacrylate backbone are reported. This chromophore was developed for introduction into single-mode nonlinear optical polymer fibres. The molecular second-order and third-order nonlinearities were estimated with quantum chemical calculations (MOPAC). The side-chain polymer shows an optical absorption maximum at 326 nm. The polymer was incorporated into the core of the fibre preform with a procedure which led to a step index profile, as measured with a preform profiler, suitable for a single-mode optical fibre. Second harmonic of the fundamental 1200 nm wave was measured in the corona poled polymer films giving the second-order susceptibility $d_{33} = 0.8$ pm/V for the polymer containing about 1.3 wt. % of the side-chain chromophore and 0.1 pm/V in a guest-host system containing 0.24 wt. % of the chromophore in the fibre preform. The coherence length of the side-chain polymer, equal to 28 μm at 1200 nm, was evaluated from the dispersion of the linear refractive indices. Degenerate four-wave mixing (DFWM) with amplified femtosecond pulses was also applied to measure the nonlinear refractive index of the co-polymer at 800 nm.
Keywords: PMMA, NLO side-chain polymer, optical fibre, poled films, second harmonic generation, coherence length, forward degenerate four-wave mixing

1. INTRODUCTION

Second-order and third-order nonlinear optical (NLO) materials suitable for incorporation into polymer optical fibres are of interest for photonics. Organic materials exhibit a large diversity in optical nonlinearities and provide a potential for being used in waveguide device configurations[1-4]. The third-order nonlinear optical properties of conjugated polymers, light transmission, solubility, and stability can vary considerably depending on the details of the chain structure and the type of substituents attached to the backbone. Our research in this area has been focussed on the highly nonlinear optical polymeric materials built of poly(*p*-phenylene vinylene) (PPV)[5-7] and π-conjugated rigid-rod molecules bearing the *p*-phenylenevinylene backbone[8-11]. Such polymers can be assembled into nonlinear slab waveguides suitable for optical signal processing. A nonlinear coupler in a channel waveguide was indeed demonstrated in a derivative of PPV[12]. The electro-optic planar waveguide devices based on highly nonlinear second-order organic chromophores are currently of great interest [13].

Plastic optical fibres based on poly(methylmethacrylate) (PMMA) represent a class of optical devices which can be fabricated in the research laboratory conditions at only moderately elevated temperatures, 100-200 °C, while the fabrication of glass optical fibres requires temperatures an order of magnitude higher. In addition to the significance of low temperature fabrication and good processibility, PMMA can be doped with a wide range of organic dopants which do not withstand extremely high temperatures but possess valuable second-order or third-order non-linear optical properties. The chromophores can be incorporated into the PMMA host by mixing or copolymerisation with methyl methacrylate (MMA). The presence of a chromophore in a core of a fibre elevates the refractive index, thus defining a

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dimension of waveguiding region for propagation of light in a fibre. A single-mode optical fibre provides an ideal geometry for optical devices to meet the requirement of a light beam of high power to be confined to a small area over a long distance in a material of large nonlinearity. Our interest is in the design and fabrication of polymer fibres for applications of second-order and third-order nonlinear optical effects.

Most work performed up to date in the field of second-order nonlinear optical properties of polymers has been concentrated on maximising the nonlinear response of the materials in order to obtain high nonlinear effect (the electrooptic effect or second harmonic generation) with the propagation lengths typical for integrated optical devices. We are reporting here on our research in which the goal was to establish a suitability of a material to be incorporated in a single-mode nonlinear plastic optical fibre for an application in which propagation lengths on the order of several meters would be required. One has to realize that such an application places numerous constraints on the choices of operating parameters and the properties of the materials used for manufacturing the fibre. With the assumption that ordinary, nonfluorinated organic polymer is to be used as the host matrix in the core of the fibre, excessive overtone absorption limits the choice of wavelengths that can be propagated with low losses from longer wavelengths end, while the tail absorption of the nonlinear chromophore will limit this choice from the shorter wavelength end. We decided therefore to evaluate the possibility of using a chromophore with a relatively short wavelength absorption, which would potentially afford a reasonably high electrooptic effect when suitably aligned but still give low absorption losses for the propagation on the order of ten meters.

We describe here the properties of a side-chain polymer in which the functionalised methacrylate mer bearing the dialkyleneoxy sulfonyl 4,4'-disubstituted distyrylbenzene (MTPV-ORSO) chromophore is a moiety built according to a simple archetype of a linear donor-conjugated bridge-acceptor structure. The conjugated bridge is a *p*-phenylenevinylene trimer, the acceptor is a sulphone group and the donor is an ether group. Fig. 1 shows the nominal structure of a copolymer (I) obtained from this chromophore.
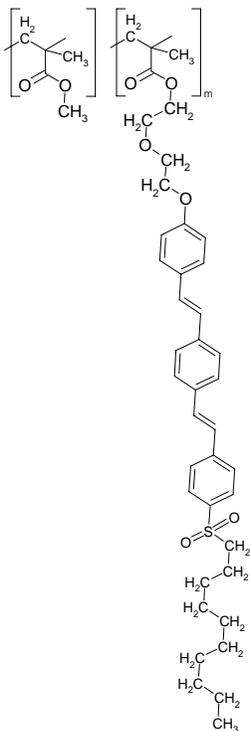

2. MATERIAL DEVELOPMENT

2.1. MOPAC computations

Estimates of the molecular parameters relevant for the optical applications were obtained for the chromophore from MOPAC-93 calculations. AM1 approximation was used for both the geometry optimization of the model molecule of the chromophore (the alkyl chain being simplified to methyl group and the polyether chain being simplified as OCH_3) and for calculation of the hyperpolarizabilities by the time-dependent coupled perturbed Hartree-Fock method. The results for the dipole moment μ and the polarizabilities: α, β and γ at zero frequency are given in Table 1.

As usual with such quantum chemical semiempirical calculations, these results should be taken with some reserve, however, it is interesting to find that MOPAC predicted the $\mu\beta$ product at zero frequency for our chromophore to be only about 30% lower than that for dimethylaminonitrostilbene, and to be comparable to that of DR1 molecule.

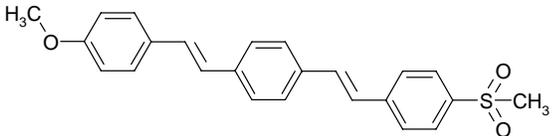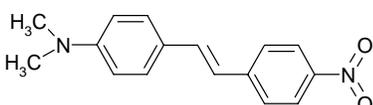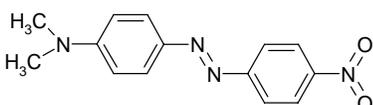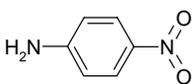Figure 1. Scheme of poly (MTPV-ORSO —co- methyl methacrylate), the polymer (I)

Table 1. Dipole moment μ, the zero frequency polarizability α, the first hyperpolarisability β and the second hyperpolarisability γ of the model molecules calculated using the MOPAC-93/AM1 semiempirical quantum chemical method.
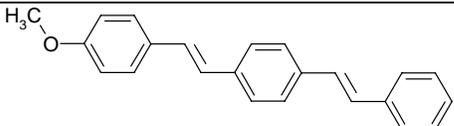
Formula	μ D	α (a.u), esu	β (a.u.), esu	γ (a.u.) esu
H₃C–O–(phenylenevinylene)₂–phenyl	1.25	276.8 41.0×10^{-23}	1274 1.10×10^{-29}	6.57×10^{6} 3.3×10^{-33}
phenyl–(vinylene-phenylene)₂–SO₂CH₃	6.2	287.4 42.6×10^{-23}	2947 2.55×10^{-29}	6.53×10^{6} 3.3×10^{-33}
H₃C–O–(phenylenevinylene)₂–phenyl–SO₂CH₃	6.6	313.6 46.5×10^{-23}	4913 4.24×10^{-29}	8.50×10^{6} 4.3×10^{-33}
(H₃C)₂N–phenyl–vinylene–phenyl–NO₂	8.7	209.6 31.1×10^{-23}	5356 4.63×10^{-29}	4.37×10^{6} 2.2×10^{-33}
(H₃C)₂N–phenyl–N=N–phenyl–NO₂	8.2	202.5 30.0×10^{-23}	4057 3.51×10^{-29}	3.11×10^{6} 1.6×10^{-33}
H₂N–phenyl–NO₂	7.3	78.1 11.6×10^{-23}	635 5.5×10^{-30}	0.016×10^{6} 8.1×10^{-36}
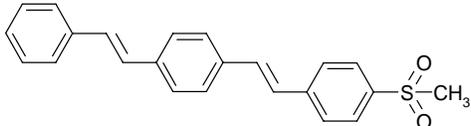
2.2. Material synthesis

The synthesis of the MTPV-ORSO chromophore monomer, using the stereoselective Wadsworth-Emmons reaction, and some of its nonlinear optical properties were described in ref[14]. An initial attempt of introducing the chromophore mer to the polymer fibre preforms by a direct bulk copolymerisation with methyl methacrylate was not successful. The product precipitated in the solid material causing strong scattering of light.

In the second approach the MTPV-ORSO monomer was copolymerised with MMA under thermal radical polymerisation conditions employing 2,2'-azobis-(2-methylpropionitrile) (AIBN) and 1-dodecanethiol[14,15]. The copolymer (I) was formed (see Figure 1). The powder was well soluble in chloroform and other solvents: N-methylpyrrolidone (NMP) or 2-ethoxyethyl acetate (Cellosolve acetate) which were used for preparation of polymer films. The estimation of the real concentration of the chromophore in the side chain copolymer (I) posed a little of a problem. The content was different from the content of the dye taken in the feed composition. The chromophore concentrations in the batches of the copolymer (I), estimated from the NMR and optical absorption spectra, were on the level of 1.3-2.3 wt. %.

Figure 2 shows absorption spectrum of the copolymer (I) in the film prepared from NMP solution by spin coating. The film contained about 2.3 wt. % of the chromophore.

The absorption band peaking at 326 - 328 nm was apparently composed of several vibronic transitions typical for the chromophore bearing the phenylenevinylene oligomer conjugated structure. It has been noticed that the absorption maximum of the chromophore after polymerisation was shifted to the shorter wavelengths in comparison to the absorption maximum of the chromophore monomer, MTPV-ORSO, which occurred at 374 nm. The origin of this shift is

not known. Possibly some degree of branching or crosslinking employing the internal double bond of the stilbene group was encountered[15].
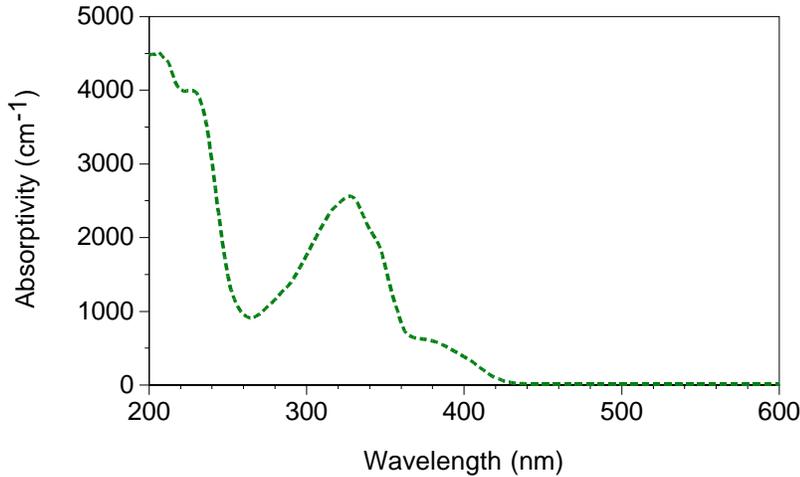

Figure 2. Absorption spectrum of the poly (MTPV-ORSO —co- methyl methacrylate),λ_{max} = 326 nm.

We developed an approach in which the powder of the side-chain polymer (I) was used for the manufacturing of a guest-host polymer system utilised in optical fibre preforms. The polymer (I) was dissolved in methyl methacrylate in amount of 19-21% by weight, filtered, and the solution was polymerised under the conditions of thermal radical polymerisation, as applied in the synthesis of neat PMMA, forming a transparent, highly fluorescent, guest-host polymer solid rod. Typically, PMMA rods were synthesised by polymerisation of MMA in the presence of the initiator, t-butyl peroxide, a chain transfer agent: 1-decanethiol or 2-butanethiol, a nonlinear optical chromophore and benzylmethacrylate (BMA) which was added to modify the refractive index of the core and the cladding of the preforms. The reaction proceeds with volume contraction but without any by-products. The concentrations of the initiator and chain transfer agent were chosen to be close to those described in[16]. A deviation from these led to mechanically unstable materials. It became clear that synthesis of high quality PMMA single-mode optical fibres posed a significant challenge when accuracy of the refractive index at the 0.1% level was required. There were also problems with bubbles formed in the preforms during polymerisation at an elevated temperature (80-90 °C, 10-14 days) and with the optical losses in the fibres.

2.3. Polymer optical fibre preforms

Polymer optical fibres have a concentric core-cladding structure consisting of a core component made of the synthetic macromolecular compound and a cladding component made of a polymer having refractive index lower than the core component. A single-mode fibre requires the core material to have the refractive index bigger then the cladding by 0.2-0.3%. For a single-mode fibre the following waveguide equation[17] is applied: $V = \dfrac{2\pi r}{\lambda}\sqrt{n_{co}^2 - n_{cl}^2} < 0.7\pi$ where n_{co}

is the core index; n_{cl} is the cladding index, and r is the fibre radius. For operating wavelengths in the low absorption region of the acrylic polymer, (0.65-0.9µm), the core radius should not exceed 5 µm or the tolerance on core-cladding index difference will become very critical leading to increased sensitivity of the fibre to bend losses. A single-mode polymer waveguide based on PMMA would have $\Delta n = n_{co} - n_{cl} = (3-5) \times 10^{-3}$ at 632.8 nm wavelength and the core diameter below 5 µm. The concentration of the chromophore and other components in the preforms could be pre-determined by the calculations of refractive indices required for the core and cladding of the fibres using the model of additivity of the molar refractivity[18] if the data were available.

We explored several methods suitable for producing single-mode polymer optical fibres[19]. Each method used a scheme of a two-stage preform production:
- Fabrication of the stage #1 preform rod, pulling of the stage #1 fibre
- Fabrication of the stage #2 preform rod, pulling of the stage #2 fibre.

We report here properties of the fibre preforms manufactured with our procedure being a modification of the approach applied in the Washington State University (WSU)[16]. It allowed us to make the preforms out of a small amount (a fraction of a gram) of the expensive-to-manufacture chromophore. The procedure consisted of five essential steps:

1.	Manufacturing of the core of the preform #1 - the polymer rod of 3.2 mm diameter was made by polymerisation of MMA mixed with about 20 wt. % of the polymer chromophore, in a glass tube under usual conditions. The procedure required a small volume of the solution, less than 1-2 cm^3, to make the core rod, typically, 10 cm long. Bubbles formed in the polymer rod during synthesis were removed by hot pressing in a custom made precise press.

2.	Manufacturing of the stage #1 preform. After the core rod had been prepared it was placed into a groove that had been carefully machined into two semi-cylindrical 12.6 mm diameter sections of an extruded Perspex rod. The machined surfaces were polished and cleaned in an ultra-sonic bath. The surfaces to be mated were then painted with a thin layer of liquid MMA; the core inserted into the groove and the upper cladding layer added. The resulting assembly was placed in a second custom made press and then in the processing oven. Pressure was applied to the assemble to fuse the core and cladding sections, while the temperature was raised to between 105 and 120 ^{o}C for 5-10 days. The end faces of the preform were polished to allow inspection of the core-cladding and cladding-cladding interfaces. The hot pressing was continued until the interfaces were hardly visible. Figure 3 shows a photograph of a completed stage #1 preform rod (P51) containing the guest-host system: 18.6 wt. % MTPV-ORSO polymer (I). The content of the MTPV-ORSO chromophore in PMMA in the core was estimated to be 0.24 wt. %.

The stage #1 preform could be also prepared by insertion of the 3.2 mm core rod into a hole in the drilled Perspex rod and compressing at an elevated temperature.
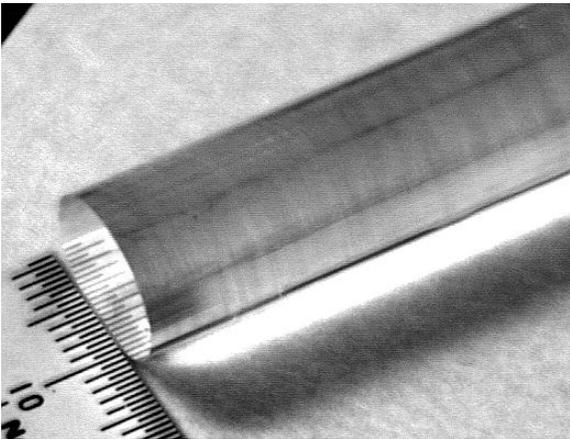

Figure 3
A view of the stage #1 fibre preform. The 3.2 mm diameter core rod composed of 18.6 wt. % of the side-chain MTPV-ORSO polymer in PMMA, was inserted in a 12.6 mm diameter Perspex rod.

3.	Manufacturing of the stage #1 fibre, 0.8 mm diameter, out of the preform #1 by pulling. The core in the fibre became 200 μm thick.

4.	Manufacturing of the stage #2 preform. The 1st stage fibre was inserted into the PMMA cladding, into the groove in Perspex rod #2, followed by a hot pressing to consolidate the preform #2;

5.	Pulling of the final fibres out of the stage #2 preform. The overall diameter was in the range 0.4-0.8 mm and the core diameter was in the range 5-10 μm.

2.4. Refractive indices of fibre preforms

The polymer fibre preforms were characterised by measurements of the refractive index with various methods. We used the preform profiler[20,21] constructed in the laboratory of the University of New South Wales to measure the profile of refractive index in the core and cladding of the preform rods.
Figure 4 shows that the 1st stage fibre preform with a step index profile suitable for preparation of the step index single-mode fibre can be obtained with our processing route.
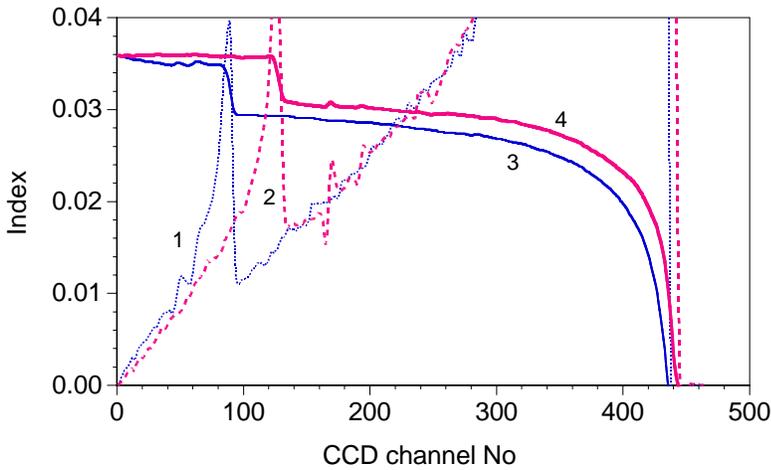
Figure 4. Refractive index step between 3.2 mm diameter core (19 wt. % the MTPV-ORSO polymer (I) in host, co-poly(methyl methacrylate-benzyl methacrylate), 4.15 wt. % BMA) and the cladding, 12.6 mm diameter Perspex (9) measured with a preform profiler at 632.8 nm. Curves 1 and 2 show the deflection of the laser beam in the left and right halves of the preform, the curves 3 and 4 show the corresponding index profiles derived from the deflection curves. The value of $\Delta n = 5.5 \times 10^{-3}$ was found.

Refractive indices were also measured in films made of the materials of the core and cladding of the preforms (see Figure 5) and slices thereof. We applied

- a Metricon prism coupler (Model 2010) to measure the waveguide mode patterns in the films prepared from the core and cladding materials; the indices were derived from the patterns found in the films deposited on a lower index substrate;

- the Metricon prism coupler operating as a refractometer providing measurements of the refractive index in 3-4 mm thick slices of the preform rods; the indices were determined from the critical angle of incidence of light leaking to a bulk substrate, ie., to the core and cladding parts of the slice brought into a contact with a prism.

The Metricon prism coupler, allowed us to measure the index with the accuracy of –0.001 and –0.0005 for the index resolution.

We found an agreement between the index data obtained with the preform profiler and measured with a prism coupler in slices of the preforms. Some deviation was found among the results obtained in films. It is believed that it is due to a solvent influence.

$$y = 6.7944E\text{-}04x^2 - 1.2781E\text{-}02x + 8.3769E\text{-}01 \quad r^2 = 9.8668E\text{-}01$$
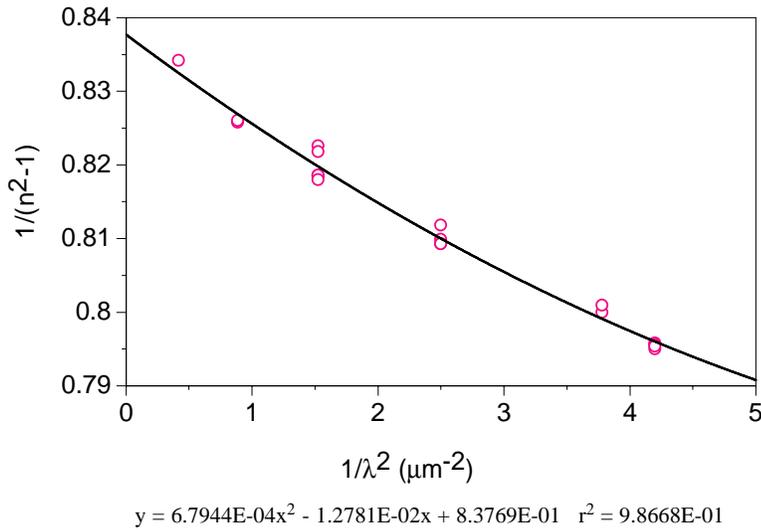
Figure 5. Refractive indices of the polymer (I), containing 1.3 wt. % of the MTPV-ORSO chromophore, measured with a Metricon prism coupler for TE and TM polarisation of the waveguide modes propagating in the film deposited on silica substrate. The index dispersion was approximated with the second-order polynomial function: $y = 6.7944 \times 10^{-4} x^2 - 1.2781 \times 10^{-2} + 0.83769$, $r^2 = 0.98668$, where $y = 1/(n^2 - 1)$, $x = 1/\lambda^2$.

3. NLO MEASUREMENTS

3.1. Second harmonic generation (SHG)

The second-order NLO coefficients of chromophores are often estimated from the second-harmonic intensity generated in poled polymer films in the Maker-fringe type experiments[4,22-26]. The oscillatory behaviour of the second-harmonic intensity vs. angle of incidence of the fundamental wave, caused by the interference pattern of generated and transmitted free and bound harmonic waves in the Maker-fringe method[27,28], is usually measured in a noncentrosymmetric medium in comparison with a standard sample. Several fringes can be observed if the sample is thicker than the coherence length l_c. The analysis of the Maker fringes can provide information about the coherence lengths and the coefficients of the second-order susceptibility tensor. Our films were thinner than l_c thus the l_c values were derived from the dispersion of refractive index of the material, see Figure 5.

A film of the polymer containing an ensemble of donor-acceptor type dipolar molecules oriented with an applied electrical field represents an anisotropic medium of the $C_{\infty v}$ symmetry (the ∞mm point group). It possesses a unique axis in the direction parallel to the electric field direction, labelled 3. The nonlinear polarisation can be described by equations taking into account components of the second-order susceptibility, d tensor, and the angles formed with incident electromagnetic field components, as appropriate for the s and p polarisations of the fundamental beam. In our experiment we used the incident light beam p polarised, thus we measured the effective d_{33} coefficient. Figure 6 shows the scheme of the experimental setup used for SHG measurements in corona-poled polymer films.

Measurements of electric-field induced second harmonic were performed with a femtosecond laser system consisting of a Clark-MXR 2001 Ti-sapphire regenerative amplifier producing 1kHz 150 fs 775 nm pulses and a Light Conversion Topas optical parametric amplifier. This system generated 100 microjoule range pulses at 1200 nm. The output beam from the Topas was properly filtered, attenuated, and used in the horizontal (p) polarization without focusing. The samples in the form of films on ITO covered glass or silica were mounted on a temperature controlled metal block which was positioned on a rotary stage to provide an incidence angle of approximately 45 degrees for the fundamental beam. The corona needle was mounted appr. 6-8 mm above the film. The voltage applied to produce the corona discharge was about 5 kV. The measurements of the second harmonic were performed with a Hamamatsu photomultiplier equipped with a suitable interference filter and connected to a HP digital scope which provided the readout of the amplitude of the second harmonic pulse through a GPIB interface to the data collection computer.
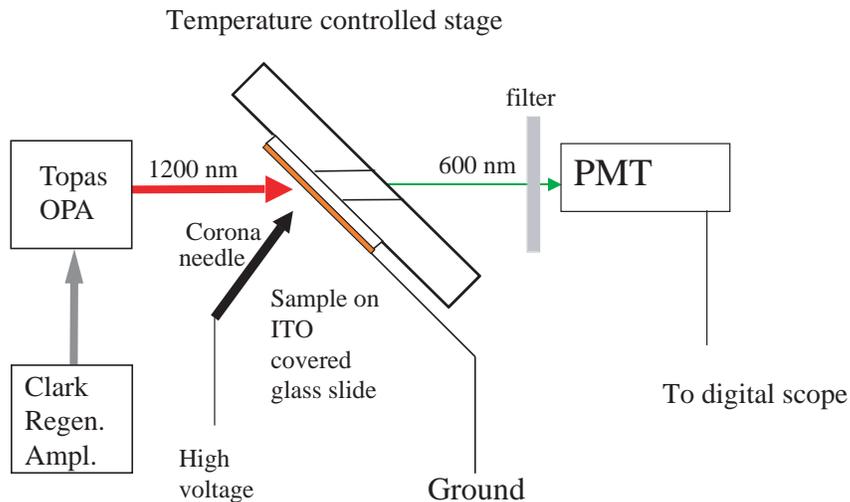
Figure 6. Scheme of the experimental setup for corona-poled SHG experiments

The SHG signals were calibrated against that at one of the Maker fringes of an x-cut quartz plate. Figure 7 shows the SHG response from the polymer (I) measured at various temperatures, induced by a repetitive switching of the poling potential.
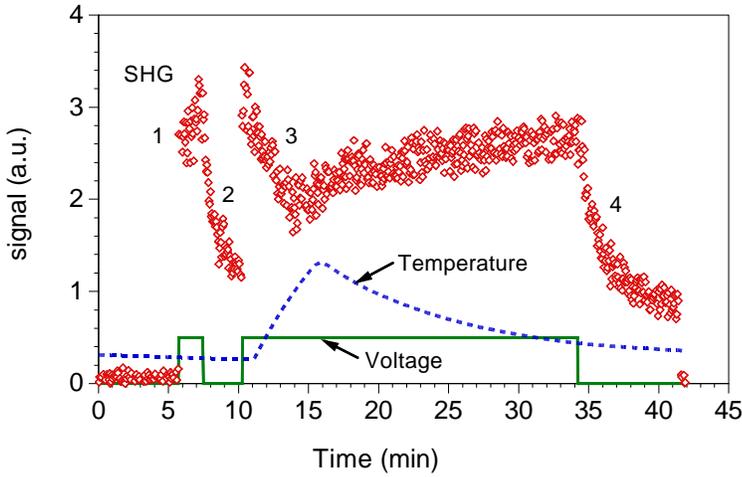

Figure 7. Second harmonic of the 1200 nm fundamental as a function of time, temperature and voltage applied to the needle electrode for poling of the film of the co-polymer (I) containing about 1.3 wt. % (1.4×10^{19} cm^{-3}) of the MTPV-ORSO chromophore. The film, 2.9 μm thick, was deposited on ITO/silica substrate from the polymer solution in N-methylpyrrolidone under nitrogen by spin coating and dried in vacuum at 65 °C for 20 hours.

The regions, indicated by numbers in the Figure, correspond to the treatment of the sample with heat and voltage applied to the corona needle. Initially the sample was exposed to laser beam at room temperature, the SHG background signal was low, about 5 mV. The SHG signal jumped up to 300 mV instantaneously when the 5kV voltage was applied to the corona needle, see the region 1. It decayed fast when the voltage was switched off, see the region 2. This shows that the sample has a tendency for cold poling. The SHG signal increased again when the voltage was switched on but it started to decay when the sample temperature increased to about 140 °C. The signal slowly increased during cooling of the film with the corona kept on, see the region 3. The second harmonic decayed partly when the voltage was switched off, see the curve 4. The sample was removed, the background was about 5 mV.

The experiment indicates that the chromophore can be oriented with electrical field induced by a corona discharge. However, the poling process did not produce a long-term orientation of the chromophore in the film. Possibly, the stability of the orientation and nonlinearity can be improved by choosing different poling conditions, careful solvent removal and chemical and physical aging[24,25] which might cause a reduction in the polymer free volume and a redistribution of void sizes thus inhibiting the relaxation of the oriented chromophore molecules. A similar SHG experiment carried on the poled film of the polymer prepared from the chloroform solution showed a slower reorientation relaxation.

The value of second harmonic susceptibility d_{33} of the polymer (I), relative to the quartz coefficient $d_{11,Q}=0.5$ pm/V, was calculated from the Eq. 1.

$$\frac{d_{eff}}{d_{eff}^{ref}} = \frac{l_c^{ref}}{l_c} \left[\frac{I_{2\omega}}{I_{2\omega}^{ref}} \frac{\eta}{\eta_{ref}} \right]^{1/2} \tag{1}$$

where l_c is the coherence length, $l_c = \lambda/4(n_{2\omega}-n_\omega)$; η is a reflection correction factor[26-28], $I_{2\omega}$ is the second harmonic intensity. The coherence lengths of quartz at the normal incidence at the fundamental wavelength 1200 nm was calculated from the dispersion equation fitting the experimental refractive indices of quartz given in[29]. The $l_{c,quartz}$ was found to be about 24 μm. The coherence length of the polymer (I) was calculated from the dispersion equation fitting the indices measured in the film of the polymer (see the caption for Figure 5). It was found to be about 28 μm. The calculations of the d coefficient proceeded with the film thickness adjusted to the 45 deg. incidence and the internal angle

28.5 deg., the effective thickness of the material was 3.3 µm. The reflection correction factor was close to 1. The nonlinear coefficient $d_{eff} = d_{33}$ of the copolymer (I), containing about 1.3 wt. % of the MTPV-ORSO chromophore, was found to be 0.8 pm/V.

The measurements of the second harmonic in a poled film prepared of the guest-host polymer system containing 0.24 wt. % of the MTPV-ORSO chromophore (the material of the fibre preform) gave the nonlinear coefficient equal to 0.1 pm/V.

3.2 Degenerate four wave mixing (DFWM)

DFWM measurements were performed at 800 nm using amplified 120 fs pulses at 30 Hz repetition rate produced by a laser system using a Coherent Mira 800D Ti-sapphire oscillator and a regenerative Ti-sapphire amplifier pumped with a Spectra Physics GCR Nd:YAG laser. The measurement setup was that of BOXCARS (forward) geometry with both the phase-matched signal and one of the two non-phase-matched DFWM signals being monitored (cf.[9,11,30]). This allowed us to determine the nonlinearity of relatively thin films of the doped PMMA even in the presence of strong DFWM signals due to the silica or glass substrates. Figure 8 shows the phase-matched and non-phase-matched signals in the film of the copolymer (I) bearing 2.3 wt. % of the MTPV-ORSO chromophore. Figure 9 shows a theoretical fit to the phase-matched experimental data, shown in the Figure 8, giving the pulse full width at half maximum (FWHM) equal to 121 fs.
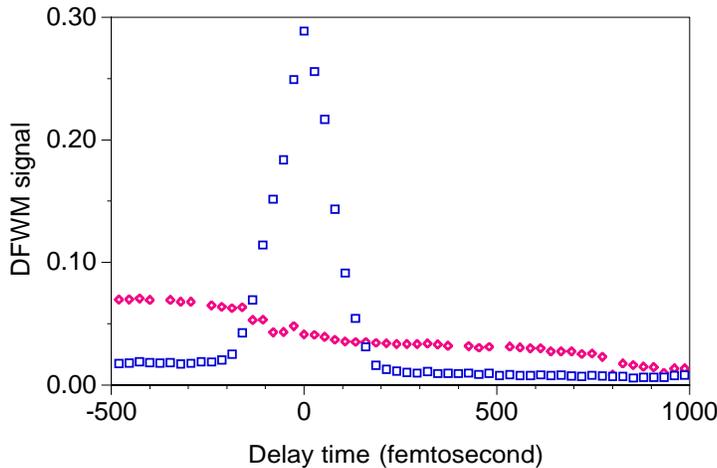

Figure 8. The phase-matched (squares) and non-phase-matched (diamonds) signals measured in an 8 µm thick film of the co-polymer (I), containing about 2.3 wt. % MTPV-ORSO chromophore, on 1mm silica substrate. Note that the delay is scanned from positive delays into negative ones (from right hand-side of the diagram to the left hand-side). The increase of the background in both signals is due to permanent grating formation
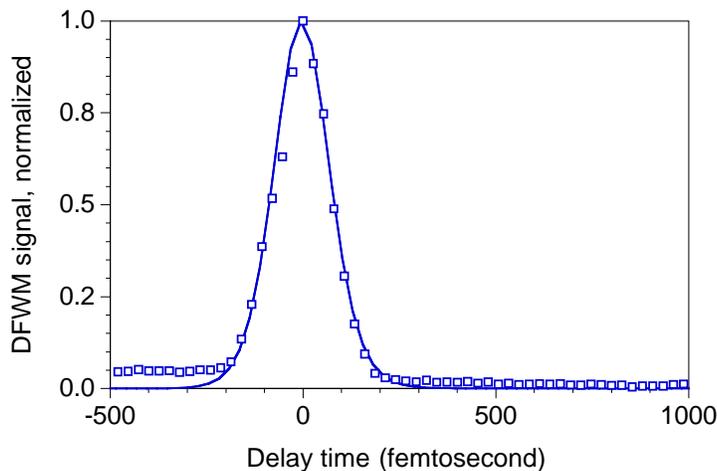

Figure 9. Fit to the experimental phase-matched DFWM measured in the 8 µm thick film of the co-polymer (I). The signal was generated mainly from the 1 mm silica glass substrate. The fit gave the pulse duration equal to 121 fs.

The DFWM measurements indicate that the polymer can easily form a permanent grating under the laser beams. These effects take place at light intensities of the order of 100 GW/cm^2 and the pulse energy of the order 1 µJ. The nonlinear refractive index, n_2, could, however, be extracted from the non-phase-matched signals measured at various incident laser powers, and was estimated to be less than (2-3) x 10^{-14} cm^2/W, when extrapolated to a neat chromophore.

4. CONCLUSIONS

Fabrication of single-mode PMMA-based optical fibres containing an NLO chromophore suitable for long propagation lengths was found to be challenging. It requires highly soluble stable materials and high precision in the manufacturing of high-quality fibre preforms.

The measurements of the linear refractive indices of the preforms with a preform profiler indicated that the applied processing route provided the required step index profile.

The nonlinear optical chromophore, MTPV-ORSO, a donor-acceptor structure based on a *p*-phenylenevinylene oligomer was designed for doping of the core component of polymer optical fibre with a wide transmission window. It shows a potential for a reasonably high second-order optical nonlinearity. The side-chain chromophore could be oriented in the films by poling with electrical field. The nonlinear susceptibility d_{33} of the copolymer containing 1.3 wt. % of the chromophore was estimated to be 0.8 pm/V, and 0.1 pm/V in the material used for manufacturing of the polymer fibre. The poled films show, however, a fast relaxation of the chromophore orientation.

The third-order nonlinearity of the side-chain polymer was detected, however it is also noted that the polymer easily forms a permanent grating under high-intensity 800 nm laser beams.

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