Synthesis and Characterization of Novel Multifunctional High-T_g Photorefractive Materials Obtained via Reactive Precursor Polymers

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Received June 22, 1999; Revised Manuscript Received January 11, 2000

ABSTRACT: We describe the synthesis of a new class of high-T_g multifunctional photorefractive polymers. They were obtained by radical copolymerization of methyl vinyl isocyanate and various N-substituted maleimides. Hole transporting carbazole moieties were attached through a variety of alkyl and phenyl spacers to the imide positions of the maleimides. In a polymer analogous reaction the reactive isocyanate groups of the precursor polymers were reacted with different hydroxyalkyl-terminated nonlinear optical chromophores. Two azo chromophores including dispersed red-1 and one pyrazolone dye were used. The resulting materials have been characterized by means of GPC, DSC, and UV/vis spectroscopy. All materials are amorphous and possess excellent solubility in common solvents such as chloroform and THF. Molecular weights range between 20 and 272 kg/mol. The glass-transition temperatures vary between 60 and 194 °C, depending on the length and the nature of the spacer groups between the maleimide rings and the carbazole moieties. Chromophore contents up to 44 mol % have been realized. Holographic experiments were performed on a device made from a multifunctionalized PR polymer plasticized such that the glass-transition temperature was $T_g = 80$ °C. The material was prepoled to break inversion symmetry and to induce macroscopic electrooptical properties. The steady-state gain coefficient (≈ 7 cm^{-1}) and diffraction efficiency of this device ($\approx 1\%$) were reduced compared with that of low-T_g materials. This is because orientational enhancement effects observed in low-T_g materials are excluded in the high-T_g regime. For the grating formation a dominant response time $\tau_1 = 100$ ms was found.

Introduction

Photorefractive (PR) materials combine photosensitivity, photoconductivity, and electrooptical (EO) activity.[1] The refractive indices of these materials can be modulated by light via a photoinduced space-charge field and the EO effect. PR phenomena have been studied for more than 30 years since their discovery in the ferroelectric single crystals $LiNbO_3$ in 1966.[2] In 1991, the PR effect was demonstrated in polymeric materials for the first time.[3] This discovery initiated intensive research activities, and many routes toward organic PR materials have been developed since.[4−6] The most extensively studied material class are composites[7−11] consisting of a polymeric binder doped with low-molecular weight components. Other approaches include low-molecular-weight multifunctional glasses[12−14] and fully functionalized polymers.[15−19]

It was noticed earlier that the PR index modulation in organic materials with rather low glass-transition temperature (T_g) was too high to be explained by a pure EO (Pockels) effect.[7] This was attributed to the "orientational enhancement mechanism",[20] in which the dipolar EO chromophores orient in situ in the space-charge field and thus introduce spatially modulated birefringence via the dynamic Kerr effect.[21] Additionally, the EO effect is enhanced. In composites operated at measuring temperatures T_m close to or above T_g ($T_m - T_g < 30$ K) the orientational birefringence overwhelms the EO effect by far, yielding very large index modulations ($\Delta n > 10^{-2}$).[8b] The response time in such materials may depend on two factors: first on the time to develop the PR space-charge field (E_{SC}) and second on the reorientation time of the EO chromophores in the developing space-charge field.

High-T_g systems ($T_m - T_g > 50$) have been studied much less intensively.[15,16a,c] Here, in the ideal case (no orientational mobility at T_m) the index modulation is solely due to the EO effect, and the temporal response is solely limited by the formation of E_{SC}, since the EO effect is instantaneous. A combination of strong EO effects, large charge-carrier generation efficiencies, and high charge mobilities could in principle produce fast and efficient PR materials. Additionally, the phase stability of single-component, high-T_g materials is superior to low-T_g composites, which may suffer from phase separation or crystallization on long time scales. In our work we focus on the synthesis of high-T_g multifunctional PR polymers.

Polymer analogous reactions using precursor polymers offer the possibility to attach functionalities labile to the polymerization conditions[22] and allow, thus, the incorporation of efficient NLO chromophores. Such precursor routes have been successfully used for the synthesis of PR materials based on polysiloxanes.[19]

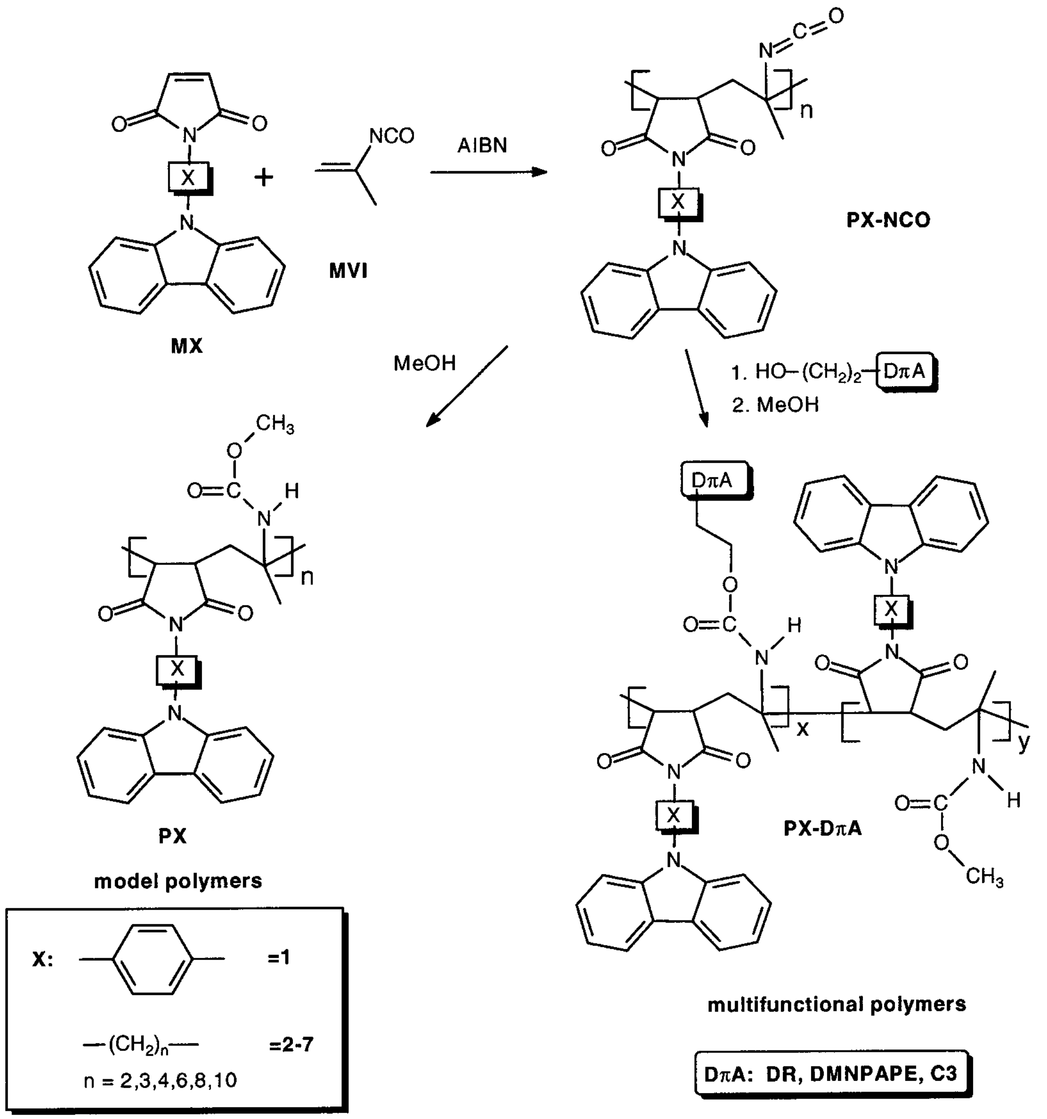
Here, we report about a new multifunctional high-T_g PR polymer system, which is prepared via a precursor route, and first measurements demonstrating its practical potential.

Results and Discussion

Polymer Synthesis. The different structural components of the polymers (Scheme 1) were selected

10.1021/ma990984g CCC: $19.00

Scheme 1. Multifunctional Copolymer System: Polymerization and Polymer Analogous Reactions



according to the following rationale: We chose five-membered maleimide rings to achieve a rigid polymer main chain with high T_g. The imide position was functionalized with carbazole moieties providing charge (hole) transport capability.

The variation of the spacer (phenyl group or alkyl chains of different lengths) between the hole conducting moieties and the imide ring allows to systematically vary the properties of the materials.

AIBN was used as radical initiator for the copolymerization of the maleimides **M1**–**M7** and methyl vinyl isocyanate **MVI**. The copolymerization of maleic anhydride with vinyl isocyanate as well as **MVI** is known to be alternating.[23] The same tendency has been found for the copolymerization of maleimide derivatives with vinyl isocyanate or **MVI**.[22] Therefore, the copolymers obtained here are presumed to be alternating, too.

By reacting the isocyanate groups of the reactive precursor polymers **PX-NCO** with an excess of methanol, model polymers **P1**–**P7** could be obtained. IR spectra of a reactive isocyanate precursor polymer with the characteristic $-N{=}C{=}O$ valence vibration signal at 2260 cm^{-1} and a model polymer where the isocyanate groups have been quantitatively reacted with methanol are shown as Supporting Information (Figure 5). In a two-step/one-pot polymer analogous reaction a variety of hydroxyalkyl-functionalized EO chromophores have been covalently attached to the reactive precursor

Scheme 2. Structures of All Chromophores Used

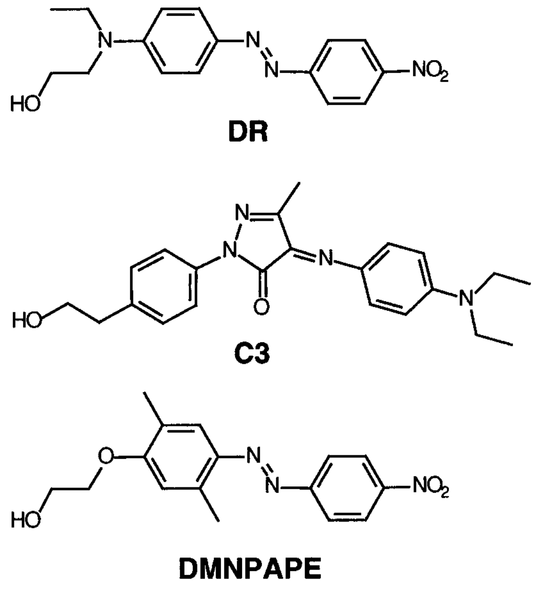


Table 1. Polymer Properties

polymer	$D\pi A$[a] [mol %]	$D\pi A$[a] [wt %]	M_p[b] [kg/mol]	T_g[c] [°C]	λ_{max}[d] [nm]	yield [%]
P1			20	194	<350	31
P2			23	182	<350	22
P3			169	162	<350	76
P4			31	131	<350	35
P5			203	110	<350	72
P6			157	83	<350	70
P7			76	60	<350	62
P5-C3	34	22	28[e]	111	515	34[g]
P5-DMNPAPE	35	19	246[f]	112	392	93[g]
P5-DRa	19	11	102[f]	112	478	19[g]
P5-DRb	36	20	248[f]	111	478	90[g]
P5-DRc	44	23	258[f]	109	478	86[g]
P6-DR	17	10	272[f]	84	478	85[g]

[a] Measured by UV spectroscopy. [b] Measured in THF with refractive index and viscosity detectors universally calibrated with polystyrene standards. [c] Measured at 10 K/min heating rate. [d] Measured in $CHCl_3$. [e] Measured in $CHCl_3$ with refractive index detector calibrated with polystyrene standard. [f] Virtual molecular weights of the polymers depend on the concentration, which can be explained by aggregation. M_p has been calculated from identical model polymers and dye contents. [g] Related to chromophore feed.

polymer forming urethane linkages.[22a] We chose we chose commercially available dispersed red-1 (**DR**), 1,2-(2,5-dimethyl-4-(*p*-nitrophenylazo)phenoxy)ethanol (**DMNPAPE**), and 1-(4-ethylhydroxyphenyl)-3-methyl-4-(4-diethylaminophenyl)imino-pyrazole-5-on (**C3**) as chromophores (**DπA**). With dibutyltin dilaurate[22] as catalyst the desired amounts of chromophore could be incorporated (Table 1). In the course of this addition reactions no ionic side products are formed, which could lead to dielectric breakdown in strong electric fields. In a second step, remaining isocyanate groups are quantitatively reacted with methanol. Unreacted chromophores were removed by extraction. NMR spectra presented in the Supporting Information (Figure 6) confirm the covalent nature of the chromophore attachment.

Polymer Properties. An overview of all polymer properties is compiled in Table 1. All polymers are soluble in chloroform and THF. The molecular weights of the model polymers range between 20 and 272 kg/mol. GPC measurements show no signs of unreacted dye for these samples.

The overall yield of polymerization as well as the molecular weight of the polymers increases with the spacer length. The polymer weight and the polymerization yield peak at **P5** with the hexyl spacer. Polymer **P3** with the propyl spacer forms an exception possessing a high yield and peak molecular weight.

DSC measurements are displayed in Figure 1. All model polymers are amorphous and show one glass transition. Increasing the length of the alkyl spacers between the maleimide unit and the carbazole moiety decreases the T_g of the corresponding copolymer. Varying the spacer length allows to vary T_g between 60 °C (10 methylene units) and 182 °C (two methylene units). The alkyl spacers act as internal plasticizers, which compensate the conformational stiffness of the polymer backbone. Because of the conformational stiffness of the phenyl spacer, the resulting polymer **P1** possesses the highest T_g of 194 °C.

Caused by the conformational stiffness, NMR spectra of the copolymers show broad signals for the polymer backbone protons even at elevated temperatures.[22] Therefore, they cannot be used for a quantitative determination of the copolymer composition and dye contents.

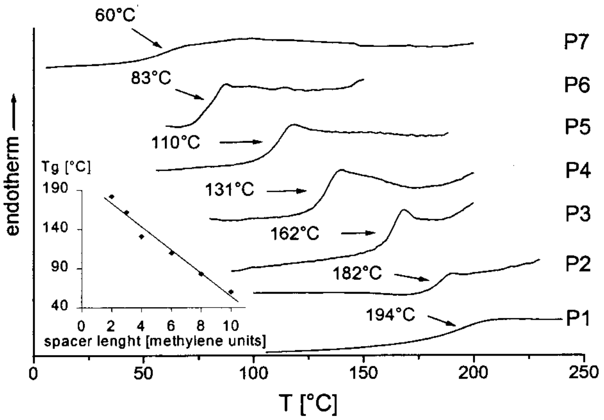


Figure 1. Glass transitions of model polymers **P1**−**P7** measured at 10 K/min.

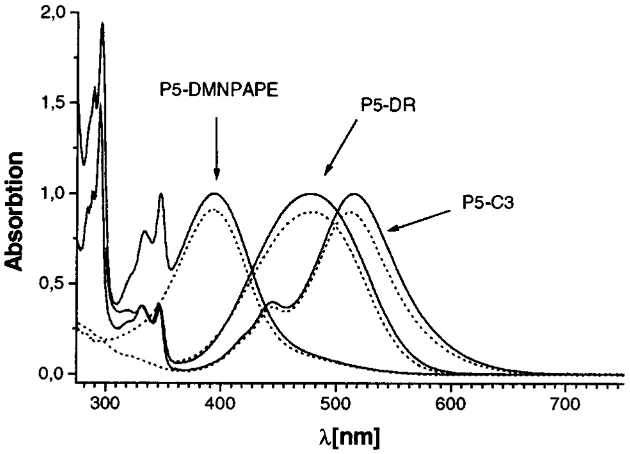


Figure 2. UV/vis spectra of multifunctional polymers **P5-DR**, **P5-DMNPAPE**, and **P5-C3** and chromophores **DR**, **DMNPAPA**, and **C3** in chloroform. λ_{max} of the chromophores attached to the multifunctional polymers (solid line) have been normalized to 1. λ_{max} of the unattached chromophores (dotted line) have been normalized to 0.8.

UV/vis spectra of the dye containing multifunctional polymers are shown in Figure 2. Absorption maxima at 330 and 345 nm originate from the carbazole moieties. Absorption maxima of the attached EO chromophores remain almost unshifted compared to the free chromophores in chlorofrom solution ($\Delta\lambda_{max}$ < 5 nm). The chromophore contents of the multifunctional polymers were determined from the absorption at λ_{max} of the attached chromophores and the extinction coefficients of the free chromophores. Dye contents ranging between 17 and 44 mol % were obtained. In relation to the chromophore feed the reactions proceeded with 85%−93% conversion.

The T_g's of the multifunctional polymers do not differ significantly from the corresponding model polymers **P1**−**P7** (Figure 3). This can be explained by the fact that the chromophores are conformationally rigid aromatic moieties so that only the short spacer group can act as a plasticizer. Multifunctional polymers with chromophore contents up to 36 mol % are amorphous. However, first signs of crystallization (endothermal peak at ≈150 °C indicative of melting of a crystalline phase, Figure 3, top curve) were detected in **P5-DRc** with 44 mol % of the chromophore **DR**.

Photorefractive Properties. For the holographic characterization of the new multifunctionalized PR polymers devices were fabricated by a melt/press tech-

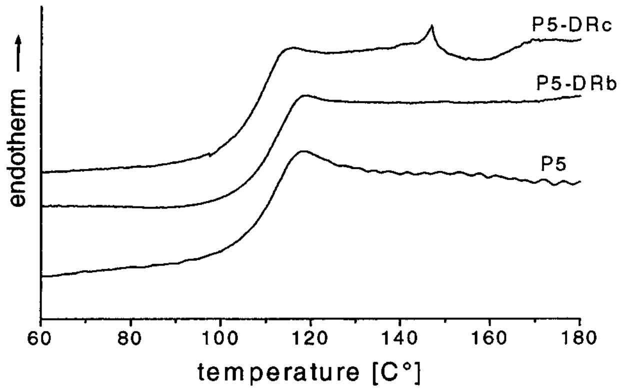
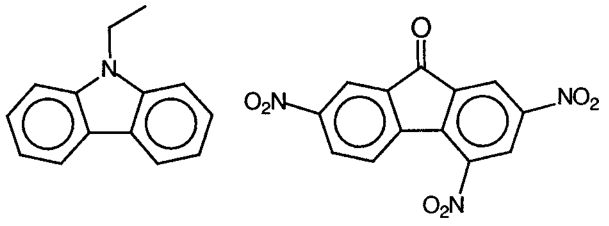


Figure 3. DSC measurements of model polymer P5 and multifunctional polymers **P5-DRb** and **P5-DRc** measured at 10 K/min.

Scheme 3. Structures of TNF and ECZ



ECZ **TNF**

nique sandwiching the composites between two ITO-coated glass substrates at elevated temperatures using glass spacer beads to adjust the film thickness to d = 105 μm.

For proof-of-principle[24] the DR-functionalized derivative of polymer **P5** (**P5-DRa**; T_g = 110 °C) was used. The sensitizer 2,4,7-trinitrofluorenone (**TNF**, Scheme 3) was added, which forms a charge transfer (CT) complex with the carbazole units, which can be optically excited for charge generation. Unfortunately, we did not succeed to obtain working devices from this material; microcracks formed after cooling to room temperature, which we attribute to mechanical stress as a result of the thermal compression. Therefore, to ease the device preparation, T_g was lowered by adding N-ethylcarbazole (**ECZ**, Scheme 3) as a plasticizer. Furthermore, **ECZ** may also act as an additional charge transport unit. The final composition of the composite was 89 wt % **P5/DRa**, 10 wt % **ECZ**, and 1 wt % **TNF**. T_g was determined to be 79 °C. The DSC measurements did not show any indication of phase separation. Within the period of our investigations, the devices were absolutely stable against phase separation.

To exhibit a macroscopic EO effect, the devices were "poled“ in an electric field (E_p = 76 V/μm) at temperatures high enough to allow sufficient rotational diffusion mobility of the EO chromophores (80 °C, 5 min). All devices showed excellent stability against dielectric breakdown under these conditions. After poling was completed, the temperature was reduced to room temperature while the field remained applied, locking in the polar order.

Two-beam coupling (TBC) and degenerate four-wave-mixing (DFWM) experiments were carried out overlapping two s-polarized writing beams ("+0" and "−0", respectively, λ = 633 nm) in the device. The external angles were α_{+0} = 50° (α_{-1} = 70°) and the external intensities were $I_{+0,\mathrm{ext}}$ = 127 mW/cm^2 ($I_{-0,\mathrm{ext}}$ = 178 mW/cm^2). The hologram was read by a weak ($I_{\mathrm{R,ext}}$ = 3 mW/cm^2) p-polarized reading beam counter propagating to "+0". The PR gain coefficient Γ_s and the internal diffraction efficiency η_{int} were calculated according to

$$\Gamma_s = \frac{1}{d}\left[\cos \alpha_{+0} \ln\left(\frac{I_{+0}(t=0,E)}{I_{+0}(t,E)}\right) - \cos \alpha_{-0} \ln\left(\frac{I_{-0}(t=0,E)}{I_{-0}(t,E)}\right)\right] \quad (1)$$

$$\eta_{\mathrm{int}} = I_{\mathrm{R,diffr}}/(I_{\mathrm{R,diffr}} + I_{\mathrm{R,transm}}) \quad (2)$$

where $I_{\pm 0}(t,E)$ is the intensity of one beam at the time t and for a given electric field E and $I_{\mathrm{R,trans}}$ and $I_{\mathrm{R,diffr}}$ are the transmitted and diffracted components of the reading beam.

Even though the devices were prepoled, still an external electric field field (anode facing toward writing beams) had to be applied in order to observe a notable PR effect unlike reported for a π-conjugated fully functionalized PR polymer, which showed two-beam coupling even without electric field.[16a,c] The field enhances the charge-carrier generation and provides the drift force for charge-carrier migration and is, thus, indispensable for the buildup of the space-charge field in our material. The steady-state gain coefficient Γ_s in TBC and the diffraction efficiency η in DFWM both increase with the applied field and reach $\Gamma_{s,\max} = -7$ cm^{-1} and $\eta_{\max} = 0.013$ at E = 95 V/μm. From the latter we can deduce $\Delta n \approx 10^{-4}$. These values are smaller than typically reported for low-T_g PR materials due to the lack of orientational enhancement.[20] Nevertheless, it is the highest diffraction efficiency (index modulation) reported so far for high-T_g PR polymer systems ($\eta = 4 \times 10^{-7}$ in the absence of a sensitizer;[15] $\Delta n = 5 \times 10^{-5}$ in ref 16a). Our gain value is much smaller than those reported in ref 16c on thin films, but note that gain values obtained for "thin" and "thick" (like in our case) devices cannot be directly compared.[25] Finally, it is interesting to note that Γ_s has opposite sign compared with similar low-T_g materials under identical field convention,[26] which is expected if the index modulation is predominantly electrooptic in nature.

We also investigated the grating buildup dynamics in TBC and DFWM (Figure 4). The data could be fitted best by a biexponential function (eq 2):

$$\frac{\eta(t)}{\eta_{\max}} = 1 - A_1 \exp\left(-\frac{t}{\tau_1}\right) - A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (3)$$

Here $\eta_{\max}$ is the steady-state diffraction efficiency, $\tau_{1,2}$ are the two exponential response times, and $A_{1,2}$ are the exponential prefactors (with $A_1 + A_2 = 1$). A similar equation applies to the gain coefficient Γ. This fitting procedure was strictly phenomenological, meaning that the two response times cannot be assigned to distinct physical processes. For the DFWM (TBC) experiment we obtained τ_1 = 0.1 s (0.04 s), τ_2 = 1.5 s (0.66 s), A_1 = 0.77 (0.81), and A_2 = 0.23 (0.19). This compares with response times of several seconds in other high-T_g systems; however, one has to keep in mind that no sensitizer was used in ref 15 and that E = 0 in ref 16a. It is also slower than the fastest composite materials known to date (a couple of milliseconds[9b,10b,11c]).

The identical experiment was repeated 20 times with intermediate erasure cycles (uniform illumination for 1 h with field applied). All traces were almost identical,

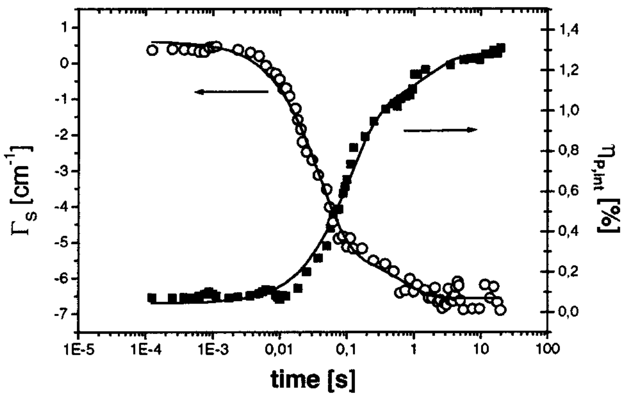


Figure 4. Temporal response of the diffraction efficiency η_p in DFWM (solid squares) and the gain coefficient η_s in TBC experiments (open circles) in **P5-DRa/ECZ/TNF** (89/10/1) at $E_0 = 95$ V/μm. Prior to recording the device was illuminated by the write beam "1" and the field was on. After 5 min the second write beam was switched on by a magnetic shutter.

indicating the excellent reproducibility of the experiment and also the good poling stability of the devices.

Finally, we need to mention that in addition to the PR index grating an "isomerization grating" develops under nonuniform illumination as commonly known for azo dyes such as **DR**.[27] Unlike for the PR grating, the strength and buildup kinetics for the isomerization grating are slightly dependent on the applied electric field. The contribution of this isomerization grating to the index modulation sensed by the reading beam and, consequently, to the diffraction efficiency η is small due to the orthogonal polarizations of the writing beams (s-polarized) and the reading beam (p-polarized). Furthermore, the buildup time of the isomerization grating is rather slow (several minutes) compared with the PR grating ($\approx$100 ms; see above). Therefore, we can attribute our observations (Figure 4) without any doubt to the formation of a PR grating within our devices as also clearly demonstrated by the observation of gain.

Conclusion

We have presented a new class of multifunctional high-T_g PR polymers. By attaching carbazole moieties to the polymer backbone through spacers of varying length, we were able to vary T_g of the materials in a broad range. Furthermore, we demonstrated the practical potential of our reactive precursor polymer by attaching three different EO chromophores, allowing to tailor the optical properties of our materials.

For proof-of-principle, one material with $T_g \approx 80$ °C was evaluated by holographic TBC and DFWM experiments. Up to now, the gain coefficient, index modulation, and diffraction efficiencies are smaller than in low-T_g systems,[4-11] which is expected due to the lack of orientational enhancement.[20] The response times were on the order of 100 ms, which is the fastest value reported for high-T_g systems so far and reasonably fast compared with most low-T_g materials.[4-11] Even faster responses are expected after incorporation of other photoconducting moieties with higher mobility than carbazole into our polymers such as triarylamines and the use of more efficient sensitizers.

Experimental Part

Materials. Commercial chemicals were used without further purifications. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from diethyl ether. Solvents where dried according to literature procedures. Monomers were prepared as described in the Supporting Information.

Instrumentation. Gel permeation chromatography (GPC) at room temperature was used to determine molecular weights of polymer samples on a Jasco PU-980 pump, PSS standard column pore size 10^3 and 10^4 Å, a Jasco RI-930 detector, a Jasco UV-975 detector, and a Viscotek T60A dual detector. A universal calibration based on polystyrene standards was used. Differential scanning calorimetry was performed on a Perkin-Elmer DSC 7 with 10 K/min heating rate. UV/vis spectroscopy was performed on a Shimadzu UV-2102 PC. A Nicolet Protégé 460 was used for IR spectroscopy. NMR were measured on a Bruker ARX 400. FD mass spectroscopy was measured on a Finnigan MAT field desorption spectrometer MAT 90 with a ZAB II-SE-SPD unit.

Polymerization: General Procedure. The method of polymerization is similar for all polymers. Therefore, one general procedure is described. The maleimide (1.5 mmol) is dissolved in a flask filled with dry dioxane (7 mL) under nitrogen atmosphere. The methyl vinyl isocyanate (MVI) is freshly distilled and added with a syringe. The volume of the flask, which is not filled with solvent, should be as small as possible. A slight excess (1.6 mmol) of the volatile isocyanate (boiling point: 69 °C) is added to compensate for the loss into the gas phase. One mole percent of azobis(isobutyronitrile) (AIBN) compared to the total amount of monomers is added. Polymerization is performed at 60 °C for 16 h. Reactive precursor polymers can be precipitated in dry diethyl ether, filtered, and dried in a vacuum at 40 °C. Most polymers have been directly converted to model or chromophore-substituted polymers. GPC was performed on the model polymers, because the reactive isocyanate groups can undergo reactions on the GPC column. All reactive precursor polymers show the characteristic IR isocyanate peak at 2260 cm^{-1} shown in the Supporting Information (Figure 5).

Model Polymers: General Procedure. To achieve model polymers, the reactive precursor polymers are dissolved in dry dioxane or have been directly converted from the polymerization solution. Dry methanol was added with a syringe, and the solution is stirred at 60 °C for 10 h under exclusion of water. The reaction can be monitored by the decrease of the isocyanate band at 2260 cm^{-1} in the IR spectra. The polymers were precipitated in 400 mL of methanol, filtered, redissolved, precipitated again, filtered, and dried in a vacuum at 40 °C. Polymers **P1**−**P4** and **P7** have been converted with 1 mL of methanol directly from the polymerization solution.

P1: 0.15 g (31%). **P2**: 0.11 g (22%). **P3**: 0.48 g (76%). **P4**: 0.17 g (35%) of white powders. **P7**: 0.4 g (62%) of light yellow powder. **P5**: 0.32 g (0.7 mmol) of poly[methyl vinyl isocyanate-*alt*-*N*-(6-(*N*-carbazole)hexyl)maleimide] was dissolved in 5 mL of dry THF and 1 mL of dry methanol. Precipitation in 400 mL of methanol: 0.25 g (72%) of white powder. **P6**: 0.2 g (0.44 mmol) of poly[methyl vinyl isocyanate-*alt*-*N*-(6-(*N*-carbazole)-octyl)maleimide] was dissolved in 5 mL of dry THF and 0.5 mL of dry methanol. Precipitation in 300 mL of methanol: 0.15 g (70%) of white powder. The properties of the polymers are summarized in Table 1.

Dye Containing Polymers: General Procedure. The reaction with hydroxyalkyl-functionalized chromophores is in principle the same as for the model compounds. Reactions carried out in chloroform and dichloromethane proved to yield lower chromophore substitutions than reactions in THF. Chromophores and precursor polymers were dissolved in dry THF, or chromophore is added directly to the polymerization mixture of the reactive precursors. One drop of dibutyltin dilaureat is added to the reaction mixture and stirred at 60 °C for 2 days under exclusion of water. In a final step an excess of dry methanol is added with a syringe to quench remaining isocyanate groups, and the reaction mixture is stirred at 50 °C for another 10 h. The polymers were precipitated in methanol, filtered, redissolved, and precipitated again. The remaining chromophore is removed in a Soxhlet extractor with diethyl ether until the solvent remains colorless. The polymer was filtered and dried in a vacuum at 40 °C. Chromophore content was measured by UV/vis spectroscopy calibrated with the low molecular weight chromophores. The properties of the polymers are summarized in Table 1.

P5-C3: 0.28 g (0.7 mmol) of poly[methyl vinyl isocyanate-*alt*-*N*-(6-(*N*-carbazole)hexyl)maleimide], 0.25 g (0.7 mmol) of 1-(4-ethylhydroxyphenyl)-3-methyl-4-(4-diethylaminophenyl)-iminopyrazole-5-on (C3), 5 mL of dry dichloromethane. Chromophore content: 34 mol % (22 wt %). Yield after extraction: 0.21 g.

P5-DMPAPE: 0.86 g (2 mmol) of poly[methyl vinyl isocyanate-*alt*-*N*-(6-(*N*-carbazole)hexyl)maleimide], 0.2 g (0.6 mmol) of 2-(2,5-dimethyl-4-(*p*-nitrophenylazo)phenoxy)ethanol (DMNPAPE), 10 mL of dry THF. Yield after extraction: 0.94 g. Chromophore content: 35 mol % (19 wt %). Yield related to chromophore feed: 93%.

P5-DRa: 0.3 g (0.7 mmol) of poly[methyl vinyl isocyanate-*alt*-*N*-(6-(*N*-carbazole)hexyl)maleimide], 0.22 g (0.7 mmol) of disperse red (DR), 5 mL of dry chloroform. Chromophore content: 19 mol % (11 wt %). Yield after extraction: 0.37 g.

P5-DRb: 1.5 g (3.5 mmol) of poly[methyl vinyl isocyanate-*alt*-*N*-(6-(*N*-carbazole)hexyl)maleimide], 0.38 g (1.2 mmol) of disperse red (DR), 20 mL of dry THF. Yield after extraction: 1.82 g. Chromophore content: 36 mol % (20 wt %). Yield related to chromophore feed: 90%.

P5-DRc: 1.5 g (3.5 mmol) of poly[methyl vinyl isocyanate-*alt*-*N*-(6-(*N*-carbazole)hexyl)maleimide], 0.55 g (1.7 mmol) of disperse red (DR), 20 mL of dry THF. Yield after extraction: 1.82 g. Chromophore content: 44 mol % (23 wt %). Yield related to chromophore feed: 86%.

P6-DR: 0.36 g (0.79 mmol) of poly[methyl vinyl isocyanate-*alt*-*N*-(8-(*N*-carbazole)octyl)maleimide], 0.49 g (1.6 mmol) of disperse red (DR), 5 mL of dry THF. Yield after extraction: 0.32 g. Chromophore content: 17 mol % (24 wt %). Yield related to chromophore feed: 85%.

Acknowledgment. This work was supported by the "Photonic" program of the Volkswagen Foundation (Germany). We gratefully thank Jürgen Wichern and Prof. P. Boldt (both University of Braunschweig, Germany) for providing the chromophore **C3**.

Supporting Information Available: Description of synthesis of monomers and DMNPAPE as well as NMR spectra and IR spectra which prove the covalent nature of the chromophore attachment. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA990984G