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Nonlinear optical active poly(adamantyl methacrylate-methyl vinyl urethane)s functionalised with phenyltetraene-bridged chromophore

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Abstract

Nonlinear optical (NLO) poly(adamantyl methacrylate-methylvinylurethane)s were prepared by functionalisation of adamantyl methacrylate vinyl isocyanate precursor polymers. A modified pathway to obtain phenyltetraene-bridged chromophore was worked out. Poled films of the polymers show high and very stable NLO response even at elevated temperatures.

Keywords: Methyl vinyl urethanes; Nonlinear optics; Second-harmonic generation

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1. Introduction

Polymers with high second-order nonlinear optical (NLO) properties are of considerable interest for the development of high-speed light modulators and switches. In order to be useful, several properties have to be optimized: the second-order response must be high, this response has to be stable at elevated temperatures and optical loss has to be minimized [1]. Therefore, research has been focussed on high glass transition (T_g) polymers that combine high NLO properties with good thermal stability. High T_g chromophore functionalised polyimides [2–10] and maleimide based polymers [11–14] are an approach to fulfill the necessary requirements.

Here, we report on the synthesis of a chromophore with extremely high nonlinearity, based on a novel substituted dicyanomethylen-dihydrofuran acceptor. To obtain this monohydroxyalkyl chromophore, we worked out a modified procedure of the method described by Dalton et al. [15] for a dihydroxyalkyl chromophore. Poly(adamantyl methacrylate-methyl vinyl isocyanate) has been chosen as polymer backbone wherein two different concentrations of the cyanate groups were incorporated. The precursor polymers were then transformed into chromophore urethane copolymers with second-order NLO properties, after poling of spincoated films. The polymers investigated show T_gs of 152 and 153 °C. Although the glass transition temperature is not in the range of the high T_g polymers mentioned above, the stability of the NLO effect is high after a prolonged time of heating at 80 °C.

2. Experimental

2.1. Materials and instrumentation

2.1.1. Materials

All starting materials were purchased from Acros Organics, Fluka, Merck or Aldrich and were used as received, unless otherwise noted. Tetrahydrofuran (THF) and dioxane were dried over a Na/K alloy.

2.1.2. Instrumentation

^{1}H- and ^{13}C NMR measurements were carried out on a Bruker Avance 300 MHz. The number average molecular weights ($\bar{M}_n$) and polydispersities ($\bar{M}_w/\bar{M}_n$) were measured by gel permeation chromatography (GPC) with a Waters HP-GPC with a tunable absorbency detector and a differential refractometer, using THF as eluent towards polystyrene standards. The UV–VIS spectra were recorded on a Varian Cary 400. Glass transition temperatures of the polymers were determined by differential scanning calorimetry

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(DSC) on a DSC 7 from Perkin Elmer with a heating rate of 15 °C min^{-1}.

2.2. Second-harmonic generation measurements

Polymer films were spincoated from a cyclohexanone solution onto ITO glass substrates, yielding high quality films. To remove any residual solvent, they were dried for at least 48 h under vacuum at a temperature about 10 °C below the boiling point of the spincoating solvent. To prevent bleaching of the chromophore during poling, the films were coated with a layer of poly vinyl alcohol. Next, they were poled by a corona discharge at a temperature 10 °C below T_g. After poling, the poly vinyl alcohol layer was removed with water. Fundamental light of 1064 nm from a Nd/YAG laser was used for the second-harmonic generation (SHG) measurements. A quartz crystal was used as reference ($d_{11} = 0.3$ mp V^{-1}). Before each measurement, deposited charges from corona poling were wiped from the surface with methanol.

2.3. Synthesis of chromophore **6** (Scheme 1)

2.3.1. Synthesis of 1,5,5-trimethyl-3-methylenecyclohexene (**1**)

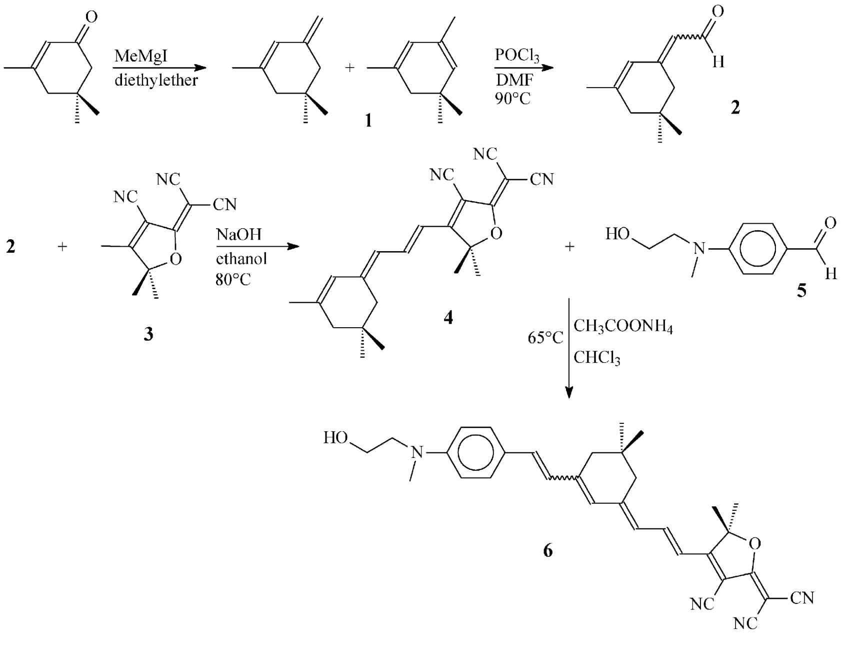
To a solution of 69.0 g (0.5 mol) of isophorone in 1500 ml of dry diethylether, a solution of methyl magnesiumiodide (200 ml of a 3 M solution in diethylether) was added dropwise at −5 °C under stirring and argon atmosphere. The reaction mixture was stirred for 24 h at room temperature, then treated by dropwise addition of a mixture of acetic acid/water (0.25:0.75 v/v) until pH 4, under cooling and stirring. The water layer was removed and extracted twice with n-hexane. The combined organic layers were dried over $MgSO_4$. After removing the solvent by evaporation under reduced pressure, the product was purified by column chromatography (silicagel; eluent: hexane/ethylacetate (95:5 v/v)) and resulted in a mixture of *cis/trans* (36/64) as a colourless oil.

Yield: 58.2 g (86%); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *trans* $\delta = 5.95$ (s, 1H), 4.73 (d, 2H), 2.01 (s, 2H), 1.85 (s, 2H), 1.75 (m, 3H), 0.91 (s, 6H); *cis* $\delta = 5.55$ (s, 1H), 5.01 (s, 1H), 1.92 (s, 2H), 1.75 (m, 6H), 0.91 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): $\delta = 142.4$, 136.0, 133.6, 128.5, 128.2, 123.0, 120.6, 108.1, 43.7, 43.1, 42.7, 30.9, 29.5, 27.2, 22.8, 22.4, 20.3.

2.3.2. Synthesis of (3,5,5-trimethylcyclohex-2-en-1-ylidene)acetaldehyde (**2**)

To 100 ml of cooled dimethylformamide, 40.4 ml of phosphorous oxychloride was added dropwise under stirring. After complete addition, the mixture was stirred for 2 h at 0–5 °C, followed by the dropwise addition of 58.2 g (0.43 mol) of compound **1**. The resulting mixture was heated for 3 h at 90 °C. After cooling down, the reaction mixture was poured in a saturated sodium acetate/water solution under stirring. After 1 h stirring, the mixture was extracted with dichloromethane (3 times). The combined organic layers were dried over $MgSO_4$. After removal of the solvent under reduced pressure, the product was purified by column chromatography (silicagel; eluent: CH_2Cl_2/EtAc (9:1 v/v)) and yielded 19.4 g (28%) of a yellow oil as a mixture of *cis/trans* (57/43).

^{1}H NMR (300 MHz, $CDCl_3$, ppm): *trans* $\delta = 9.85$ (d, 1H, $J = 8.1$ Hz), 6.95 (s, 1H), 5.55 (d, 1H, $J = 8.1$ Hz), 2.10 (s, 2H), 2.02 (s, 2H), 1.90 (s, 3H), 1.05 (s, 6H); *cis* $\delta = 9.75$



Scheme 1. Synthesis of chromophore **6**.

(d, 1H, $J = 8.4$ Hz), 6.05 (s, 1H), 5.75 (d, 1H, $J = 8.4$ Hz), 2.65 (s, 2H), 2.02 (s, 2H), 1.85 (s, 3H), 1.05 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): $\delta = 191.2$, 190.1, 157.3, 157.2, 148.8, 125.5, 125.2, 123.7, 45.7, 38.4, 28.1, 24.8, 1.1.

*2.3.3. Synthesis of 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (**3**)*

The synthesis was carried out as described in a previous paper [16], starting from 3-hydroxy-3-methyl-2-butanone (10.0 g, 100 mmol) and 2 equiv. of malononitrile in the presence of $LiOC_2H_5/C_2H_5OH$.

Yield = 17.8 g (90 %); m.p. = 197.5 °C

*2.3.4. Synthesis of [3-cyano-5,5-dimethyl-4-[3-(3,5,5-trimethylcyclohex-2-en-1-ylidene)prop-1-enyl]furan-2(5H)-ylidene]malononitrile (**4**)*

In a round bottomed flask, 4.85 g (0.03 mol) of compound **2** was mixed with 5.9 g (0.03 mol) of **3** in 150 ml of absolute ethanol together with 0.23 g (6 mmol) of sodiumhydroxide. After 3 h of stirring at 80 °C, the mixture was stored in the refrigerator overnight. The crystals formed were removed by filtration, purified by column chromatography (silicagel; eluent: CH_2Cl_2) and finally recrystallised from methanol yielding 3.45 g (35%) of purple crystals; m.p. 215–218.4 °C.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 8.01$ (dd, 1H, $J = 11.7$, 15.4), 6.27 (d, 1H, $J = 15.4$), 6.19 (d, 1H, $J = 11.7$), 2.35 (s, 2H), 2.15 (s, 2H), 1.93 (s, 3H), 1.75 (s, 6H), 1.05 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): $\delta = 176.1$, 174.0, 154.7, 150.1, 144.6, 126.4, 125.7, 115.7, 112.3, 111.5, 111.4, 97.1, 95.3, 56.0, 45.8, 39.5, 31.7, 28.3, 26.4, 24.9; MS: $m/z = 345$ (M^+), 330 ($M^+ - CH_3$), 315 ($M^+ - C_2H_6$).

*2.3.5. 4-[N-(2-hydroxyethyl)-N-methylamino]benzaldehyde (**5**)*

4-[*N*-(2-hydroxyethyl)-*N*-methylamino]benzaldehyde (**5**) was prepared as described in a previous paper [17].

*2.3.6. Synthesis of chromophore (**6**)*

A mixture of 3.63 g (0.02 mol) of **5** together with 7.0 g (0.02 mol) of **4** and 0.65 g (8 mmol) of ammonium acetate in 140 ml of $CHCl_3$ was heated under stirring for 60 h at 65 °C. At ambient temperature, the reaction mixture was washed twice with water. After drying over $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by column chromatography (silicagel; eluent: CH_2Cl_2/EtAc (9:1 v/v)). Pure chromophore was obtained as a mixture of *cis/trans* (21/79) after recrystallisation from acetonitrile, yielding 1.0 g (10%) of dark-blue crystals; m.p. 225.4–227.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): *tran*: $\delta = 8.01$ (dd, 1H, $J = 12.1$, 14.8), 7.38 (d, 2H), 6.85 (m, 4H), 6.34 (d, 1H, $J = 12.1$), 6.26 (d, 1H, $J = 14.8$), 3.85 (t, 2H), 3.55 (t, 2H) 3.01 (s, 3H), 2.35 (m, 4H), 1.75 (s, 6H), 1.05 (s, 6H); *cis*: $\delta = 8.01$ (dd, 1H, $J = 12.1$, 14.8), 7.41 (d, 2H), 6.81 (m, 4H), 6.20 (d, 1H, $J = 14.8$), 6.12 (d, 1H, $J = 12.1$), 3.85 (t, 2H), 3.55 (t, 2H) 3.01 (s, 3H), 2.35 (m, 4H), 1.75 (s, 6H), 1.05 (s, 6H); UV ($CDCl_3$): $\lambda_{max}(\varepsilon) = 666$ nm (27,400 l mol^{-1} cm^{-1}); UV (THF): $\lambda_{max}(\varepsilon) = 654$ nm (36,950 l mol^{-1} cm^{-1})

2.4. Polymer synthesis (Scheme 2)

*2.4.1. Synthesis of methyl vinyl isocyanate (**7**)*

Compound **7** was prepared via a Curtius reaction from methacryloyl azide and was redistilled prior to use [18].

B.p. = 67–69 °C, IR: 2267.1 cm^{-1} (–N=C=O).

*2.4.2. Synthesis of adamantyl methacrylate (**8**)*

Methacryloylchloride, 8.3 g (78.8 mmol) was added dropwise under cooling to a stirred solution of 10.0 g (65.7 mmol) of 1-adamantanol and 12.0 g (119.0 mmol) of triethylamine in 100 ml of dichloromethane. After 3 days of stirring in the refrigerator, the organic layer was treated with a bicarbonate-solution followed by water. After drying over $MgSO_4$ and removal of the solvent under reduced pressure, followed by column chromatography (silicagel; eluent: CH_2Cl_2), pure **8** was obtained as an oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 6.03$ (s, 1H), 5.47 (q, 1H), 2.25 (s, 9H), 1.85 (s, 3H), 1.65 (s, 6H).

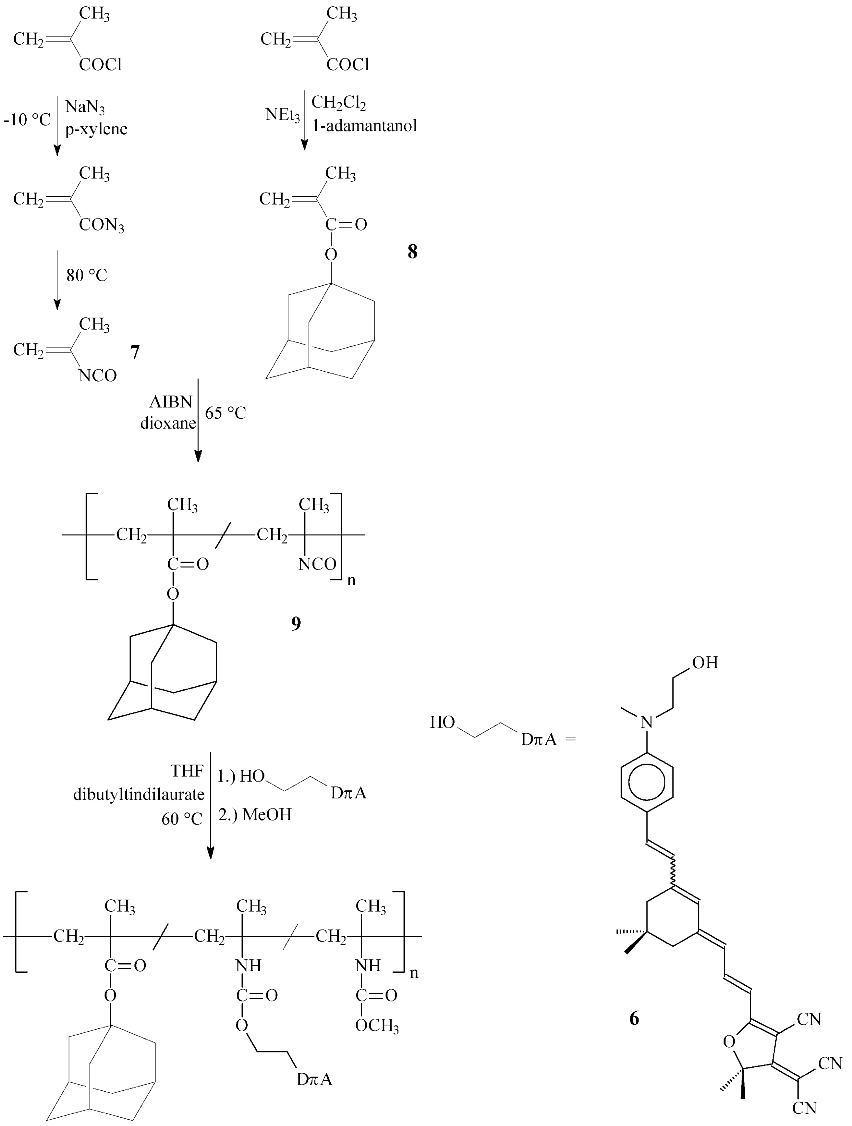
*2.4.3. Synthesis of poly(adamantyl methacrylate-methyl vinyl isocyanate) (**9**)*

The copolymerisations were carried out in a mole ratio of adamantyl methacrylate/methyl vinyl isocyanate 85/15 ($\mathbf{P_1}$) and 80/20 ($\mathbf{P_2}$) in 20 ml of dioxane solution, under argon atmosphere at 65 °C in the presence of 1 wt% of 2,2′-azobisisobutyronitrile (AIBN) for 24 h. The resulting copolymer solution was cooled, precipitated in dry diethylether under argon atmosphere, filtered and finally dried under reduced pressure. Yields up to 70% were obtained.

2.5. Chromophore functionalisation of precursor polymers (Scheme 2)

A general procedure is as follows: prior to use, the chromophore, copolymers and solvent were thoroughly dried. Chromophore **6** and copolymers $\mathbf{P_1}$ and $\mathbf{P_2}$ were dissolved in THF (ratios given in Table 1) in a sealed reaction vessel. The mixture was purged with argon followed by the addition of dibutyltin dilaurate in appropriate concentration. After 48 h of stirring at 60 °C, methanol (50 μl) was added and heating was continued for 48 h. After cooling, the polymer was precipitated in methanol, filtered and dried under reduced pressure. This procedure was repeated until the filtrate was colourless.

Several functionalisations were carried out in this way. Data from GPC-, DSC-, and UV–VIS-measurements are given in Table 1.



Scheme 2. Synthesis of precursor polymer and functionalisation.

3. Results and discussion

3.1. Synthesis of chromophore *6*

To get access to a mono-hydroxyalkyl CLD-type chromophore, a modified procedure of Dalton's reported method [15] on the synthesis of di-hydroxyalkyl CLD-type chromophores was used. While Dalton et al. worked out a step by step route to synthesise the phenyltetraene-bridged chromophore, we started synthesis by transforming isophorone into his methylene derivative by reaction with methyl magnesiumiodide followed by a Vilsmeyer reaction.

Table 1
Properties of chromophore-functionalised polymers **P_1**-5 wt% and **P_2-13 wt%** as well as the concentration of the different components for functionalisation

Polymer	mol%[a] NCO-groups	# mg Polymer	# mg Chrom. **6**	# μl dibutyltin dilaurate	# ml THF	$\bar{M}_n$[b] (g mol^{-1})	$\frac{\bar{M}_w}{\bar{M}_n}$	T_g[c] (°C)	wt%[d] (%)
P_1-5 wt%	6.3	299	114	150	15	49930	1.52	153	5.3
P_2-13 wt%	11.9	360	227	190	20	27290	1.68	152	13

[a] Measured by ^{1}H NMR from the methyl urethane copolymer.
[b] Measured by GPC in THF, towards polystyrene standards.
[c] Glass transition temperature, measured by DSC.
[d] Weight percent of NLO-dye in polymer from spectrophotometric measurements.

In the next step, reaction with 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran **3** under basic conditions resulted in acceptor molecule **5** which was coupled with donor aldehyde **5** to form chromophore **6**. This synthetic way had the advantage that the hydroxyl group of **5** not had to be protected by a silyl- or acetyl-group.

3.2. Synthesis of precursor copolymers

In a first attempt to synthesize a functionalised copolymer, the chromophore was transformed into his methacrylate monomer by reaction with methacryloyl chloride under basic conditions. Attempts, however, to make copolymers with adamantyl methacrylate failed.

Therefore, another route was developed. Adamantyl methacrylate was polymerised with methyl vinyl isocyanate in different concentrations under radical conditions to give precursor polymers $\mathbf{P_1}$ and $\mathbf{P_2}$. Adamantyl methacrylate could easily be obtained by reaction of methacryloyl chloride and 1-adamantanol in the presence of triethylamine. Column chromatography resulted in pure monomer.

Methyl vinyl isocyanate was made available via a Curtius reaction from methacryloyl azide [18].

The precursor polymer compositions were measured by ^{1}H NMR of the methyl urethane derivative. By choosing the integrated value at 2.15 ppm corresponding to 9 H of the adamantyl-monomer as a reference, the number of protons at 3.6 ppm corresponding to the methylurethane-unit, allowed us to calculate the concentration of incorporated isocyanate monomer. The methyl urethane derivatives were obtained by treatment of the precursor polymers with methanol in the presence of dibutyltin dilaurate as catalyst. Copolymers $\mathbf{P_1}$ and $\mathbf{P_2}$ contained 6.3 and 11.9 mol% of isocyanate-groups, respectively. GPC-analysis of the methyl urethane derivatives of $\mathbf{P_1}$ and $\mathbf{P_2}$ showed molecular weights ($\bar{M}_n$) of, respectively, 42,700 and 30,450 g mol^{-1}. Both methyl urethane derivatives showed a polydispersity ($\bar{M}_w/\bar{M}_n$) of 1.4.

3.3. Functionalisation of copolymers

Precursor polymers $\mathbf{P_1}$ and $\mathbf{P_2}$ were partly functionalised with mono-hydroxyalkyl chromophore under the same reaction conditions as for the above mentioned methyl urethane copolymers. The remaining isocyanate groups were converted into a methyl urethane group by reaction with methanol in a second step. The structure of the resulting terpolymer is given in Scheme 2. Absorption measurements of the functionalised polymers $\mathbf{P_1}$ and $\mathbf{P_2}$ in THF allowed us to calculate the weight percent (wt%) of NLO-dye incorporated in the copolymers. The same values were obtained by use of ^{1}H NMR in CDCl$_3$. The wt%, molecular weights, polydispersities and T_gs are given in Table 1. No decomposition temperatures (T_d) below 200 °C were observed.

Table 2
Wavelength of maximum absorption (λ_{max}) and second-harmonic coefficients ($d_{33}(2\omega)$ and $d_{33}(0)$) of spincoated films of chromophore functionalised polymers

Polymer	λ_{max} [a] (nm)	$d_{33}(2\omega)$ [b] (pm V^{-1}	$d_{33}(0)$ [c] (pm V^{-1})
$\mathbf{P_1}$-5 wt%	660.2	54.2	18.0
$\mathbf{P_2}$-13 wt%	655.8	30.9	10.0

[a] Measured after corona poling.
[b] Measured at 1064 nm.
[c] Extrapolated to zero frequency using the two-level model [19].

The glass transition temperatures of $\mathbf{P_1}$ (5.3 wt% chromophore) and $\mathbf{P_2}$ (13 wt% chromophore) are, respectively, 12 and 11 °C higher than for poly(adamantanyl methacrylate) ($T_g = 141$). Although T_g*s* around 150 °C were observed, a high and very stable NLO effect is present.

3.4. Second harmonic generation measurements

The second harmonic generation results from corona poled films are summerised in Table 2. The polymers showed $d_{33}(2\omega)$ values of 54.2 and 30.9 pm V^{-1} for **$\mathbf{P_1}$-5 wt%** and **$\mathbf{P_2}$-13 wt%**, respectively (measured at 1064 nm of induced light), leading to high off-resonant values [18] of 18.0 and 10.0 pm V^{-1}. Pure trans chromophore would have given higher SHG effects but as a mixture of *cis*/*trans* was obtained, the values are lower than expected. Off-resonant values of 18 and 10 pm V^{-1} for chromophore loads of 5 wt%, respectively, 13 wt% could be measured. These results tend to a polymerstructure which is randomly arranged. Blocky copolymers would have given much lower $d_{33}(0)$ values because of chromophore interactions, which is not the case.

Furthermore, a SHG-effect of 18.0 pm V^{-1} can be compared with the results obtained for chromophore

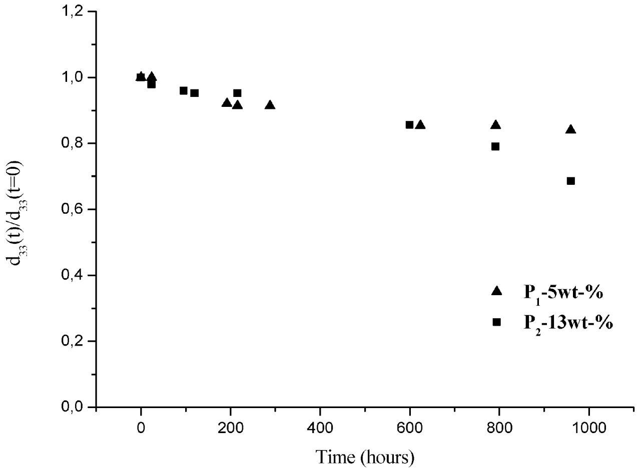


Fig. 1. Plot of the normalized SHG-effect as a function of time at 80 °C under nitrogen atmosphere.

functionalised high T_g polyimides synthesised by Luping Yu et al. [4,20–22] and others [5,7–9]. Off-resonant values up to 27 pm V^{-1} are reported. Also comparable values are obtained with chromophore functionalised high T_g polymaleimides [11,14,23] possessing off-resonant values up to 23 pm V^{-1}. The T_gs of **P_1-5 wt%** and **P_2-13 wt%** are much lower than those obtained with high T_g polyimides and polymaleimides but the fact that the remaining NLO-response is high after heating for a prolonged time, makes these materials interesting for the development of devices.

A plot of $d_{33}(t)/d_{33}(t=0)$ versus time at a temperature of 80 °C under nitrogen atmosphere, is shown in Fig. 1. It can be seen that the second harmonic signal does not significantly changes over 960 h, since 68–84% of the nonlinearity remained.

In summary, we have shown that chromophore functionalised methyl vinyl urethane copolymers possess a fairly high NLO response for a low chromophore content even at elevated temperatures.

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