Reactions on Vinyl Isocyanate/Maleimide Copolymers: NLO-functionalized Polymers with High Glass Transitions for Nonlinear Optical Applications

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ABSTRACT: A new reactive copolymer system with high, but still variable glass-transition temperatures was synthesized. This was accomplished by copolymerizing various N-substituted maleimides with methylvinyl or vinyl isocyanate, so that a polymer with a 1:1 composition of the two monomers is obtained. Further functionalization is then possible with any nucleophile known from comparable low molecular weight reactions. With different substituents attached to the imide-ring, T_g can be adjusted between 120 and 210 °C. Two effects of the substituent at the imide nitrogen are observed. Bulky groups reduce the mobility of the chain and lead to high T_g values. A similar tendency is found for smaller, less flexible substituents. In this case, the inter- and intramolecular forces of hydrogen-bonding (urethanes) contribute to the effects for high T_g's. The potential of these copolymers was highlighted here for NLO chromophores. A variety of different NLO chromophores was attached to the polymer backbone by reaction of a hydroxyalkyl-containing chromophore with the isocyanate groups, thereby forming urethane linkages between chromophore and polymer. The polymers functionalized in this way show nearly unchanged glass transition temperatures and offer thus the possibility to prepare NLO polymers with high T_g values and good solubility. It is important that even base labile NLO chromophores and systems labile to radical conditions can be fixed easily. The advantage of this system is highlighted by the fixation of NLO chromophores with tricyanovinyl (**C2**), tricyanochinodimethane (**C3**) and heterocyclic acceptors (**C4**). With one of these systems a d_{33} value of 53 pm/V could be obtained for a loading with only 12 wt % of chromophore.

Introduction

Second-order nonlinear materials may play an important role for integrated optical telecommunication components such as switching and routing devices. NLO-chromophore-functionalized polymers are of high interest due to their ultrafast electronic response (f_{BW} 60 GHz),[1] their relatively large linear electrooptic coefficients (r_{33} 55 pm/V at 1300 nm),[2] and their simple processing techniques.[3,4] In addition to the molecular hyperpolarizability β of the embedded NLO chromophore, the magnitude of the macroscopic nonlinear effect is determined by the number density of chromophores within the polymer and their degree of noncentrosymmetrical orientation. The net polarization is usually achieved by aligning the chromophore dipoles in a high static electrical field, while the polymer is heated to a state of elevated mobility close to its glass transition temperature (T_g). A major difficulty with these materials is the long term relaxation of the NLO chromophores back into the isotropic state. The common method to suppress this reorientation is to synthesize rigid polymer backbones exhibiting high glass-transition temperatures. However, with increasing T_g (and/or higher chromophore density) solubility- and phase-separation problems become more likely to appear. Since there are a lot of requirements to obtain optimal properties, it is difficult to combine these in only one system. On a chemical basis, this requires a very variable system, that allows modifications with respect to, e.g., glass transition or chromophore, in a simple manner.

Most of the polymer systems designed for nonlinear optical (NLO) applications in the last years are synthesized either by radical polymerization of chromophore containing monomers or by step growth reactions yielding polyesters, polyurethanes or polyimides.[5−10] However, each of these two strategies has some major disadvantages that limit their use. In radical polymerizations it is observed that chromophores act as retarder or inhibitor and thereby decrease yields and molecular weights. In special cases promising NLO chromophores are not compatible with the conditions of radical polymerizations.[11−12] In the case of the step-growth reaction, the monomers have to survive the reaction conditions (either high temperatures or acidic or basic conditions).

Compared to these two possibilities described, there exists one alternative, that is described only in fewer papers (for a selection of newer papers, see refs 11−15). A polymer analogous reaction allows it to attach NLO chromophores to the backbone of a reactive precursor polymer without exposing the chromophores to aggressive conditions. The polymer chain formed in a polymerization step before is not influenced during the polymerization by any chromophores present in the reaction mixture. This concept defines an elegant

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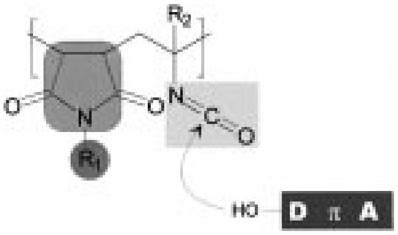
Scheme 1. General Functionalization Scheme of the Polymer Analogous Reaction of Hydroxy-Functionalized NLO-Chromophores to the Backbone of a Precursor Polymer



strategy to a great variety of NLO polymers from one precursor polymer.

In this paper, we present the synthesis of a novel polymer system prepared by radical copolymerization of vinyl isocyanates with N-substituted maleimides.[15−17] In a second step the NLO chromophores are introduced by reaction of the polymeric isocyanates with hydroxyl or amino groups linked via an alkyl spacer to the end of the chromophores, thus forming a urethane linkage between polymer chain and chromophore.

Results and Discussion

To fulfill the requirements of a useful NLO material (e.g. high glass-transition temperatures, good solubility, high loading with NLO chromophores), the different structural parts of the polymer were selected for the following reasons. The different N-substituted maleimides were used because the rotation around the C−C bonds in the five-membered ring structure is prevented. This leads to a more rigid polymer main chain resulting in higher glass transition temperatures (in copolymers with styrene and *N*-phenylmaleimide T_g's of about 235 °C have been found). In addition to the stiff polymer chain the substituents at the imide position of the maleimides allow a systematic shift of T_g between 80 and 210 °C parallely influencing the solubility. The vinyl isocyanates as comonomer units are used to introduce the reactive isocyanate groups into the polymer chain. They are converted into urethane linkages after the polymer analogous reaction with NLO chromophores containing hydroxyalkyl- or aminoalkyl spacers. For a schematic illustration of the copolymers see Scheme 1.

A. Synthesis. The maleimide monomers are accessible via two different synthetic routes depending on the substituent at the imide nitrogen (for an alternative route using furan as protecting group see ref 17). The most common method for preparing maleimides is the reaction of a primary amine with maleic anhydride to the corresponding maleamic acid, which is followed by the cyclization to the imide with acetic anhydride.[18] The temperatures needed for this second step depend on R_1 (70−120 °C). For aliphatic amines generally higher temperatures are needed. The pentafluorophenyl derivative gives almost quantitative yields at about 50 °C. More bulky substituents such as diphenylmethyl or trityl are introduced via the corresponding halide, which is converted to the desired product with the silver salt of the unsubstituted maleimide.[19] Vinyl isocyanates are known in the literature and are usually prepared by a Curtius rearrangement reaction of an acrylic or methacrylic acid chloride.[20] The acid chloride is first converted into the azido derivative with sodium azide in a two-phase system of water and toluene (vinyl isocyanate) or xylene (methylvinyl isocyanate). The Curtius rearrangement takes place at about 70 °C, and after nitrogen is split off, the free isocyanate is obtained. For an overview of all used monomers see Scheme 2.

The copolymerization of the two monomers is performed in toluene or dioxane (to keep precursor polymers in solution—see Experimental Part) at 70 °C with AIBN as radical initiator. After a polymerization time of about 16 h, the polymers can be precipitated in dry inert solvents. The copolymerization of maleic anhydride with vinyl as well as methylvinyl isocyanate is known to be alternating.[21−23] The same tendency can be found for the copolymerization of maleimide derivatives with vinyl or methylvinyl isocyanate, especially when both monomers are used in equimolar amounts (slight excess of isocyanate component—see Experimental Part). The elemental analysis of all polymers showed a 1:1 composition of comonomers, and so the polymers can be regarded as almost alternating copolymers with one reactive isocyanate group per repeating unit. All synthesized reactive copolymers are summarized in Table 1. Their structure is presented in Scheme 3.

To test the reactivity of isocyanate groups in the polymer, a functionalization with various nucleophiles was tried. As can be seen from Figure 1, both alcohols and amines can be used for a quantitative conversion of the isocyanate groups (the properties of the resulting polymers are compiled in Tables 2−4). However the conditions needed are very different. With butyl- or dibutylamine the reaction is completed after some minutes (50 °C, molar ratio amine to isocyanate 1:1). For methanol the reaction is not yet completed after 2.5 h, if the same conditions (equimolar) are used. A complete conversion within about 1 day can however be achieved, if a large excess (100 mol per mole of isocyanate) is used. For methanol or ethanol this large excess is obviously no problem, and unreacted alcohol is easily removed during the workup of the polymer (precipitation). For long chain alcohols such as octadecyl alcohol (see Table 3) or the NLO chromophores **C1**−**C4** (see Scheme 2 and Table 4) the use of a large excess is, however, not desirable, because the unreacted alcohol cannot be easily removed from the functionalized polymer. In addition the NLO chromophores are often only available in small quantities. Therefore their conversion with the isocyanate groups has to be catalyzed with dibutyltin dilaurate (see Figure 2). With this catalyst a nearly quantitative conversion can be achieved within 1−2 days for equimolar systems.

Despite the lower reactivity of hydroxyl groups as compared to amino groups we used only hydroxyl group containing NLO chromophores for the following reasons: at first, hydroxyl functionalized NLO chromophores are synthetically more easily accessible; second, amino groups react with some of the strong, base labile acceptor groups in modern NLO chromophores. A typical example for this are the chromophores with tricyanovinyl or tricyanochinodimethane groups (**C2** and **C3**), which do react with amine groups, but can be functionalized with hydroxyl groups. In addition these NLO chromophores decompose during radical polymerization conditions.[11,12] The precursor polymers **Pr1** to **Pr11** are however perfect for their fixation.

In this paper we will present results for four different NLO-chromophores (**C1**−**C4**). Disperse red (**C1**) is commercially available and was used to test the reaction conditions. **C2** and **C3** are representatives of highly

Scheme 2. Summary of All Used Monomers and Chromophores

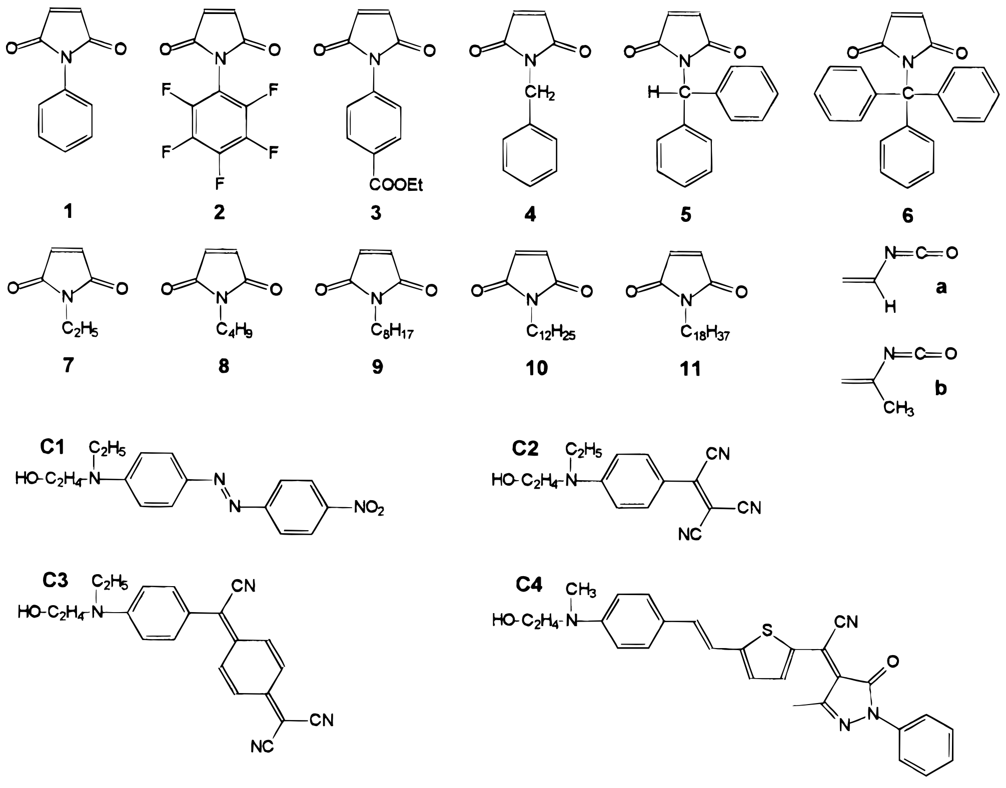


Table 1. Structures, Conversions, Molecular Weights and Characterization of the Reactive Precursor Polymers Pr1−Pr11[b]

no.	R$_1$ (imide component)	R$_2$ (isocyanate component)[a]	yield	M_n	anal. found	anal. calcd
Pr1	phenyl	CH$_3$	92.5	15 000	C, 65.65; H, 5.03; N, 10.74; O, 18.58	C, 65.62; H, 4.72; N, 10.93; O, 18.73
Pr2	pentafluorphenyl	CH$_3$	91	17 800	C, 48.89; H, 2.33; N, 8.23	C, 48.57; H, 2.04; N, 8.09
Pr3	(4-carboxyethyl)phenyl	CH$_3$	92	10 700	C, 62.01; H, 4.80; N, 8.46; O, 24.73	C, 62.19; H, 4.91; N, 8.53; O, 24.37
Pr4a	benzyl	CH$_3$	80	25 700	C, 66.34; H, 5.50; N, 10.13; O, 18.03	C, 66.66; H, 5.22; N, 10.36; O, 17.76
Pr4b	benzyl	H	80	31 400	C, 65.37; H, 4.50; N, 10.86; O, 19.27	C, 65.63; H, 4.69; N, 10.94; O, 18.74
Pr5a	diphenylmethyl	CH$_3$	91	54 800	C, 72.77; H, 5.40; N, 7.91; O, 13.92	C, 72.82; H, 5.23; N, 8.09; O, 13.86
Pr5b	diphenylmethyl	H	87	62 900	C, 72.44; H, 4.33; N, 8.61; O, 14.62	C, 72.29; H, 4.82; N, 8.43; O, 14.46
Pr6a	trityl	CH$_3$	75	14 200	C, 76.03; H, 5.33; N, 6.49; O, 12.15	C, 76.76; H, 5.25; N, 6.63; O, 11.36
Pr6b	trityl	H	72	18 600	C, 76.38; H, 4.74; N, 7.07; O, 11.81	C, 76.47; H, 4.90; N, 6.86; O, 11.76
Pr7	ethyl	CH$_3$	89	28 200	C, 57.63; H, 5.99; N, 13.47; O, 22.91	C, 57.69; H, 5.81; N, 13.45; O, 23.05
Pr8	butyl	CH$_3$	82	24 500	C, 60.89; H, 6.95; N, 11.96; O, 20.20	C, 61.00; H, 6.82; N, 11.86; O, 20.32
Pr9	octyl	CH$_3$	84	40 000	C, 65.75; H, 8.51; N, 9.48; O, 16.26	C, 65.73; H, 8.27; N, 9.58; O, 16.42
Pr10	dodecyl	CH$_3$	68	26 300	C, 69.56; H, 8.83; N, 7.95; O, 13.66	C, 69.28; H, 8.67; N, 8.09; O, 13.68
Pr11	octadecyl	CH$_3$	88	29 700	C, 72.42; H, 10.88; N, 6.34; O, 10.36	C, 72.18; H, 10.25; N, 6.48; O, 11.09

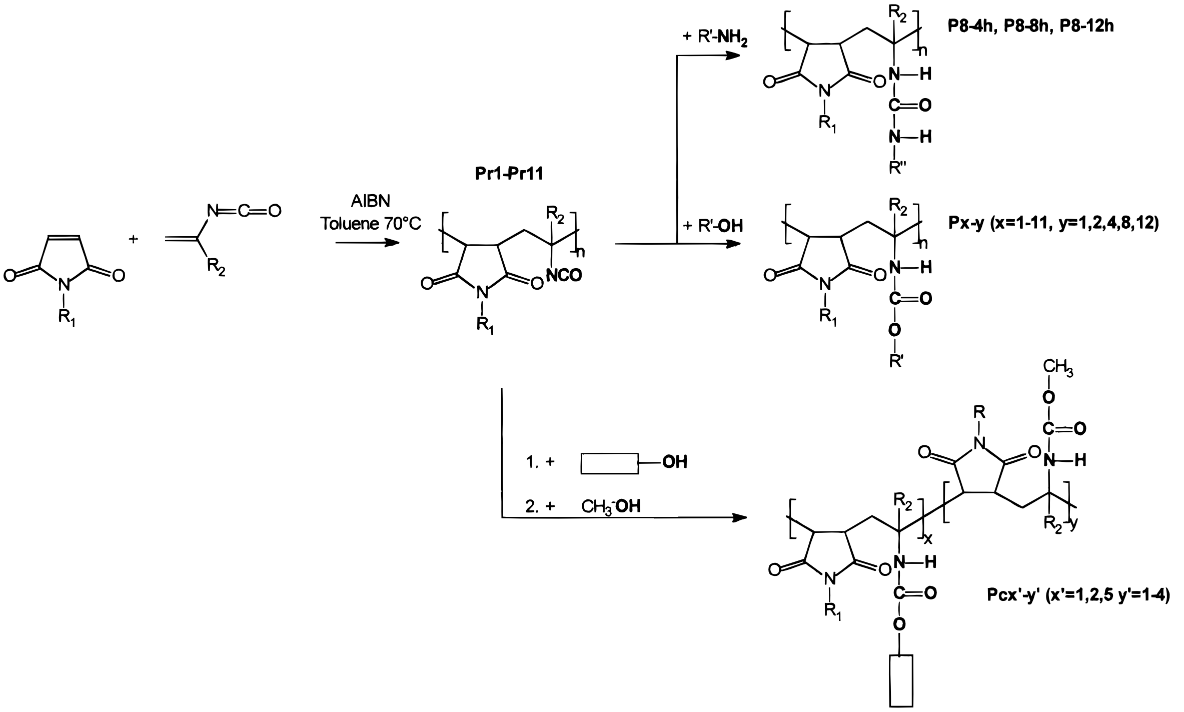
[a] Key: H, vinyl isocyanate; CH$_3$, methylvinyl isocyanate. [b] The molecular weights were determined by GPC (gel permeation chromatography) compared to polystyrene after reaction of the polymers with methanol (see Table 2). All polymers were polymerized in toluene (exception: Pr4A and Pr6A in dioxane). Dry diethyl ether was used for precipitation (exception: hexane for Pr9; acetonitrile for Pr10; acetone for Pr11).

efficient NLO chromophores with tricyanovinyl and tricyanoquinodimethane acceptors, respectively.[24] **C2** is synthetically more easily available, while **C3** has the higher molecular hyperpolarizability ($\beta = 326 \times 10^{-50}$ C m^3/V^2 at 1064 nm, $\mu \cdot \beta = 0.125 \times 10^{-75}$ C^2 m^4/V^2), because the quinoid acceptor moiety in **C3** provides a more extended π-system. Chromophore **C4** consists of a π-bridge which constitutes a highly efficient conjugating unit in connection with strong donor and acceptor groups.[25,26] The pyrazolidene acceptor is a favorable alternative to tricyanovinyl ($\mu \cdot \beta = 0.146 \times 10^{-75}$ C^2 m^4/V^2). The heterocycle possesses enhanced chemical stability when compared to tricyanovinyl, especially toward nucleophiles, e.g., amino and hydroxy groups. Therefore **C4** is a good compromise between stability and NLO efficiency.

Chromophore **C3** was synthesized by reaction of commercially available (2-ethylanilino)-1-ethanol with 7,7,8,8-tetracyanoquinodimethane (TCNQ) in a modified two-step one-pot procedure similar to that described by Bespalov et al.[27] (see Scheme 4): the initially formed addition product need not be isolated but can be converted "in-situ" into a deeply colored dye by irradiation with UV light (366 nm). The product is conveniently isolated in pure form and good yield by filtering off the precipitate and washing.

Compound **C4** was obtained by reaction of 6-methyl-4-([(*E*)-2-(2-thienyl)-1-ethenyl]anilino)-1-hexanol (**14**) with the malononitrile **15** in ethanol (see Scheme 4). The addition product splits off HCN upon irradiation with UV light (254 nm), and the push−pull substituted chromophore is formed in moderate yield. The *E*-

Scheme 3. Reaction Scheme of Polymerization and Polymer Analogous Reaction with Alcohols, Amines and OH-Functionalized NLO-Chromophores



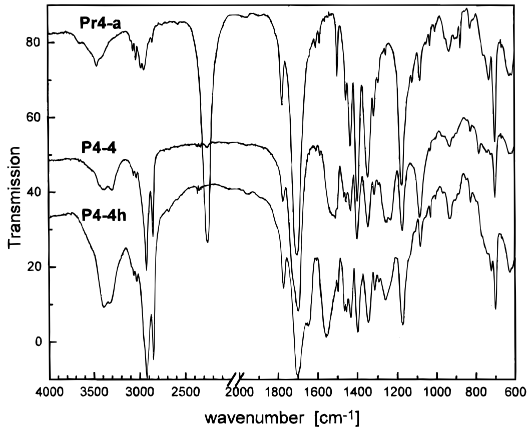


Figure 1. IR spectra for completeness of the polymer analogous reaction of polymer Pr4-a and the reaction with butanol and butylamine yielding the polymers P4−4 and P4−4h.

configuration of the central ethylenic unit is confirmed by ^{1}H NMR ($^{3}J = 15.9$ Hz).

The optimization of the reaction conditions for the fixation of NLO chromophores (and also the long chain alcohols of Table 3) was performed with disperse red (**C1**). As can be seen from Figure 2a the kinetics for the uncatalyzed reaction depends on the type of polymer used. Polymers prepared from vinyl isocyanate react more quickly, but the conversion seems to be limited to values of about 25% for unknown reasons. For polymers with methylvinyl isocyanate monomer units the reaction proceeds more slowly but does not saturate. Generally the reactivity decreases with increasing bulkiness of the substituent at the imide ring.

Figure 2b shows the effect of adding dibutyltin dilaurate as catalyst. In this way a conversion of about 80 mol % can be achieved within 2 days. The remaining isocyanate groups are reacted with methanol to obtain a unreactive polymer. The polymers functionalized with NLO chromophores and used for further investigation are compiled in Table 4. They are all prepared by a catalyzed reaction.

B. Properties of the Model Systems. To test the solid-state properties of the polymer backbones independent of the type of further functionalization, DSC measurements of the polymers **P1−1** to **P11−1** were performed. In these polymers the isocyanate groups of the precursor polymers **Pr1** to **Pr11** have been reacted with methanol. Representative DSC measurements are displayed in Figure 3. All results are compiled in Table 2.

All polymers are amorphous and display a glass transition. As can be seen from Figure 3 the T_g values increase on increasing the bulkiness of the substituent at the imide ring from 120 to 210 °C. For polymers with flexible alkyl chains lower T_g values are found (see also Table 3 for comparison). In addition polymers derived from methylvinyl isocyanate (R_2: CH_3) show about 20 °C higher T_g values than polymers derived from vinyl isocyanate (R_2: H). Judged from the polymer backbone these copolymers are thus promising for NLO polymers, as they combine high T_g values with a good solubility, necessary for spin coating.

It should be noted that there is another possibility to obtain polymers of this type with high T_g values.[17] Polymers with a very small substituent at the imide ring—methyl or especially hydrogen—give very high T_g values too. This is probably due to a more intensive hydrogen bonding. These polymers show however, a poor solubility and need *t*-BOC-protecting groups for solubilization and processing. They show the high T_g values only after deprotection.[17]

To test the influence of long alkyl chains on the glass transition temperature the polymers of Table 3 were prepared. Increasing the length of the alkyl chain leads in these polymers to a strong decrease of the T_g value (see Figure 4). This is probably a result of two effects working in parallel. Long alkyl chains act as intramolecular softeners. At the same time they hinder the

Table 2. Structures, Molecular Weights, Glass Transitions, and Characterization of the Model Polymers that Were Reacted with Methanol[b]

no.	R_1 (imide component)	R_2 (isocyanate-component)[a]	yield	M_n	T_g (°C)	anal.	
						found	calcd
P1−1	phenyl	CH_3	79	15 000	215	C, 61.75; H, 5.64; N, 9.41; O, 23.20	C, 62.49; H, 5.59; N, 9.72; O, 22.20
P2−1	pentafluorphenyl	CH_3	85	17 800	175	C, 47.73; H, 3.41; N, 7.84	C, 47.63; H, 2.93; N, 7.40
P3−1	(4-carboxyethyl)phenyl	CH_3	82	10 700	not det.	C, 59.43; H, 5.51 N, 7.40; O, 27.66	C, 60.00; H, 5.59; N, 7.77; O, 26.64
P4a−1	benzyl	CH_3	86	25 700	155	C, 64.15; H, 6.37; N, 8.78; O, 20.70	C, 63.57; H, 6.00; N, 9.27; O, 21.17
P4b−1	benyzl	H	81	31 400	133	C, 65.87; H, 4.95; N, 10.52; O, 18.66	C, 62.50; H, 5.55; N, 9.72; O, 22.23
P5a−1	diphenylmethyl	CH_3	88	54 800	186	C, 69.08; H, 6.02; N, 7.20; O, 17.70	C, 69.83; H, 5.86; N, 7.40; O, 16.91
P5b−1	diphenylmethyl	H	91	62 900	166	C, 72.88; H, 4.50; N, 8.21; O, 14.41	C, 69.23; H, 5.49; N, 7.69; O, 17.59
P6a−1	trityl	CH_3	65	14 200		C, 73.46; H, 5.67; N, 6.25; O, 14.62	C, 73.99; H, 5.77; N, 6.16; O, 14.08
P6b−1	trityl	H	73	18 600	215	C, 75.98; H, 4.95; N, 7.02; O, 12.05	C, 73.64; H, 5.45; N, 6.36; O, 14.55
P7−1	ethyl	CH_3	93	28 200	183	C, 54.67; H, 6.98; N, 11.26; O, 27.09	C, 55.46; H, 5.92; N, 11.76; O, 26.86
P8−1	butyl	CH_3	80	24 500	132	C, 58.10; H, 7.57; N, 10.37; O, 23.96	C, 58.19; H, 7.51; N, 10.44; O, 23.85
P9−1	octyl	CH_3	75	40 000	107	C, 62.96; H, 8.84; N, 8.35; O, 19.85	C, 62.94; H, 8.70; N, 8.64; O, 19.73
P10−1	dodecyl	CH_3	89	26 300	96	C, 66.83; H, 9.47; N, 7.20; O, 16.50	C, 66.29; H, 9.54; N, 7.36; O, 16.82
P11−1	octadecyl	CH_3	54	29 700	93	C, 69.98; H, 10.54; N, 5.92; O, 13.56	C, 69.79; H, 10.41; N, 6.03; O, 13.77

[a] Key: H, vinyl isocyanate; CH_3, methylvinyl isocyanate. [b] Molecular weights were measured by GPC compared to polystyrene standards. Glass transitions were determined by DSC (heating rate 10 K/min). Yields are the amounts of isolated polymer where isocyanates have been converted to 100%.

Table 3. Structures and Glass Transitions of Model Systems with Longer Alkyl Side Chains at Urethane or Urea Groups

no.	R_1 substituent (imide component)	R_2 (isocyanate component)	isocyanate converted with	T_g (°C)
P7−2	-ethyl	CH_3	ethanol	169
P7−4	-ethyl	CH_3	butanol	139
P7−8	-ethyl	CH_3	octanol	110
P7−12	-ethyl	CH_3	dodecanol	107
P7−18	-ethyl	CH_3	octadecanol	105
P8−2	-butyl	CH_3	ethanol	121
P8−4	-butyl	CH_3	butanol	110
P8−12	-butyl	CH_3	dodecanol	103
P8−18	-butyl	CH_3	octadecanol	98
P8−4h	-butyl	CH_3	butylamine	135
P8−8h	-butyl	CH_3	octaylamine	127
P8−12h	-butyl	CH_3	dodecylamine	118
P8−18h	-butyl	CH_3	octadecalamine	115

hydrogen bonding between the urethane group (N−H) and the imide ring (C═O).

Another important property of these materials is their thermal stability. Here especially the thermal back-reaction of the urethanes to isocyanates and alcohols is important, since this reaction would lead to a loss of the NLO chromophores. To test the thermal stability thermogravimetric measurements of selected systems were performed (see Figure 5). They show thermal stability of the system up to about 200 °C. Above this temperature the thermal back-reaction sets in, as determined by the IR spectrum of the evaporated material, which is that of methanol. This reaction is finished at about 275 °C, when the theoretical weight loss due to evaporation of methanol is reached. At still higher temperatures the polymer backbone degrades. This thermal back reaction will definitely limit the stability of the polar order above 200 °C. Since the NLO chromophores do however not evaporate—like methanol—they will stay in the polymer and react again with the isocyanate groups during cooling. In this context another point is noteworthy: there are—to our knowledge—no good NLO chromophores available that survive long annealing times above 200 °C in any case (see next section).

C. Properties of NLO Polymers. In the next step the solid-state properties of the polymers functionalized with NLO chromophores were investigated. DSC curves show the glass transition and at higher temperatures the onset of the thermal decomposition of the chromophores. The resulting properties are compiled in Table 4. It should be noted that high degrees of functionalization can be achieved, (i) if the solubility of the precursor polymer is sufficient (this is not the case for **Pr1** (Table 1) yielding polymer **Pc 1−1** (Table 4)) and (ii) if sufficient amounts of chromophore are available. From the chromophores **C3** and **C4** only smaller quantities were available. Therefore the loading with NLO chromophores was reduced to obtain enough NLO polymer for the characterization of the NLO properties.

A comparison of the T_g values of the model polymers (Table 2) and the NLO polymers (Table 4) shows that the NLO modification does not lead to a decrease of T_g. This can be explained by the fact that the chromophores are stiff aromatic moieties, and only the spacer part can act as softener. This effect may be supported by hydrogen bonding, which can occur between the urethane group (N−H) and the acceptor of the NLO chromophores. Thus NLO polymers with a T_g above 180 °C are easily accessible.

These high T_g values raise another question, that of the thermal stability of the chromophore during poling, which has to be done around T_g. If corona poling is used, the polymeric film is in contact with air. Therefore, oxygen may play a crucial part in determining the stability of the dye. Thermal stabilities of chromophores are often determined by DSC measurements showing the decomposition. This method gives good results for a comparison of different chromophores, but the values obtained are usually higher than those measured isothermally[28−30] (sometimes up to 100 °C). In our case they are well above T_g. We used here UV-spectroscopy to follow isothermally the decomposition of the π-system of the chromophore within the polymer matrix. This method has the advantage that it monitors directly the properties necessary for nonlinear optical effects. It is sensitive to small changes of the NLO chromophore, such as the addition of oxygen, which might limit the π-conjugation, but which may not show up in DSC− or thermogravimetric measurements. In Figure 6 the changes of the UV spectra of a polymer with a tricyanochinodimethane acceptor (chromophore **C3**) are shown. At 180 °C the chromophore is still quite stable, and after 1 h—a time sufficient for poling—90% of the optical density is still present. At 195 °C only 80% of the optical density is left after 1 h. Evaluating the optical density of this chromophore showed an interesting influence of the polymer matrix (see Figure 7).

Table 4. Summary of NLO-Polymers[a]

no.	R_1 substituent (imide component)	R_2 (isocyanate component)	chromophore	chromophore content		λ_{max} (nm)			M_n	T_g (°C)
				x	wt %	chromophore	polymer			
Pc1−1	phenyl	CH_3	C1	0.085	14.1	480	480	481	16 250	205
Pc2−1	pentafluorophenyl	CH_3	C1	0.494	30	499.5	490	460.5	24 400	182
Pc2−2	pentafluorophenyl	CH_3	C2	0.193	16.5	518.5	512.5	505	19 950	190
Pc2−3	pentafluorophenyl	CH_3	C3	0.095	8	675	665	654.5	19 200	191
Pc2−4	pentafluorophenyl	CH_3	C4	0.31	35	671	662.5	640	24 370	182
Pc5−1	diphenylmethyl	CH_3	C1	0.28	20	480	479	476	66 250	180
Pc5−3a	diphenylmethyl	CH_3	C3	0.02	1.8	675	677.5	676.5	55 700	181
Pc5−3b	diphenylmethyl	CH_3	C3	0.09	7.8	675	677	676.5	58 850	181
Pc5−3c	diphenylmethyl	CH_3	C3	0.15	12	675	677	670.5	61 550	170

[a] Solution properties of the NLO-polymers were measured in $CHCl_3$ except for polymer Pc2−1, which was dissolved in 1:1 $CHCl_3$−DMF. Molecular weights were determined by adding the amount of chromophore determined by UV-spectroscopy to the value of the model systems determined by GPC (see Table 2).

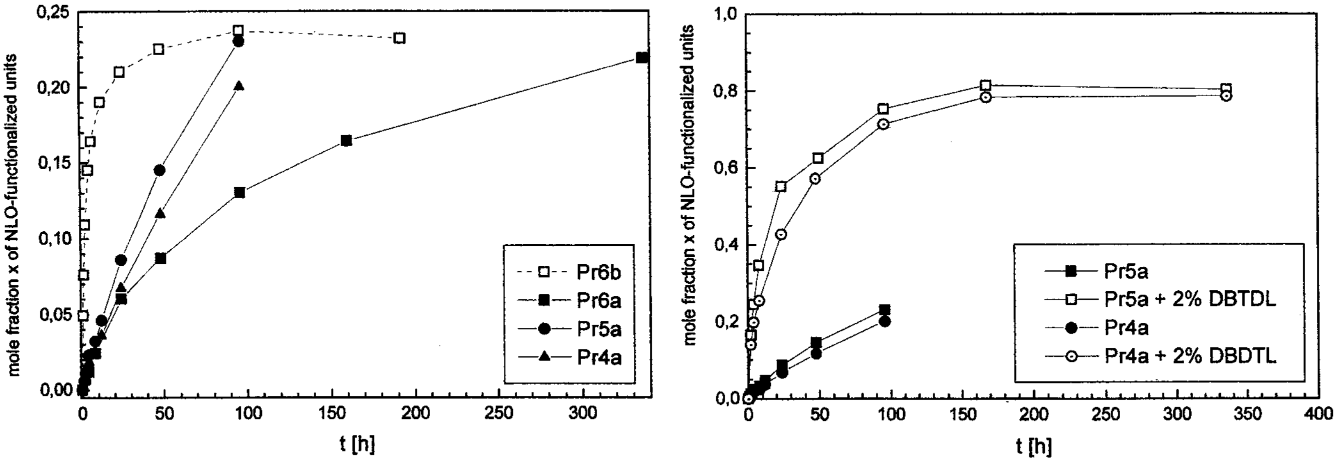
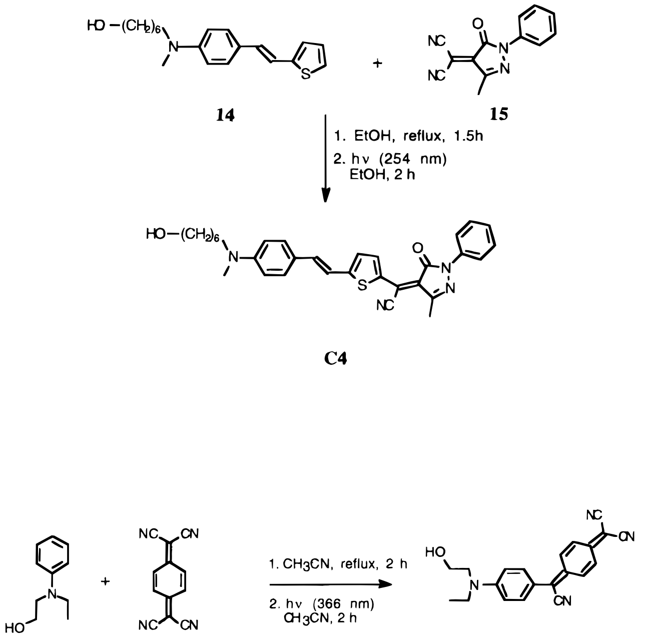


Figure 2. Left: kinetics of the polymer analogous reaction and the dependence on the substitution of the backbone. Right: kinetics of the polymer analogous reaction when using dibutyltin dilaurate as catalyst.

Scheme 4. Synthesis of Chromophores C3 and C4



14 15

C4

C3

In Figure 7 the kinetics of the thermal decomposition of chromophore **C3** is compared for a polymer matrix with a perfluorated substituent at the imide ring (**Pc2−3**) and one with diphenylmethyl at the imide ring (**Pc5−3b**). Both systems have nearly the same glass transition temperature, and they are functionalized with the same amount of chromophores. In all cases the thermal stability is considerably higher in the perfluorated matrix. This can—in this case—however not just be due to differences of the solubility of the matrix for oxygen or water, since similar effects are observed also in a vacuum. The higher stability of chromophore **C3** in the perfluorated matrix should therefore result from changes of the local order in both polymers.

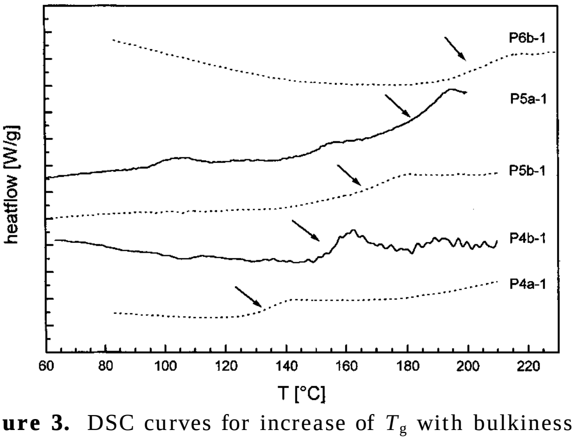


Figure 3. DSC curves for increase of T_g with bulkiness of substituents and shift of T_g with additional CH_3 group at the polymer main chain in the series of the methylvinyl isocyanate copolymers.

Finally the thermal stability of chromophore **C4** was investigated (see Figure 8). The thermal stability of this chromophore in the perfluorated matrix is lower than that of chromophore **C3**. Nevertheless the stability would be high enough for a poling at 180 °C.

The electrooptical properties of the polymers functionalized with disperse red 1 (polymers **Pc1−1**, **Pc-**

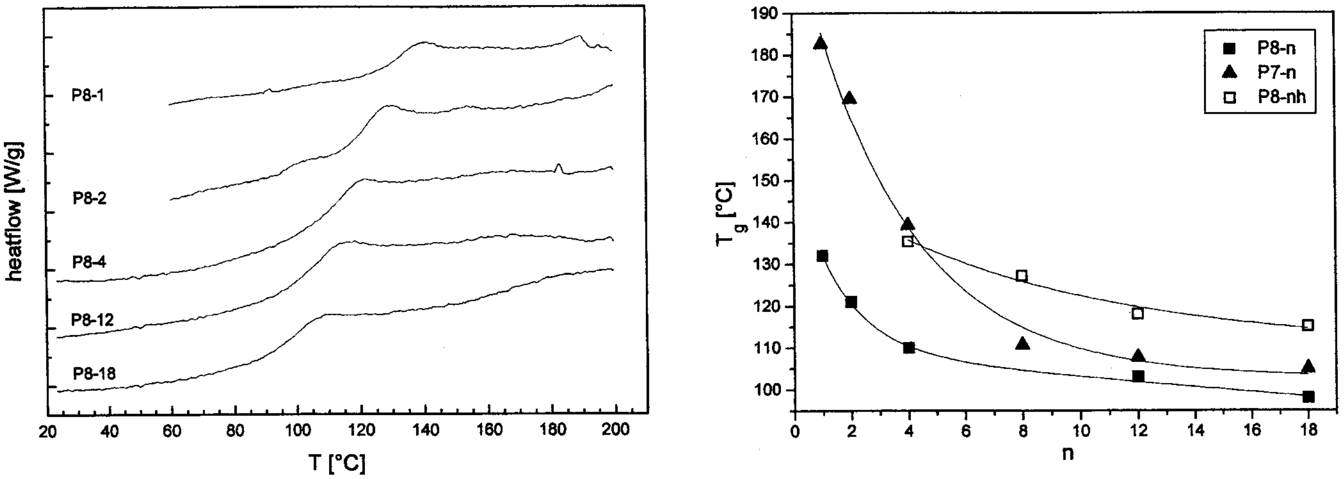


Figure 4. Right: DSC curves vs side chain length at urethane for polymer series P8-*n*. Left: DSC plot of T_g vs side chain length at the maleimide component for polymer series P7−*n* and P8−*n* (urethane side groups) and for P8−*n*h (urea side groups).

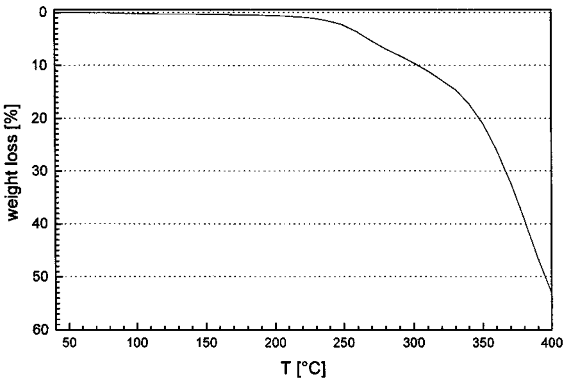


Figure 5. TGA of polymer P2−1 (rate 10 K/min, nitrogen atmosphere).

2−1 and **Pc5−1**) were already investigated in detail in ref 31. These measurements showed a good thermal stability of the poled structure and, e.g., a half-life time (determined from the relaxation of the electrooptic coefficient r_{33}) of 2 years at 80 °C for polymer **Pc5−1**.

The polymer films in this study were prepared on glass slides by spin casting from cyclohexanone solutions. The samples with typical thickness of about 1 μm were corona poled at the individual T_g (see Table 5). The absorption spectra taken before and after the poling process indicated a loss of 15−20% of optical density in all cases. This is mostly due to the efficient poling process as indicated by the large ratio d_{33}/d_{13} = 5−6 (Table 5), but also partly due to degradation of the chromophore units at the elevated temperatures required for the poling. The films were brought in contact with a grounded aluminum foil to remove residual surface charges.

To determine the frequency-doubling coefficients *d*, the poled films were characterized by the Maker−fringes technique (fundamental 1064 nm, second harmonic 532 nm) relative to x-cut quartz (d_{11} = 0.5 pm/V). Possible absorption at both wavelengths was taken into account using the formalism proposed by Herman and Hayden.[32] The derived d_{33} and d_{13} values are given in Table 5, assuming the validity of Kleinman symmetry (i.e., $d_{13} = d_{15} = d_{32} = d_{24}$).

The polymers **Pc2−3** and **Pc5−3a−c** are functionalized with the chromophore **C3** at different concentrations. A linear dependence of the d_{13} and the d_{33} coefficients on the chromophore content is observed for the polymers containing the diphenylmethyl substituent (Figure 9), reaching up to 53 pm/V for the highest-substituted polymer **Pc5−3c**. The fact that the dependence is linear shows that antiparallel correlations between the chromophores, leading to aggregates which cannot be aligned by the electric field, do not occur at these concentrations. In contrast, our investigations on guest/host systems containing **C3** at various concentrations in PMMA revealed a sublinear dependence of d_{33} on the number density *N* of the chromophore.[33] The largest value achieved was 42 pm/V for $N = 2.5 \times 10^{-4}$ ($d_{33}/d_{13} \gg 4.8$). Obviously, the SHG coefficients of the doped system are larger than those in the functionalized polymer for an identical number density of the chromophore despite the reduced poling efficiency given by the ratio of the *d* coefficients d_{33}/d_{13}. This can be explained by the reduced rotational mobility of the chromophores when linked to the polymer backbone. Furthermore, the poling in the polymer had to be performed at higher temperature (180 vs 100 °C in the PMMA matrix), which also reduces the degree of poling.

In the polymer with the pentafluorophenyl substituent the SHG-coefficient was found to be larger (**Pc2−3**, d_{33} = 45 pm/V) than for the diphenylmethyl substituent at a similar concentration (**Pc5−3b**, d_{33} = 30 pm/V). This may be explained by several factors: (i) the slightly larger chromophore content in **Pc2−3** compared with **Pc5−3b**; (ii) the larger number density of the chromophores in the pentafluorophenyl compared with the diphenylmethyl substituted polymers at equal chromophore content; (iii) the higher thermal stability of the chromophore in the perfluorated matrix, rendering the number density of the intact chromophores in **Pc2−3** larger (see above, Figure 8); (iv) the better poling efficiency achieved in **Pc2−3** compared with **Pc5−3b** as indicated by d_{33}/d_{13} (see Table 5); (v) the higher polarity of the pentafluorophenyl polymer.

One might argue that the values reported here are resonance enhanced; however, this argument is difficult to apply in the case of the chromophore C3 due to the following reasons.

(i) The absorption band of **C3** lies between 532 and 1064 nm; i.e., there is an optical "window" in the region around 532 nm (compare with Figure 7). In this case, the two-level model typically used to describe the dispersion of the SHG coefficients cannot be applied.

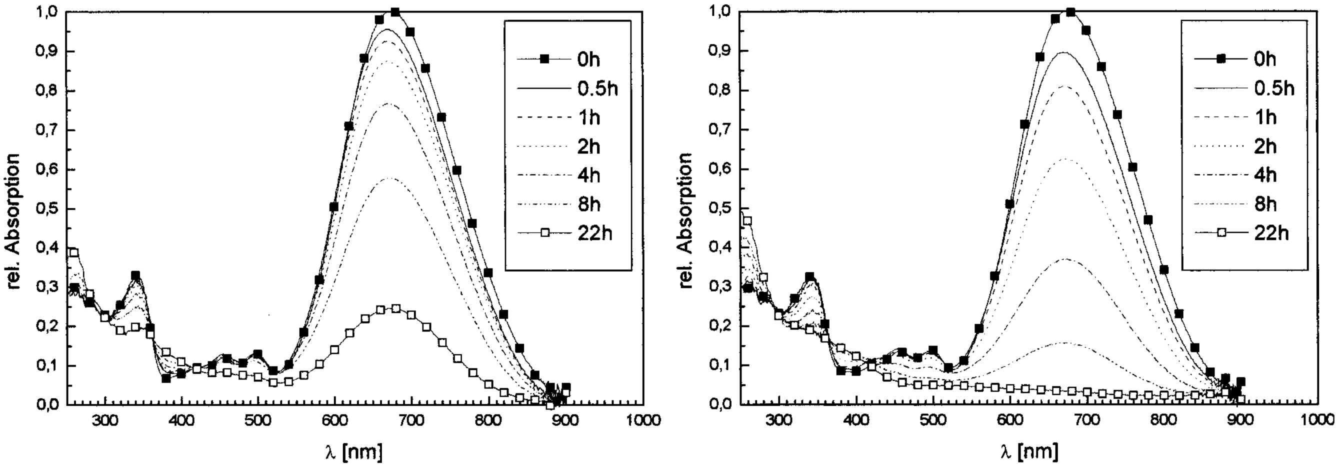


Figure 6. UV spectra of Polymer Pc5−3b at 180 °C (left) and 195 °C (right) under air atmosphere demonstrating the thermal stability of chromophore C3 over a period of ca. 1 day.

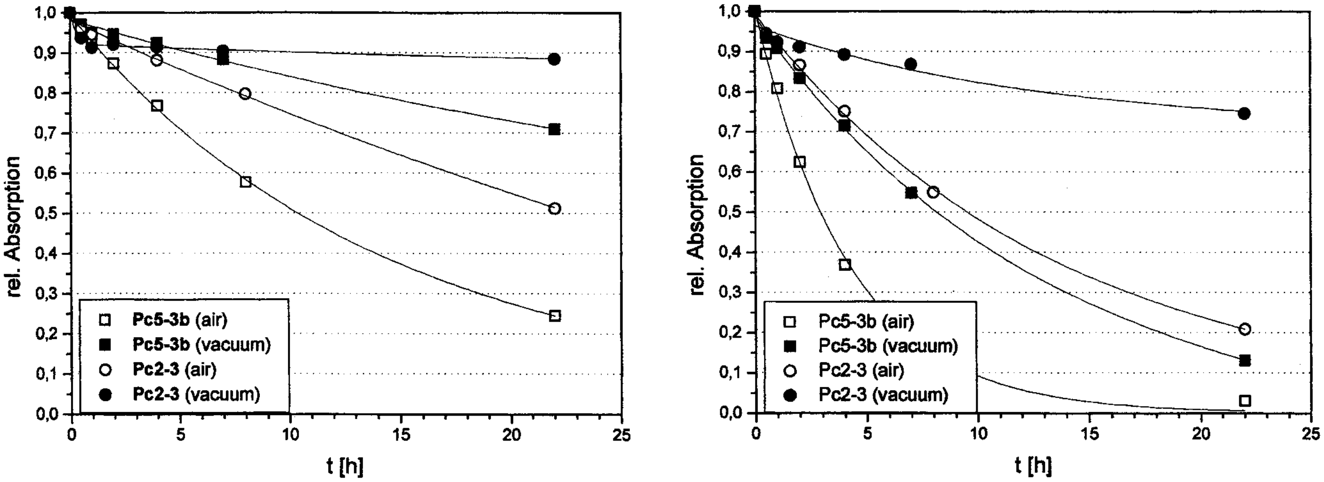


Figure 7. Comparison of thermal stabilities of polymers Pc5−3b (diphenylmethyl substituent) and Pc2−3 (pentafluorophenyl substituent) at 180 °C (left) and 195 °C (right) under different conditions (air (top) or vacuum (bottom)).

(ii) Wavelength-dependent measurements on different chromophore systems[34,35] show, that a resonance enhanced maximum of the frequency-doubling coefficients occurs near the absorption maximum. But when the second harmonic is shifted beyond λ_{max} toward shorter wavelengths, the frequency-doubling coefficients decrease significantly similarly to the usual case at the longer wavelengths. Our own wavelength-dependent measurements on the guest/host system **C3** (1.7×10^{-4} mol/cm^3) in polyetherimide revealed a d_{33} value of 19 pm/V for 1064 nm/532 nm, while for 1400 nm/700 nm, i.e., near the absorption maximum, a strongly resonance-enhanced d_{33} value of 80 pm/V was found.[36] These considerations should hold when **C3** is linked to a polymer.

Finally, we obtained a large $d_{33} = 100$ pm/V for the polymer **Pc2−4**, which is mostly due to the high chromophore content (31%) and the efficient poling ($d_{33}/d_{13} = 5.9$). Furthermore, the value is somewhat resonance enhanced due to the proximity of the second harmonic wavelength to the wavelength of maximum absorption (compare with Figure 8).

Conclusion

Copolymers from maleic imides and vinyl or methylvinyl isocyanates offer a flexible reactive polymer system, in which the T_g values can be varied between 120 and 210 °C depending on the substituent at the imide ring. They can be used for the fixation of alcohols or amines with various functional groups. The potential of these copolymers was highlighted here for NLO chromophores. It allows the fixation of chemically labile NLO chromophores, which do not tolerate radical polymerization or basic conditions, to prepare NLO polymers with T_g values of about 180 °C. The resulting polymers show sufficient solubility for the spin coating of thin polymer films of high optical quality. For one system a d_{33} value of 100 pm/V for a loading with 31% of chromophores (**C4**) was found (this value is however somewhat inflated by the overlap of second harmonic frequency and absorption band).

Experimental Part

The solvents used were dried according to literature procedures where inert media (no reactions with reactive isocyanates) are required. The films for UV measurements of the thermal stabilities were spin-coated on quartz slides from cyclohexanone solutions. They were not dried under extreme conditions to prevent any destruction before UV measurements.

Monomer Synthesis. All maleimides were synthesized according to modified literature procedures. All maleimides except **5** and **6** are available from maleic anhydride and the corresponding amine.[18,37,38] Monomers **5** and **6** are prepared by a coupling reaction of the silver salt of the unsubstituted

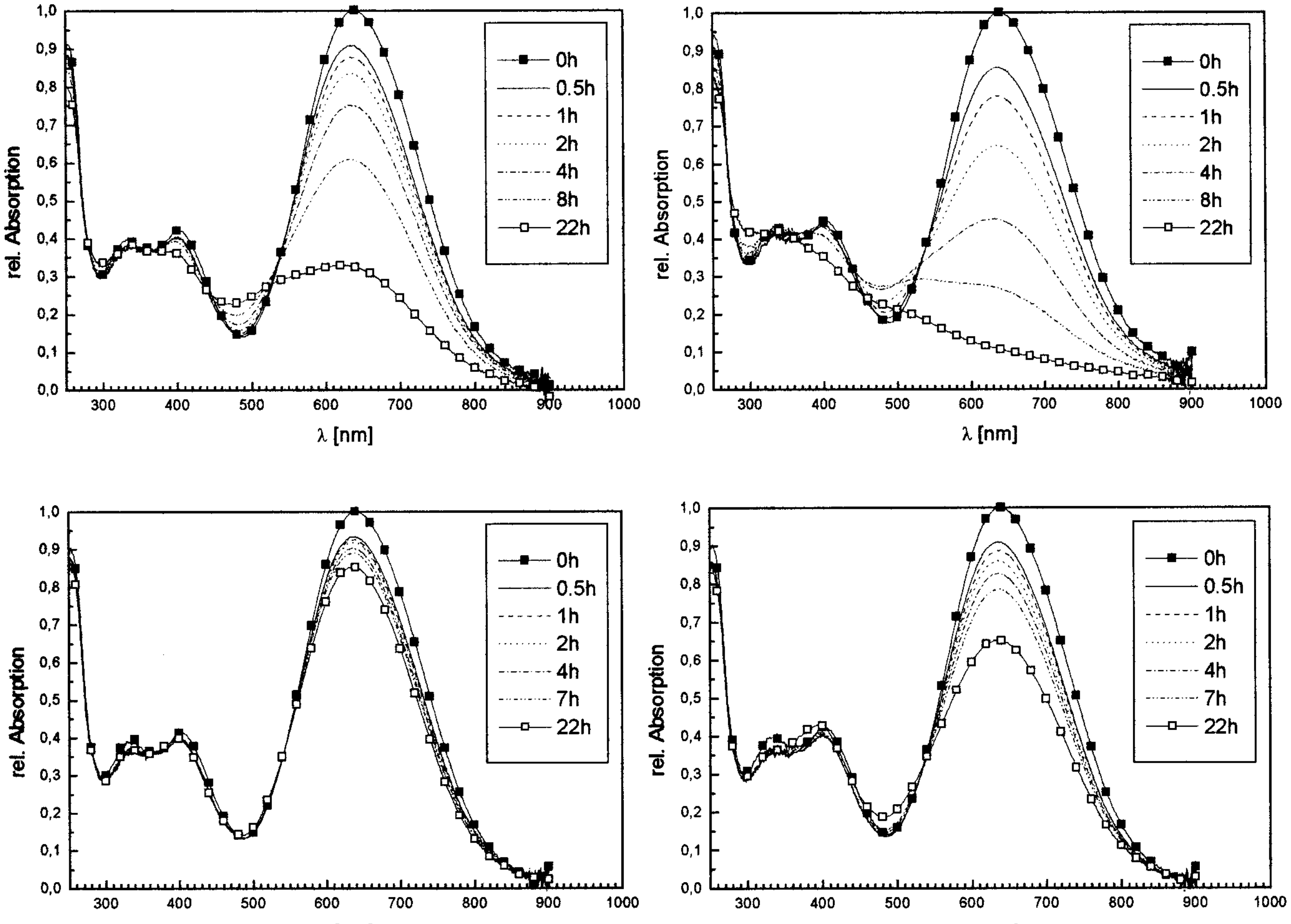


Figure 8. Thermal stability of chromophore C4 in polymer Pc2−4 at 180 °C (left and 195 °C (right) in air (upper curves) and in vacuo (lower curves).

Table 5. Nonlinear Optical Properties of Various Polymers as Determined by Frequency Doubling

polymer	chromophore content *x*	chromophore number density[a] (10^{-4} mol/cm^3)	d_{33} (pm/V)	d_{13} (pm V)	d_{33}/d_{13}
Pc2−3	0.095	2.8	45	8	5.6
Pc2−4	0.31	7.18	100	17	5.9
Pc5−3a	0.02	0.62	6	1	6
Pc5−3b	0.09	2.52	30	6	5
Pc5−3c	0.15	4.2	53	11	4.8

[a] This value was estimated assuming a density of $\rho \approx 1.2$ g/cm^3 for the polymers.

maleimide and the corresponding halides.[19] *N*-Ethylmaleimide was commercially available from Aldrich. As one example for the synthesis of maleimides starting with maleic anhydride, the synthesis of N-pentafluoromaleimide is described in detail.

(Pentafluorophenyl)maleimide (2). 5 g (27 mmol) sample of pentafluoroaniline and 2.67 g (27 mmol) of maleic anhydride are mixed in 10 mL of chloroform. The reaction is stirred overnight, and the yellow solution turns white with the desired product as a solid precipitate. This intermediate product can be separated by filtration and is used for the following imidization reaction without further purification. (yield: 7.6 g, 99%).

The *N*-pentafluorophenylmaleamicacid (7.6 g, 27 mmol) is dispersed in 15 mL of acetic anhydride and 1.5 g sodium acetate is added. This mixture is heated to 70 °C for approximately 4 h. During this time the educts dissolve, and with further reaction time, the desired products precipitates. After the reaction mixture was cooled to room temperature, the excess of acetic anhydride is hydrolyzed with about 100 mL of ice-cold water. The separated solid is washed with water, dried, and purified on a silica column with methylene chloride as eluent.

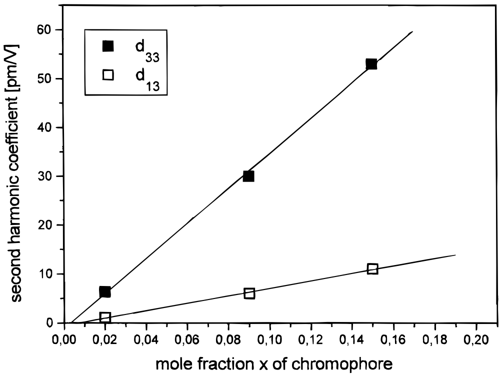


Figure 9. Dependence of the frequency-doubling coefficients d_{33} and d_{13} on the chromophore content for the polymers Pc5−3a−c determined by the Maker−fringe technique. The lines are guide to the eye.

Yield: 5.4 g (75%). ^{1}H NMR, δ (ppm): 6.95 (s, 2H).

Methylvinyl Isocyanate (13).[20,22,39,40] 39 g (0.6 mole) sample of sodium azide is dissolved in 140 mL of water and cooled to ca. −10 °C. Then 42 g (0.4 mole) of methacrylic acid chloride in 140 mL of xylene is added slowly, so that the reaction temperature does not exceed −5 °C. After complete addition of the acid chloride, the mixture is stirred for another hour. Then the organic phase of the two-phase reaction mixture is separated and washed once with saturated sodium carbonate solution and twice with water. Before this solution is used further, it is dried carefully over sodium sulfate. To decompose the acid azide, 10 mL of xylene is put into a flask and heated to 80 °C. The solution of the azide is added slowly, and the nitrogen evolution is controlled. After the reaction is complete, the product is separated by destillation. The crude products has a boiling point between 61 and 72 °C (lit. 69 °C)[20] and is distilled freshly before every polymerization. In the remaining reaction mixture residues of isocyanate are destroyed by adding small amount of propylamine.

Yield: 14.86 g (54%). ^{1}H NMR, δ (ppm): 1.95 (s, 3H), 4.55 (s, 1H), 4.7 (s, 1H).

The monomer **12** (vinyl isocyanate) is synthesized in a similar manner. Because of the lower boiling point, the product distills off during the decomposition of the azide.

Chromophores. Disperse Red 1 was commercially available from Aldrich and purified by column chromatography before use.

***N*,*N*-((2-Hydroxyethyl)ethyl)-4-(tricyanovinyl)aniline (C2).** A 7.20 g (43.11 mmol) sample of *N*-(2-hydroxyethyl)-*N*-ethylaniline is dissolved in 25 mL of absolute DMF. Then 4.90 g (37.5 mmol) of tetracyanoethylene is added portionwise, so that the temperature does not rise far above room temperature. If necessary, cooling with an ice bath prevents a fast temperature increase. After complete addition the mixture is heated to ca. 60 °C for about 10 min. *Caution!* Care has to be taken because of the poisonous HCN evolved during this process, and the reaction is carried out in an efficient hood. The crude product can be separated by filtration after cooling to 0 °C. Further purification is possible by column chromatography (silica gel) with hexane/ethyl acetate 1:2 as eluent.

Yield: 8.76 g (88%). ^{1}H NMR, δ (ppm): 1.25 (t, 3H), 3.65 (2d, 4H), 3.9 (d, 2H), 6.8 (d, 2H), 8.05(d, 2H).

Compounds **14** and **15** were synthesized as described in refs 41 and 42, respectively.

(*Z*)-2-[5-((*E*)-2-{4-[(6-Hydroxyhexyl)(methyl)amino]phenyl}-1-ethenyl)-2-thienyl]-2-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-4-pyrazolinylidene)acetonitrile (C4). To a stirred solution of 0.33 g (1.05 mmol) of **14** in 125 mL of dry ethanol is added 0.25 g (1.05 mmol) of 2-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-4-pyrazolinylidene)malononitrile (**15**). The mixture is heated at reflux for 1.5 h under nitrogen atmosphere. The green solution is cooled and transferred into a photoreactor equipped with a medium-pressure mercury lamp (Heraeus, TQ150) and is irradiated through a quartz glass filter at room temperature for 2 h. *Caution!* Care has to be taken because of the poisonous HCN evolved during this process, and the reaction was carried out in an efficient hood. The resulting blue-green solution is evaporated to dryness, and the dark residue is purified by flash filtration (CH_2Cl_2, R_f = 0.1, and CH_2Cl_2/ethyl acetate, volume ratio 10:1, R_f = 0.3), followed by recrystallization from ethanol, yield 0.17 g (0.32 mmol, 31%) **C4** as dark blue crystals, mp 170 °C.

^{1}H NMR ($CDCl_3$, 400 MHz), *d*: 8.27 (d, ^3J = 4.44 Hz, 1H, thiophenediyl proton), 7.96−7.94 (m, 2H, phenylene protons), 7.45−7.41 (m, 4H, phenyl protons), 7.31 (d, ^3J = 15.93 Hz, 1H, $C_6H_4{-}CH{=}C\mathit{H}{-}$), 7.23−7.18 (m, 1H, phenyl proton), 7.16 (d, ^3J = 4.44 Hz, 1H, thiophenediyl proton), 7.00 (d, ^3J = 15.93 Hz, 1H, $C_6H_4{-}C\mathit{H}{=}CH{-}$), 6.65−6.63 (m, 2H, phenylene protons), 3.65 (m, 2H, $HOC\mathit{H}_2{-}$), 3.36 (m, 2H, $-CH_2N$), 3.00 (s, 3H, $N{-}CH_3$) 2.63 (s, 3H, $-CH_3$), 1.65−1.55 (m, 5H, CH_2 and OH), 1.45−1.36 (m, 4H, CH_2).

UV/vis (chloroform): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) = 672 (38 905).

MS (70 eV): *m/z* (%) = 524 (78) [M$^+$].

Anal. Calcd for $C_{31}H_{32}N_4O_2S$ (524.68): C, 70.97; H, 6.15; N, 10.68; S, 6.11. Found: C, 71.02; H, 6.19; N, 10.73; S, 6.12.

2-{4-Cyano[[4-ethyl(2-hydroxyethyl)amino]phenyl]-methylene-2,5-cyclohexadienylidene}malononitrile (C3). A stirred solution of 1.0 g (6.05 mmol) of 2-(ethylanilino)-1-ethanol and 1.24 g (6.05 mmol) of 7,7,8,8-tetracyanoquinodimethane in 100 mL of dry acetonitrile is heated at reflux for 2 h. The resulting green solution is cooled to room temperature and transferred into a photoreactor where it is irradiated as described above for **C4**. *Caution!* Care has to be taken because of the poisonous HCN evolved during this process, and the reaction is carried out in an efficient hood. The dark green solution is filtered and the crystalline product is washed twice with ice-cold methanol and diethyl ether. The filtrate is concentrated to about $^1/_5$th of its initial volume and heated at reflux for a few minutes. When this is cooled to ambient temperature, another fraction of the product precipitates, which is washed as described above. Yield: 1.24 g (4.72 mmol, 78%) of **C3** as dark green crystals, mp 238 °C.

^{1}H NMR 400 MHz (DMSO-d_6), *d*: 7.72−7.63 (m, 4H, aromatic protons), 7.23−7.01 (m, 4H, quinoid protons), 4.64−5.23 (bs, 1H, OH), 3.72−3.63 (m, 6H, CH_2), 1.20 (t, 3H, CH_3).

UV/vis (chloroform): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) = 680 (53 580).

MS (70 eV): *m/z* (%) = 342 (28) [M$^+$].

Anal. Calcd for $C_{21}H_{18}N_4O$ (342.40): C, 73.67; H, 5.30; N, 16.36. Found: C, 73.36; H, 5.25; N, 16.51.

Polymer Synthesis. The method of polymerizing is similar for all the monomers used and is performed under similar conditions. Therefore one general procedure is described, and then only the exemptions (polymerization or precipitation solvent) for every special polymer are noted.

The polymerization solvent is filled into a dry nitrogen flask. The two comonomers are filled in under a continuous nitrogen flow to prevent the polymerization mixture to come into contact with oxygen. Finally about 2−3 mol % of AIBN compared to the total amount of monomers is added, and the reaction flask is closed. Since the polymerization is performed at about 70 °C, the volume in the flask, which is not filled with liquid should be as small as possible. The polymerization is performed at 70 °C for 16−20 h. For some of the maleimide monomers it is necessary to heat to the reaction temperature to get a clear solution. After the reaction is complete, the polymers can be precipitated into dry diethyl ether (in most cases). The polymerization solvents were chosen to keep the polymers in solution. The precipitated polymers can be separated by filtration and are dried at ca. 40 °C in vacuo.

Pr1. Poly(methylvinyl isocyanate)-*alt*-(*N*-phenylmaleimide). Polymerization: 2 g (11.55 mmol) of *N*-phenylmaleimide (**1**); 1.15 g (13.86 mmol) of methylvinyl isocyanate (**13**); 25 mL of dioxane; 37 mg of (0.23 mmol) AIBN; precipitation solvent, diethyl ether.

Yield: 2.74 g (92.5%).

Pr2. Poly[methylvinyl isocyanate-*alt*-*N*-(pentafluorophenyl)maleimide]. Polymerization: 7.5 g (28.5 mmol) of *N*-pentafluorophenylmaleimide (**2**); 2.85 g of (34.2 mmol) methylvinyl isocyanate (**13**); 90 mL of dioxane; 93.6 mg (0.6 mmol) AIBN; precipitation solvent, diethyl ether.

Yield: 8.98 g (91%).

Pr3. Poly[methylvinyl isocyanate-*alt*-*N*-(4-carboxyethyl)phenylmaleimide]. Polymerization: 2.46 g (10 mmol) of *N*-(4-carboxyethyl)phenylmaleimide (**3**); 1 g (12 mmol) of methylvinyl isocyanate (**13**); 20 mL of toluene; 32.8 mg (0.2 mmol) of AIBN; precipitation solvent, diethyl ether.

Yield: 3.03 (92%).

Pr4a. Poly(methylvinyl isocyanate-*alt*-*N*-benzylmaleimide). Polymerization: 2.5 g (13.35 mmol) of *N*-benzylmaleimide (**4**); 1.33 g (16.03 mmol) of methylvinyl isocyanate (**13**); 30 mL of dioxane; 44 mg (0.3 mmol) of AIBN; precipitation solvent, diethyl ether.

Yield: 2.88 (80%).

Pr4b. Poly[(vinyl isocyanate)-*alt*-(*N*-benzylmaleimide)]. Polymerization: 2.5 g (13.35 mmol) of *N*-benzylmaleimide (**4**); 1.1 g (16.03 mmol) of vinyl isocyanate (**12**); 30 mL of dioxane; 44 mg (0.3 mmol) of AIBN; precipitation solvent, diethyl ether.

Yield: 2.73 g (80%).

Pr5a. Poly[methylvinyl isocyanate-*alt*-*N*-(diphenylmethyl)maleimide]. Polymerization: 5.17 g (24 mmol) of *N*-(diphenylmethyl)maleimide (**5**); 2.4 g (28.8 mmol) of methylvinyl isocyanate (**13**); 40 mL of toluene; 100 mg (0.6 mmol) of AIBN; precipitation solvent, diethyl ether.

Yield: 6.56 (91%).

Pr5b. Poly[vinyl isocyanate-*alt*-*N*-(diphenylmethyl)maleimide]. Polymerization: 2.5 g (11.6 mmol) of *N*-(diphenylmethyl)maleimide (**5**); 960 mg (13.92 mmol) of vinyl isocyanate (**12**); 40 mL of toluene; 37 mg (0.23 mmol) of AIBN; precipitation solvent, diethyl ether.

Yield: 2.87 g (87%).

Pr6a. Poly[methylvinyl isocyanate-*alt*-*N*-(triphenylmethyl)maleimide]. Polymerization: 1.5 g (4.42 mmol) of *N*-(triphenylmethyl)maleimide (**6**); 0.4 g (5.3 mmol) of methylvinyl isocyanate (**13**); 30 mL of dioxane; 7.3 mg (0.04 mmol) of AIBN; precipitation solvent, diethyl ether.

Yield: 1.4 g (75%).

Pr6b. Poly[vinyl isocyanate-*alt*-*N*-(triphenylmethyl)maleimide]. Polymerization: 2 g (5.89 mmol) of *N*-(triphenylmethyl)maleimide (**6**); 490 mg (7.07 mmol) of vinyl isocyanate (**12**); 30 mL of dioxane; 9.7 mg (0.07 mmol) of AIBN; precipitation solvent, diethyl ether.

Yield: 1.73 g (72%).

Pr7. Poly(methylvinyl isocyanate-*alt*-*N*-ethylmaleimide). Polymerization: 2.5 g (20 mmol) of *N*-ethylmaleimide (**7**); 1.99 g (24 mmol) of methylvinyl isocyanate (**13**); 30 mL of toluene; 65.6 mg (0.4 mmol) of AIBN; precipitation solvent, diethyl ether.

Yield: 3.70 g (89%).

Pr8. Poly(methylvinyl isocyanate-*alt*-*N*-butylmaleimide). Polymerization: 3.68 g (24 mmol) of *N*-butylmaleimide (**8**); 2.39 g (29 mmol) of methylvinyl isocyanate (**13**); 40 mL of toluene; 100 mg (0.6 mmol) of AIBN; precipitation solvent, diethyl ether.

Yield: 4.66 g (82%).

Pr9. Poly(methylvinyl isocyanate-*alt*-*N*-octylmaleimide). Polymerization: 4 g (19.1 mmol) of *N*-octylmaleimide (**9**); 1.9 g (23 mmol) of methylvinyl isocyanate (**13**); 40 mL of toluene; 62.4 mg (0.4 mmol) of AIBN; precipitation solvent, hexane.

Yield: 4.70 g (84%).

Pr10. Poly(methylvinyl isocyanate-*alt*-*N*-dodecylmaleimide). Polymerization: 2 g (7.55 mmol) of *N*-phenylmaleimide (**10**); 0.76 g (9.15 mmol) of methylvinyl isocyanate (**13**); 20 mL of toluene; 25 mg (0.15 mmol) of AIBN; precipitation solvent, acetonitrile.

Yield: 1.78 g (68%).

Pr11. Poly(methylvinyl isocyanate-*alt*-*N*-octadecylmaleimide). Polymerization: 2.65 g (7.6 mmol) of *N*-phenylmaleimide (**11**); 0.76 g (9.15 mmol) of methylvinyl isocyanate (**13**); 20 mL of toluene; 25 mg (0.15 mmol) of AIBN; precipitation solvent, acetone.

Yield: 2.89 g (88%).

Reaction with Alcohols. General Procedure. All model polymers that are functionalized with simple alcohols (see Tables 2 and 3) can be synthesized by the following general procedure: The precursor polymer (Pr) is dissolved in chloroform to approximately 5 wt %. The corresponding alcohol is added in equimolar amounts. In case of the methanol-functionalized systems, a large excess of the alcohol can be used, since most of the polymers are precipitated in methanol. For longer chain alcohols it becomes more important to use only an equimolar amount because of separation problems after the reaction. Finally about 2 mol % of dibutyltin dilaurate as catalyst is added and the closed reaction flask is heated to about 50 °C for 1−2 days. Reaction times depend strongly on the side-chain length and can be checked by IR spectroscopy. A complete reaction is indicated when the NCO signal at 2260 cm^{-1} has disappeared. The polymers are precipitated in methanol, redissolved and precipitated again. Exceptions in precipitation solvents are as follows: polymers **P7−*n*** (hexane), **P8−1, P8−2, P8−4,** and **P8−12** (hexane). For a summary of the synthesized model polymers and their properties see Tables 2 and 3. All yields that are mentioned are the amounts of isolated polymer which is functionalized to 100%.

Reaction with Amines. General Procedure. In principle the reaction of the precursor polymers with the corresponding amines is the same as described as for the reaction with alcohols. The only difference is the much faster reaction. The amines are introduced into the reaction mixture in equimolar amounts, and a reaction time of 2−3 h (IR control) is enough to get a complete reaction at room temperature. The urea-functionalized polymers summarized in Table 3 can be precipitated in methanol. It should be mentioned that yields indicate the amount of isolated polymer, which is functionalized to 100%.

Reaction with Chromophores. General Procedure. The reaction of the precursor polymers with OH-functionalized chromophores is in principle the same as for the model systems. The precursor polymer is dissolved (chloroform or DMF dependent on precursor) and the amount of chromophore used is added. Again 2 mol % of dibutyltin dilaurate is added, and the closed flask is heated to 50 °C for a certain reaction time. After that time an excess of methanol is added to the reaction mixture to convert all remaining isocyanates to urethanes. After all isocyanate groups are converted (IR control) the polymer can be precipitated in methanol. To remove remaining low molecular weight chromophores, the polymer is dissolved again and reprecipitated. Larger amounts of remaining chromophores can be extracted in a Soxhlet extractor. Drying of the polymers can be done in vacuo at 60 °C. A characteristic property after the functionalization is the mole fraction of chromophore functionalized units *x*, which is determined by UV spectroscopy. The molecular weights were determined by measuring the methanol functionalized model systems (Table 2) and adding the amount of chromophore determined by UV spectroscopy. This method leads to more comparable values than measuring the chromophore functionalized systems themselves in the GPC because aggregation effects of the polar chromophores can be excluded.

Pc1−1. Polymer analogous reaction: 1 g (3.9 mmol) of **Pr1**; 491 mg (1.6 mmol) of **C1**; 50 mg (0.1 mmol) of dibutyltin dilaurate; 25 mL of chloroform + 10 mL of DMF; reaction time, 3 days and then addition of excess methanol (ca. 0.5 mL).

Yield: 800 mg ($x = 0.085$).

Anal. Calcd: C, 62.59; H, 5.55; N, 10.50; O, 1.36. Found: C, 62.56; H, 6.02; N, 10.46; O, 20.96.

Pc2−1. Polymer analogous reaction: 820 mg (2.37 mmol) of **Pr2**; 744 mg (2.37 mmol) of **C1**; 50 mg (0.1 mmol) of dibutyltin dilaurate; 20 mL of THF; reaction time, 4 days and then addition of excess methanol (ca. 0.5 mL).

Yield: 1.10 g ($x = 0.494$).

Anal. Calcd: C, 57.31; H, 3.85; N, 11.86. Found: C, 56.34; H, 3.94; N, 10.94.

Pc2−2. Polymer analogous reaction: 500 mg (1.44 mmol) of **Pr2**; 385 mg (1.44 mmol) of **C2**; 45 mg (0.1 mmol) of dibutyltin dilaurate; 15 mL of chloroform; reaction time, 3 days and then addition of excess methanol (ca. 0.5 mL).

Yield: 570 mg ($x = 0.193$).

Anal. Calcd: C, 50.21; H, 3.08; N, 9.17. Found: C, 49.81; H, 3.66; N, 9.70.

Pc2−3. Polymer analogous reaction: 1 g (2.89 mmol) of **Pr2**; 494 mg (1.44 mmol) of **C3**; 36 mg of dibutyltin dilaurate; 30 mL of chloroform; reaction time, 4 days and then addition of excess methanol (ca. 0.5 mL).

Yield: 1.02 g ($x = 0.095$).

Anal. Calcd: C, 49.78; H, 3.05; N, 8.18. Found: C, 50.35; H, 3.55; N, 8.08.

Pc2−4. Polymer analogous reaction: 900 mg (2.6 mmol) of **Pr2**; 400 mg (0.76 mmol) of **C4**; 30 mg of dibutyltin dilaurate; 15 mL of chloroform; reaction time, 5 days and then addition of excess methanol (ca. 0.5 mL).

Yield: 1.29 g ($x = 0.31$).

Anal. Calcd: C, 54.97; H, 3.74; N, 8.55; S, 1.87. Found: C, 52.42; H, 3.78; N, 2.15; S, 2.15.

Pc5−1. Polymer analogous reaction: 1.5 g (4.33 mmol) of **Pr5a**; 407 mg (1.3 mmol) of **C1**; 15 mL of DMF; reaction time, 6 days and then addition of excess methanol (ca. 0.5 mL).

Yield: 1.72 g ($x = 0.28$).

Anal. Calcd: C, 68.78; H, 5.71; N, 9.55; O, 15.96. Found: C, 68.68; H, 5.71; N, 9.72; O, 15.89.

Pc5−3a. Polymer analogous reaction: 700 mg (2.02 mmol) of **Pr5a**; 207.5 mg (0.606 mmol) of **C3**; 10 mL of chloroform; reaction time, 4 days and then addition of excess methanol (ca. 0.5 mL).

Yield: 565 mg ($x = 0.02$).

Anal. Calcd: C, 69.95; H, 5.84; N, 7.57; O, 16.64. Found: C, 67.67; H, 5.91; N, 7.25; O, 19.17.

Pc5−3b. Polymer analogous reaction: 500 mg (1.44 mmol) of **Pr5a**; 494 mg (1.44 mmol) of **C3**; 20 mL of DMF; reaction time, 8 days and then addition of excess methanol (ca. 0.5 mL).

Yield: 600 mg ($x = 0.09$).

Anal. Calcd: C, 70.35; H, 5.77; N, 8.13; O, 15.75. Found: C, 69.42; H, 5.77; N, 8.41; O, 16.40.

Pc5−3c. Polymer analogous reaction: 700 mg (2.02 mmol) of **Pr5a**; 207.5 mg (0.606 mmol) of **C3**; 20 mg of dibutyltin dilaurate; 20 mL chloroform; reaction time, 4 days and then addition of excess methanol (ca. 0.5 mL).

Yield: 540 mg ($x = 0.15$).

Anal. Calcd: C, 70.65; H, 5.72; N, 8.57; O, 15.06. Found: C, 67.71; H, 5.82; N, 8.26; O, 18.21.

Solutions of the copolymers in cyclohexanone are spin cast onto glass substrates, yielding films of about 1 mm thickness, as determined with a Dektak D3 profilometer. Refractive indices at 532 and 1064 nm of unpoled samples are measured using a prismn coupler (Metricon model 2010). The films are corona-poled at the polymer's T_g to induce the noncentrosymmetric orientation of the chromophores, necessary for second-order nonlinear optical effects. The samples are cooled to room temperature while the field is still applied. Second harmonic coefficients relative to quartz have been measured at 1064 nm using the Maker−fringes technique. The data are evaluated using a theoretical function given by Herman et al.,[38] taking into account absorption if necessary. The poling induced birefringence is neglected.

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References and Notes

(1) Wang, W.; Chen. D.; Fettermann, H. R.; Shi, Y.; Steier, W.H.; Dalton, L. R. *Appl. Phys. Lett.* **1995**, *67*, 1806.

(2) Ahlheim, M.; Barzoukas, M.; Bedworth, P. V.; Blanchard-Desce; Fort, A.; Hu, Z.-Y.; Marder, S. R.; Perry, J. W.; Runser, C.; Staehelin, M.; Zysset, B. *Science* **1996**, *271*, 335.

(3) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31.

(4) Dalton, L. R.; Harper, A. W.; Wu, B.; Gosn, R.; Laquindanum, J.; Liang, Z.; Hubbel, A.; Xu, C. *Adv. Mater.* **1995**, *7*, 519.

(5) Teraoka, I.; Jungbauer, D.; Reck, B.; Yoon, D. Y.; Twieg, R.; Willson, C. G. *J. Appl. Phys.* **1991**, *69*, 2568.

(6) Xu, C.; Wu, B.; Dalton, L. R.; Ranon, P. M.; Shi, Y.; Steier, W. H. *Macromolecules* **1992**, *25*, 6716.

(7) Weder, C.; Neuenschwander, P.; Suter, U. W.; Pretre, P.; Kaatz, P.; Günter, P. *Macromolecules* **1994**, *27*, 2181.

(8) Kawatsuki, N.; Dörr, M.; Schmidt, H.-W. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 1013.

(9) Servay, T. K.; Winkelhahn, H.-J.; Schulze, M.; Boeffel, C.; Neher, D.; Wegner, G. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 1272.

(10) Zentel, R.; Baumann, H.; Scharf, D.; Eich, M.; Schoenfeld, A.; Kremer, F. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 121.

(11) Jen, A. K.-Y.; Liu, Y.-J.; Cai, Y.; Rao, V. P.; Dalton, L. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2711.

(12) Drost, K. J.; Rao, V. P.; Jen, A. K.-Y. *J. Chem. Soc., Chem. Commun.* **1994**, 369.

(13) Müller, H.; Nuyken, O.; Strohriegel, P. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 125.

(14) Ahlheim, M.; Lehr, F. *Macromol. Chem. Phys.* **1994**, *195*, 361.

(15) Dörr, M.; Zentel, R. *Macromol. Chem., Rapid. Commun.* **1994**, *15*, 935.

(16) Dörr, M.; Zentel, R.; Boldt, P.; Wichern, J.; Eich, M.; Sprave, M.; Vydra, J. *Proc. SPIE* **1995**, *2527*, 105. Dörr, M. Ph.D. Thesis, Universität Mainz, Germany, 1996.

(17) Dörr, M.; Zentel, R.; Sprave, M.; Vydra, J.; Eich, M. *Adv. Mater.* **1997**, *9*, 225.

(18) *N*-Phenylmaleimide: *Organic Synthesis*; John Wiley and Sons: New York, 1973; Collect. Vol. V, p 944. Metha, N. B.; Phillips, A. P.; Fu, F.; Brooks, R. E. *J. Org. Chem.* **1960**, *25*, 1012.

(19) Schwartz, A.; Lerner, M. *J. Org. Chem.* **1974**, *39*, 21.

(20) Sato, M. *J. Org. Chem.* **1961**, *26*, 770. König, K. H. *Tetrahedron* **1990**, *46*, 7729.

(21) Mormann, W.; Schmalz, K. *Makromol. Chem, Rapid Commun.* **1992**, *13*, 377.

(22) Mormann, W.; Schmalz, K. *Macromolecules* **1994**, *27*, 7115.

(23) Mormann, W.; Grimm, A. *Macromol. Chem. Phys.* **1997**, *198*, 1281.

(24) Boldt, P.; Wichern, J.; Zippel, St.; Dörr, M.; Zentel, R.; Bräuchle, C.; Dietrich R.; Meerholz, K. *Proc. SPIE* **1996,** *2852*, 2.

(25) Rao, V. P.; Jen, A. K.-Y.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1118.

(26) Boldt, P.; Bourhill, G.; Bräuchle, C.; Jin, Y.; Kammler, R.; Müller, C.; Rase, J.; Wichern, J. *J. Chem. Soc., Chem. Commun.* **1996**, 793.

(27) Bespalov, B. P.; Titov, V. V.; Pankratov, A. A. *J. Org. Chem. USSR (Engl. Transl.)* **1972**, *8*, 1701.

(28) Moylan, C. R.; Twieg, R. J.; Lee, V. Y.; Swanson, S. A.; Betterton, K. M.; Miller, R. D. *J. Am. Chem. Soc.* **1993**, *115*, 12599.

(29) Moylan, C. R.; Twieg, R. J.; Lee, V. Y.; Miller, R. D.; Volksen, W.; Thackara, J. I.; Walsh, C. A. *Proc. SPIE* **1994**, *2285*, 17.

(30) Moylan, C. R.; Miller, R. D.; Twieg, R. J.; Lee, V. Y.; McComb, I. *Proc. SPIE* **1995**, *2527*, 151.

(31) Eich, M.; Beissinghoff, H.; Knödler, B.; Ohl, M.; Sprave, M.; Vydra, J.; Eckl, M.; Strohriegl, P.; Dörr, M.; Zentel, R.; Ahlheim, M.; Stähelin, M.; Zysset, B.; Liang, J.; Levenson, R.; Zyss, J. *Proc. SPIE* **1994**, *2285*, 104.

(32) Herman, W. N.; Hayden, L.-M. *J. Opt. Soc. Am. B* **1995**, *12*, 416.

(33) Dietrich, R.; Meerholz, K.; Bräuchle, C.; Wichern, J.; Boldt, P. *Chem. Phys. Lett.* **1998**, in press.

(34) Lundquist, P. M.; Yitzchaik, S.; Zhang, T.; Kanis, D. R.; Ratner, M. A.; Marks, T. J.; Wong, G. K. *Appl. Phys. Lett.* **1994**, *64*, 2194.

(35) Otomo, A. Jäger, M.; Stegeman, G. I.; Flipse, M. C.; Diemeer, M. *Appl. Phys. Lett.* **1996**, *69*, 1991.

(36) Dietrich, R.; Meerholz, K.; Bräuchle, C., in preparation.

(37) Yamaguchi, H.; Minoura, Y. *J. Polym. Sci., Part A* **1970**, *8*, 929.

(38) Metha, N. B.; Phillips, A. P. *J. Org. Chem.* **1960**, *25*, 1012.

(39) Hart, R.; van Dormael, A. *Bull. Soc. Chim. Belg.* **1956**, *65*, 571.

(40) Butler, G. B.; Monroe, S. B. *J. Macromol. Sci.*−*Chem.* **1971**, *A5*, 1063.

(41) Drost, K. J.; Jen, A. K.-Y.; Rao, V. P.; Mininni, R. M. *Mater. Res. Soc. Symp. Proc.* **1994**, *328*, 517.

(42) Junek, H.; Klade, M.; Sterk, H.; Fabian, W. *Monatsh. Chem.* **1988**, *119*, 993.

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