

Synthesis and properties of a ROMP backbone polymer with efficient, laterally appended nonlinear optical chromophores†

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The synthesis and properties of a new ROMP backbone polymer bearing lateral donor–acceptor-substituted (*E*)-diethynylethene ((*E*)-hex-3-ene-1,5-diyne) chromophores are described. The polymer with an average of 40 monomeric repeat units is readily soluble in common organic solvents such as tetrahydrofuran, dichloromethane and chloroform. Good optical-quality films were obtained by spin coating. The third-order susceptibility $\chi^{(3)}$ at a wavelength of 1907 nm was determined to be 100 times greater than that of fused silica. After electrical poling, the polymer also showed a significant second-order nonlinear optical coefficient (d_{33}) value, which decays by a factor of two over a period of one month at room temperature.

Efficient nonlinear optical (NLO) materials attract much attention in view of their potential applications in areas such as optical signal processing, optical computing and telecommunications, and a wide range of compounds extending from inorganic crystals to organic π -chromophores have been explored for application in NLO devices.^{1–6} Among them, organic polymers have advantages with regards to ease of fabrication and integration into macroscopic devices, tailorability—allowing the chemical structure and properties to be fine-tuned for a given nonlinear optical process—, low dielectric constants, fast nonlinear optical response times and large off-resonance nonlinear optical susceptibilities.²

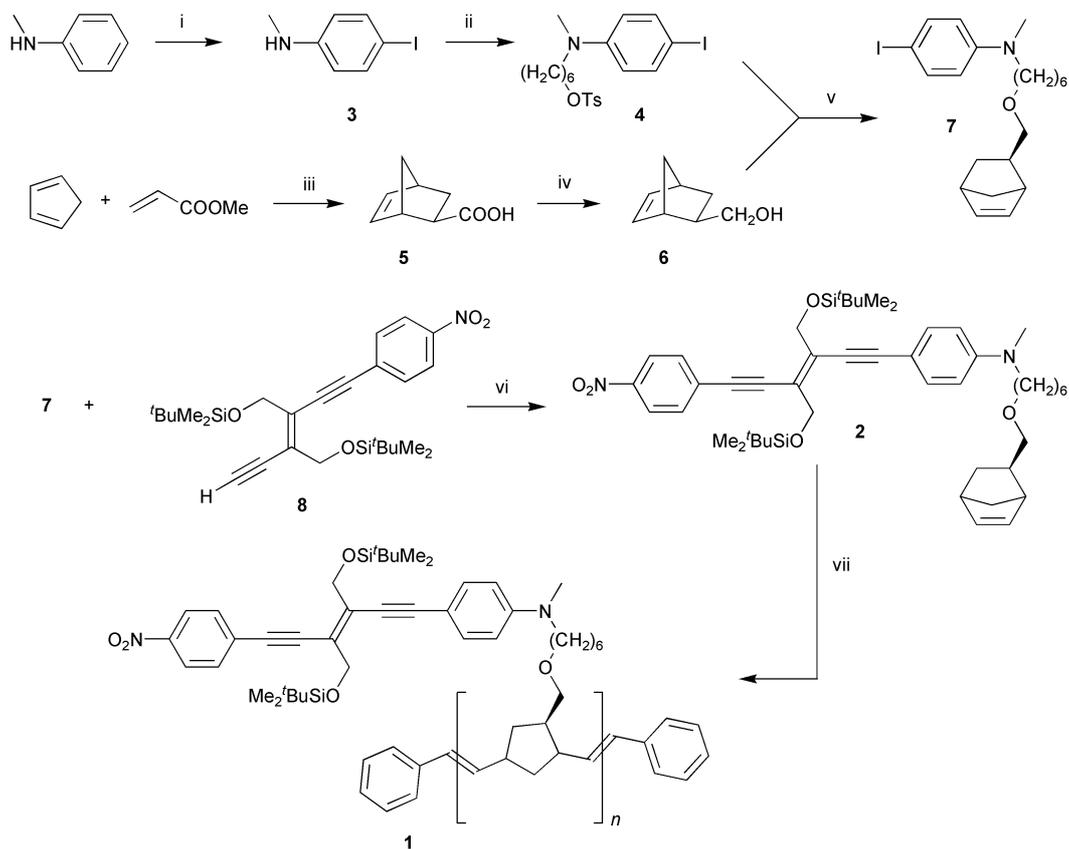
During the past decade, we targeted the understanding of structure–property relationships for second- and third-order nonlinear optical susceptibilities by studying comprehensive series of powerful new one- and two-dimensional NLO chromophores. These compounds are donor– (e.g. 4-dimethylaminophenyl) acceptor– (e.g. 4-nitrophenyl) substituted derivatives of 1,2-diethynylethene (DEE, (*E*)-hex-3-ene-1,5-diyne)³ and tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne)⁴ featuring fully planar π -chromophores. They are synthetically accessible *via* short and high-yielding protocols and have high thermal stability in air.

Here we describe the synthesis by ring-opening metathesis polymerisation (ROMP)⁵ and physical investigation of the novel polymer **1** (Scheme 1) bearing donor–acceptor-substituted DEEs as NLO-active side-chain chromophores. The preparation of linear polymers of low polydispersity, featuring precisely positioned side-chain chromophores and possessing desirable properties such as high solubility, ease of processability and low viscosity has become an attractive target, in particular for the development of optoelectronic devices.⁶ ROMP has been shown in the last several years to be a useful technique for achieving low polydispersities across a wide array of molecular weight,⁷ but so far only a few reports have appeared in which this polymerisation technique has been adopted as a useful synthetic route to polymers bearing NLO-active chromophores as side-chains.⁸ We also opted for ROMP polymers since they offer good solubility, required for using spin coating techniques, and transparency of the polymer backbone.

The norbornenyl derivative **2**, with the NLO-chromophore appended *via* an *exo*-ether linker to the bicyclic framework, was chosen as the ROMP monomer.⁹ This monomer was selected because it is known to add irreversibly to a living ROMP polymer chain,¹⁰ permitting access to homopolymers and block copolymers of low polydispersity. It is well documented that *exo*-norbornenyl derivatives polymerise more readily than *endo*-isomers.^{10a}

For the preparation of **2** (Scheme 1; for full protocols, see ESI†) commercially available *N*-methylaniline was iodinated to give **3**. *N*-Alkylation with 6-bromohexanol followed by esterification with *p*-toluenesulfonyl chloride afforded **4**. *exo*-Norbornenylcarboxylic acid **5** was prepared by the Diels–Alder reaction between freshly distilled cyclopentadiene and methyl acrylate, followed by *exo*–*endo* equilibration and saponification. The *endo*-isomer was subsequently removed by iodolactonization⁹ to afford **5** in 18% overall yield. Reduction with LiAlH₄ gave alcohol **6** that was etherified with **4** to provide **7**. Sonogashira cross-coupling¹¹ of aryl iodide **7** with *p*-nitrophenyl-substituted DEE **8**^{1a} afforded the red-colored monomer **2**, featuring a donor–acceptor-substituted chromophore. The metathesis reaction of **2** was carried out with the commercial catalyst [RuCl₂(PCy₃)₂CHPh] in THF under Ar. No change in color or viscosity was observed during the

† Electronic Supplementary Material (ESI): Full details of the synthesis of polymer **1** and comparison of the ¹H-NMR spectra of **1** and monomer **2**. See <http://www.rsc.org/suppdata/jm/b3/b314789d/>



Scheme 1 Reagents and conditions: i, I₂, NaHCO₃, H₂O, rt, 45 min, 40%; ii, 6-bromohexanol, K₂CO₃, n-BuOH, Δ, 72 h, 60%; then *p*-toluenesulfonyl chloride, pyridine, CH₂Cl₂, rt, 18 h, 84%; iii, CH₂Cl₂, Δ, 24 h; then NaOMe, Δ, 4 h; then aq. NaOH, Δ; then I₂, KI, NaHCO₃, H₂O; 18%; iv, LiAlH₄, Et₂O, rt (9 h) and Δ (45 min), 90%; v, NaH, THF, 0 °C (30 min) and rt (2 h), 62%; vi, [PdCl₂(PPh₃)₂], CuI, NEt₃, rt, 24 h, 60%; vii, [RuCl₂(PCy₃)₂CHPh], THF, rt, 2 h, then benzaldehyde, rt, 1 h; quantitative yield. Cy = cyclohexyl.

transformation. After all of **2** had reacted (thin layer chromatography (TLC) control), the metathesis reaction was irreversibly terminated by addition of an excess of benzaldehyde, yielding polymer **1** in nearly quantitative yield.

Analytical gel permeation chromatography (GPC, calibrated by polystyrene and poly(triacetylene) standards) analysis of **1** revealed the formation of a polymer of low polydispersity with an average of 40 monomeric repeat units. The polymer was highly soluble in common organic solvents such as tetrahydrofuran, dichloromethane and chloroform. The ¹H-NMR (CDCl₃, 300 MHz) of **1** is well defined featuring broadened peaks compared to the spectrum of monomer **2** (see ESI†). The resonances of the appended DEE chromophores in **1** appear nearly unchanged. The resonance for the olefinic protons of the norbornene ring in **2** (6.05–6.13 ppm) have disappeared and a new broad peak around 5.1 ppm is observed, belonging to the protons of the ethene-1,2-diyl moieties connecting the monomeric repeat units in **1**.

High-quality thin films of polymer **1** were made by spin coating of a solution of **1** (concentration 2–10 wt%) in CH₂Br₂ at 40 °C using a spinning rate of 300 min⁻¹ for 4 s and 1500–3000 min⁻¹ for 40 s. The film was subsequently dried at 70 °C for 15 h. This procedure afforded films with good optical quality having a thickness range of 0.2 to 3 μm. Differential scanning calorimetry (DSC) analysis of polymer **1** was carried out under nitrogen at a heating rate of 20 °C min⁻¹ and revealed the glass transition temperature (*T*_g) at 40.0 °C, indicating that polymer **1** is amorphous and is in a glassy stable state at room temperature.

The linear and nonlinear optical properties of spin-coated thin films of polymer **1** were measured. A Perkin-Elmer Lambda 9 spectrometer was used to measure the absorption. The Kramers–Kronig relations were used to calculate the corresponding dispersion of the refractive index (Fig. 1). To

obtain an absolute value of the refractive index, we scaled the refractive index curve using the absolute refractive index values determined at the two telecom wavelengths of 1.313 μm and 1.55 μm. The absolute value of the refractive index was measured by the waveguide grating–coupling technique¹² using *s*-polarized light. The results are marked on the refractive index curve as two crosses (Fig. 1).

We first assessed the second-order nonlinear optical response of electrically poled spin-coated thin films of polymer **1**, having thicknesses ranging from 200 to 300 nm, by second-harmonic generation (SHG) experiments using a fundamental wavelength of 1064 nm. To pole the thin films we used the standard technique of corona poling in a needle to plane configuration¹³ applying voltages between 6.5 to 9 kV. The polar orientation at room temperature is achieved by electric field poling close to the glass transition temperature of the sample and subsequent cooling. Because of the symmetry of the poling field, the resulting second-order susceptibility tensor has only the two independent elements *d*₃₃ and *d*₃₁ (= *d*₁₅ = *d*₃₂ = *d*₂₄ if Kleinman symmetry can be applied) with the 3-axis along the poling field. After poling, the nonlinear coefficients were measured by the Maker fringe method.^{14,15} The laser used was a Nd-YAG laser emitting 100 ps pulses at a wavelength of 1064 nm. Quartz serves as reference with a *d*₁₁ coefficient of 0.3 pm V⁻¹.¹⁶ The 532 nm second-harmonic wavelength in this experiment is slightly inside the absorption band of the polymer film.

In the Maker fringe experiment, we measured second-harmonic generation as a function of the incidence angle. One experiment was performed with the polarization of both beams (the fundamental and the second harmonic) in the incidence plane (*p* → *p*). In another experiment, the polarization of the fundamental wave was set to be perpendicular to the incidence plane (*s* → *p*). The resulting curves of second-harmonic

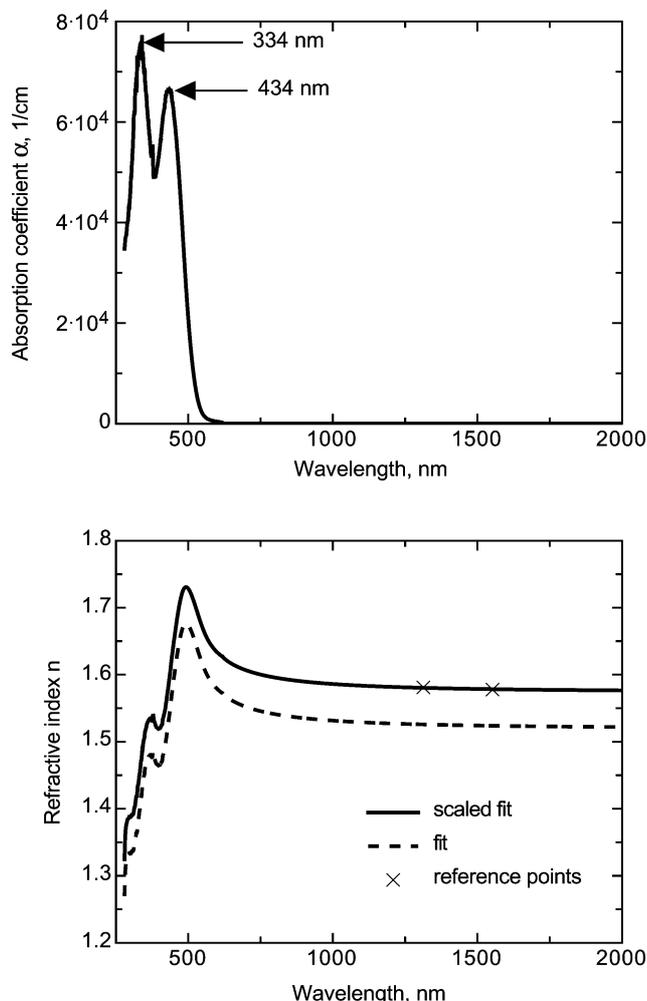


Fig. 1 Absorption (top) and refractive index (below) of polymer **1** as function of the wavelength.

intensity vs. incidence angle were compared with the theoretical prediction¹⁴ and with the results obtained using a quartz crystal as a reference to obtain the values of the nonlinear optical susceptibilities of the polymer film. From the $s \rightarrow p$ experiment we directly obtained $d_{31} = 10 \pm 2 \text{ pm V}^{-1}$. From the $p \rightarrow p$ experiment we obtained $d_{33} = 30 \pm 10 \text{ pm V}^{-1}$, using a fixed ratio $d_{33}/d_{31} = 3$ while fitting the experimental data (a ratio of 3 between these two coefficients is expected whenever the dipole energy, leading to the molecular orientation during poling, is much smaller than the thermal energy kT). Thus, both the $s \rightarrow p$ and the $p \rightarrow p$ experiments consistently deliver a value of $d_{33} = 30 \pm 5 \text{ pm V}^{-1}$.

Fig. 2 describes the poling process. It is a plot of the SHG signal and temperature vs. time. This plot clearly shows that (i)

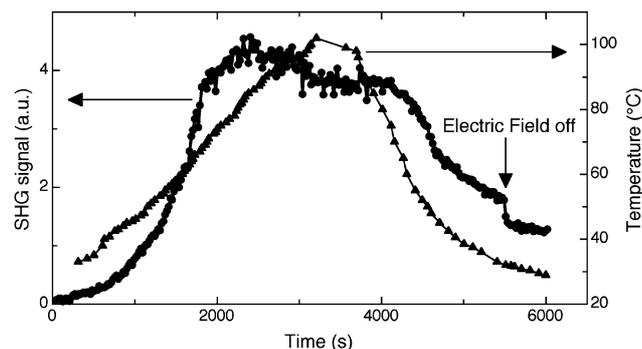


Fig. 2 Poling process: plot of the SHG-signal and temperature vs. time.

the SHG signal increases with increasing temperature, and that (ii) the electric-field-induced nonlinearity reaches a plateau at a value of about $d_{33} = 80 \text{ pm V}^{-1}$ (with the electric field applied). The initial rapid decrease (taking place at a time of 4000–5200 s) of the nonlinearity upon cooling can be ascribed to a first fast reorientation of the chains at temperatures close to the T_g value of polymer **1**. The later abrupt decrease (taking place at the later time of 5200–6000 s, and at a lower temperature) is due to the removal of the applied electric field. In order to estimate the time-dependence of the orientational stability of the poled polymer films at room temperature, SHG measurements were repeated on the same films after one month. In spite of the low T_g value, the nonlinear optical coefficients were found to be as high as half of the initially measured values. Of course, a higher T_g would improve material performance over time by increasing its orientational stability at a temperature higher than room temperature. An increase of the T_g value could be achieved, for example, by decreasing the length of the alkyl chain between the NLO chromophores and the polymer backbone.

Third-harmonic generation (THG) was performed both in solution and in thin films at a fundamental wavelength of $1.907 \mu\text{m}$. Such a long fundamental wavelength was chosen to avoid any resonance effect. The fundamental and third-harmonic wavelengths were not in absorption bands of the investigated polymer. As a reference for the calibration we used $\chi_{fs}^{(3)} = 1.62 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$ ($1.16 \times 10^{-14} \text{ esu}$) for fused silica.^{16,17} In a chloroform solution, we measured the third-order nonlinearity of a single chromophore (**2**) to be $\gamma = 355 \pm 28 \times 10^{-36} \text{ esu}$. For the low-polydispersity polymer **1** with an average of 40 side-chain chromophores, we obtained $\gamma = 14500 \pm 600 \times 10^{-36} \text{ esu}$, which is about 40 times the value of a single chromophore. We conclude that there are no interactions between the side-chain chromophores in solution. In thin films, the third-order nonlinearity $\chi^{(3)}$ was measured to be about 100 times that of fused silica. An extrapolation of $\chi^{(3)}$ from γ gives a $\chi^{(3)}$ value of about 170 times that of fused silica. This reduction in the expected $\chi^{(3)}$ has already been observed in poly(triacetylene) thin films.¹⁸ Intermolecular interactions in the solid-state reduce the third-order nonlinearity $\chi^{(3)}$ of thin films.

In summary, we have synthesized *via* high-yielding procedures the new ROMP polymer **1** which features good processability and promising optical and nonlinear optical properties. A high off-resonance third-order nonlinearity $\chi^{(3)}$ was measured in a thin film of **1**, with an average of 40 chromophore-containing repeat units, which was about 100 times the nonlinearity of fused silica. Polymer **1** has a significant d_{33} value, comparable to those of other polymers containing highly conjugated donor–acceptor chromophores,^{19–21} and it is easily oriented under corona poling conditions. Although the relatively low glass transition temperature does not allow the orientation to be completely frozen during corona poling, being detrimental to its long-term stability, this might be very interesting for applications in photorefractivity and dynamic holography, where the dipolar chromophores must react to small local changes in the electric field. The general strategy applied to the synthesis of **1** should readily allow further adjustment and optimisation of properties, such as viscosity, T_g , SHG and THG, in future work by varying the time of polymerisation, the linker length between the polymer backbone and the photoactive chromophore and the NLO-chromophore itself.

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