Facile Attachment of Nonlinear Optical Chromophores to Polycarbonates

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Received August 19, 2008
Revised Manuscript Received October 8, 2008

Introduction. Second-order nonlinear optical (NLO) polymers are being intensively investigated because of their potential application in high-speed electro-optic (EO) devices with very broad bandwidth and low driving voltage.[1−5] Covalent attachment of NLO chromophores to polymers backbones can effectively increase chromophore loading, prevent phase separation, and result in a better dipole alignment stability than the guest−host systems.[4,6] There are two major ways to achieve chemical incorporation of a NLO chromophore into a polymer.[4,7,8] One method is to functionalize the chromophore with suitable chemical groups to give a monomer that can eventually react to form a copolymer.[9−11] Although the so obtained side-chain NLO polymers have shown several advantages, such as a high-temperature alignment stability and good mechanical properties, this approach often requires tedious procedures for the synthesis of the appropriate chromophore-containing monomers. The other method is to covalently connect the chromophore, either directly or using a linker or spacer, to a prepolymerized macromolecule possessing a suitable pendent functionality for the attachment.[12−14] This procedure is particularly attractive for high NLO dyes, which are often prone to chemical degradation under the polymerization conditions.[15,16]

While polycarbonates have widely been employed as a host material for NLO chromophores (amorphous polycarbonate, APC, in particular), thanks to good optical properties, high T_g, and good processability,[5,17] to the best of our knowledge, there are no synthetic procedures that provide a convenient modular approach to attach NLO chromophores to the polycarbonate backbone.

Moore and Brittain have reported a strategy to NLO polycarbonates in which first a chromophore was attached to the bisphenol functionality.[18] The chromophore was used to make cyclic carbonate oligomers which were eventually converted to polycarbonates via ring-opening polymerization in solution.

Recently, we have reported a synthetic methodology to side-chain NLO polycarbonates, requiring the synthesis of donor-containing dihydroxy monomers, followed by copolymerization and post-tricyanovinylation.[19] In this procedure, the polycarbonate backbones were achieved by condensation polymerization of equimolar amounts of a dihydroxy-containing monomer with the commercially available bis(chloroformates) of bisphenol A or Z. This class of compounds, however, is expensive, and not many derivatives are readily attainable, requiring the prior laboratory preparation in case monomers with different properties are needed. Furthermore, the general applicability of this procedure is limited by the small availability of postfunctionalization reactions, which restricts the selection of chromophores.[11]

Recently, a procedure to synthesize polycarbonates has been described based on the polycondensation polymerization of bisphenol derivatives with triphosgene (bis(trichloromethyl)carbonate).[20,21] This methodology has two main advantages over the former one: (i) virtually any dihydroxy-containing monomer can be used; (ii) the monomer-to-monomer ratio is not limited to equimolarity, but can easily be varied over a wide range, or even more than two different dihydroxy monomers can be employed. This results in a greatly improved versatility in tuning the physicochemical properties (i.e., rigidity, T_g, thermal stability) of the final material.

This Communication deals with a versatile synthesis of NLO side-chain polycarbonates, as depicted in Scheme 1. It is based on the reaction of a carboxylic acid-containing polycarbonate with appropriately functionalized chromophores. The introduction of the chromophore in the final reaction step also allows a great flexibility, both in forming the polymer backbone and in controlling the amount of chromophore incorporated. In addition to the synthesis, the characterization, the thermal properties as well as the second-order nonlinearity of the synthesized polymeric materials is described.

Results and Discussion. *Synthesis.* To synthesize a polycarbonate with a pendent anchoring group, 4,4-bis(4-hydroxyphenyl)valeric acid (**1**) was chosen as diphenolic monomer. It is known that its carboxylic acid group causes cross-linking and branching when directly polymerized with phosgene.[22] Therefore, to obtain well-defined, linear polycarbonates, the carboxylic group was first protected by esterification with *tert*-butanol (Scheme 2). The obtained bisphenol **2** was then condensed with bisphenol Z (**4**) using triphosgene and pyridine as a base in the presence of a few mol % of phenol as chain terminator to give polymer **PC-Z-*t*But** with M_n in the range of ∼10 000 to ∼15 000 and a polydispersity of ∼2 and a good solubility.[23]

Subsequently, the *tert*-butyl groups in polymer **PC-Z-*t*But** were quantitatively cleaved with trifluoroacetic acid at room temperature, achieving polycarbonate **PC-Z** with free pendent carboxylic acid groups. The completion of the reaction was checked by the consistent reduction of the C−H stretching band at around 2900 nm in the IR spectrum and the complete disappearance of the singlet of the *tert*-butyl group at 1.41 ppm in the ^{1}H NMR spectrum.

Polymers that contain fluorine in or along the backbone possess many desirable physical properties. In general, fluoropolymers exhibit high thermal stabilities, enhanced chemical resistance, and decreased intermolecular attractive forces (which turns in a better solubility) compared to their hydrocarbon analogues.[24,25] The optical loss by absorption due to the vibration overtones of the polymer at the key telecommunication wavelength of 1.3 μm is also minimized by substituting hydrogen with fluorine.[26]

To obtain a polycarbonate with high fluorine content, bisphenol AF (**4**) was used, containing two CF_3 groups instead of the cyclohexyl moiety in bisphenol Z (**3**). Following the same procedure described above, monomer **2** was copolymerized in a 1:2 ratio with bisphenol AF (**4**) to obtain polycarbonate **PC-AF** (Scheme 2).

The polycarbonates **PC-Z** and **PC-AF** are soluble in polar solvents, such as THF, DMF, and cyclopentanone, with polymer **PC-AF** showing the best solubility. This might be explained

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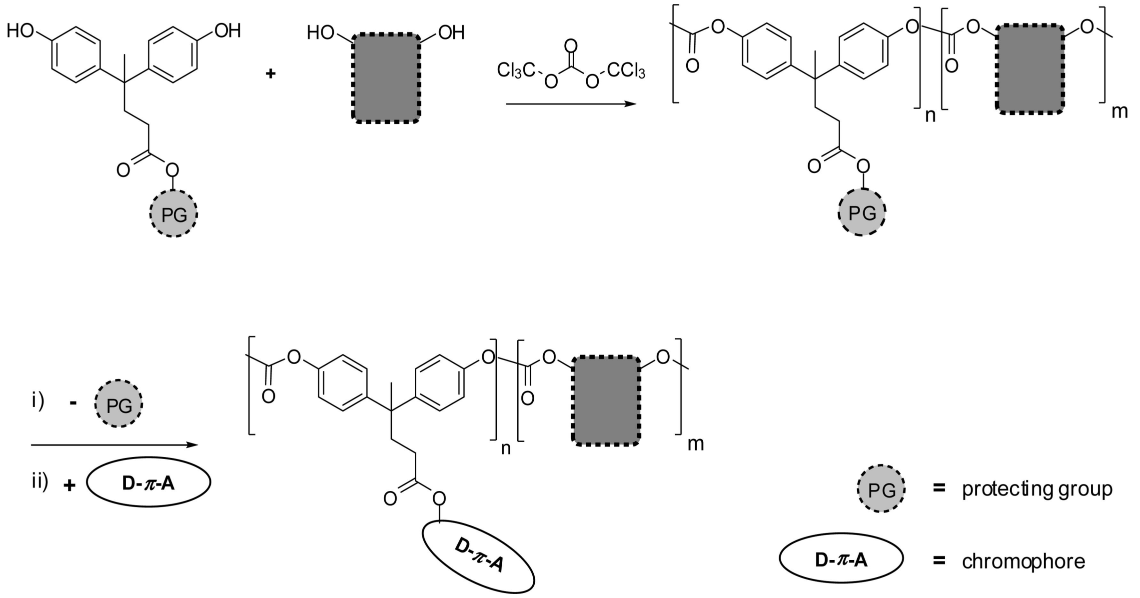
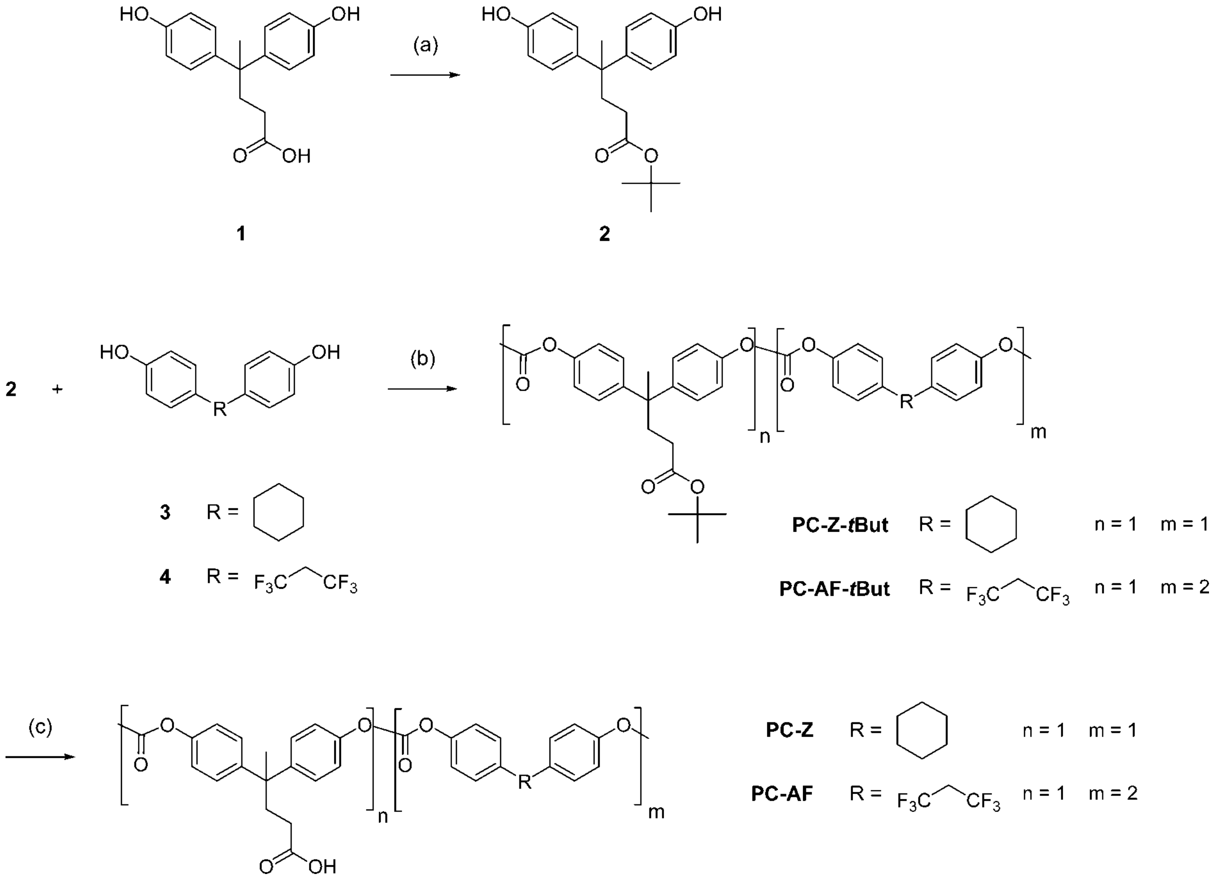
10.1021/ma801875w CCC: $40.75

Scheme 1. General Strategy for the Synthesis of Side-Chain NLO Polycarbonates



Scheme 2. Synthesis of the PC-Z and PC-AF Polycarbonates[a]

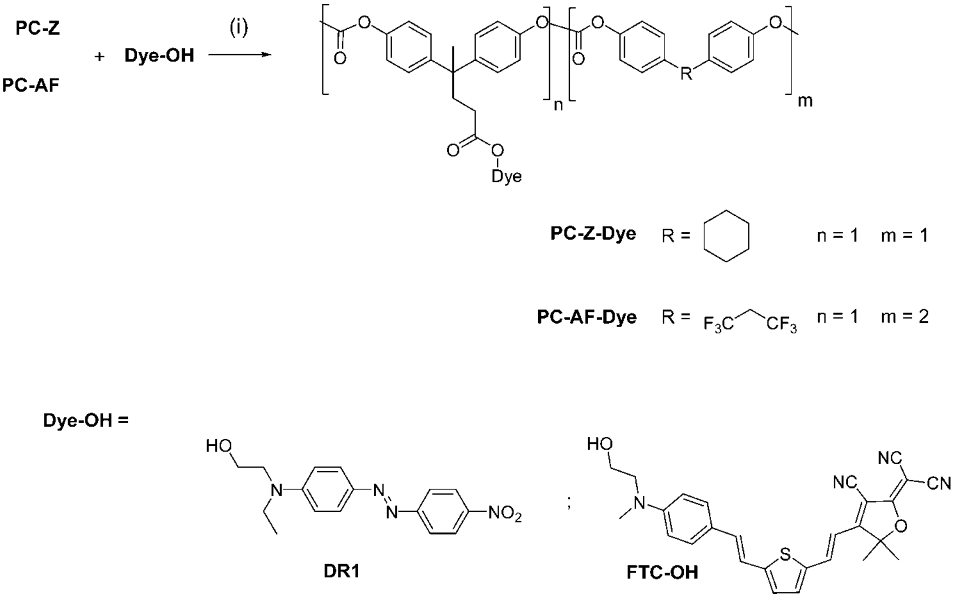


[a] Reagents and conditions: (a) trifluoroacetic anhydride, *tert*-butanol, THF, rt; (b) triphosgene, pyridine, THF, CH_2Cl_2, rt; (c) CF_3COOH, CH_2Cl_2, rt.

either by the presence of the hexafluoropropylidene moiety reducing intermolecular packing or by the smaller content of carboxylic acid groups.

The hydroxyethyl group containing chromophores **DR1** and **FTC-OH** (Scheme 3) were attached to the polycarbonate backbones using 1,3-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridium-4-toluenesulfonate (DPTS) as the coupling agents.[27] This methodology has been reported to provide efficient anchoring of high-$\mu\beta$ dyes, such as the **CLD** and **FTC** type, to a wide variety of polymers and dendrimers.[28−31] After attaching the chromophores a new peak appeared in the ^1H NMR spectra at about 4.18 ppm, that was assigned to the oxymethylene protons ($-OCH_2-$) of the ester linkage with the dye. The degree of functionalization was determined either

Scheme 3. Dye Attachment to the Polycarbonates PC-Z and PC-AF[a]



[a] Reagents and conditions: (i) DCC, DPTS, CH_2Cl_2, THF, rt.

Table 1. Summary of the Thermal, Physical, and Optical Properties of the NLO Polycarbonates

	λ_{max}[a] (nm)	T_d^5[b] (°C)	T_g (°C)	M_w	M_w/M_n	chrom density (wt %)	r_{33} (pm/V)
PC-Z-DR1	476	347	202	14 500	2.3	29	22[c]
PC-Z-FTC	624	282	186	16 200	2.1	35	26[d]
PC-AF-DR1	475	385	189	16 800	2.0	20	16[c]
PC-AF-FTC	629	303	174	19 300	2.4	24	38[d]

[a] λ_{max} was measured in THF. [b] T_d^5 is defined as the point at which 5% weight loss has occurred in the polymer. [c] Measured at 830 nm. [d] Measured at 1300 nm.

on the basis of the peak area of the methylene protons of the pendent group (at 2.0−2.3 ppm) and the area at 4.2 ppm that corresponds to the $-OCH_2-$ protons or by quantitative analysis of the UV spectra of their solution in THF. In all cases, attachment efficiencies of over 70% were obtained (Table 1).

All NLO polymers containing the **DR1** and **FTC** chromophores have a good solubility in high boiling solvents, such as cyclopentanone.

Polymer Physical Properties and Processing. The thermal properties of the polymers were determined by DSC and TGA measurements. All NLO side-chain polycarbonates have a high T_g (>174 °C) and excellent thermal stabilities (Table 1). The T_g of these polymers varied from 174 to 202 °C, depending on the structure and the density of the attached choromophores. Weight losses of less than 5% were observed up to 280 °C. In general, the NLO polymers containing the bisphenol Z monomer show sensibly higher T_g values (11−15 °C) compared with the corresponding polymers containing the bisphenol AF monomer, while the former ones possess higher decomposition temperatures T_d^5 (21−38 °C). Moreover, the fact that polymers containing the thermally most stable **DR1** chromophore (T_d > 347 °C) also possess the highest T_d^5 of the NLO polymers suggests that the thermal properties of NLO polycarbonates can be further improved if thermally more stable chromophores are chosen.

UV spectra of the NLO polymers were recorded in CH_2Cl_2, and the λ_{max} values are reported in Table 1. All polymers exhibit strong absorption maxima in the visible region attributed to the $\pi-\pi^*$ charge-transfer band of NLO chromophores and show colors ranging from red to blue (Figure 1).

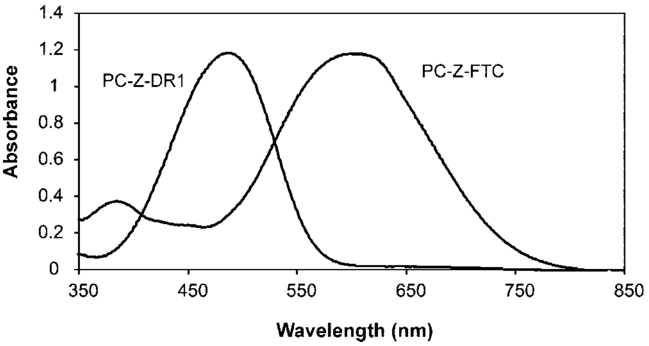


Figure 1. Absorption spectrum of the **PC-Z-DR1** and **PC-Z-FTC** polymers in THF.

To minimize the optical loss contributed from absorption, it is important to have the material with its absorption band edge far away from the operating wavelength of EO devices. Therefore, the **PC-Z-FTC** and **PC-AF-FTC** polymers are suitable for use at 1300 nm, while the polymers containing the **DR1** chromophore are more appropriate to be used at 830 nm. Accordingly, the measurements of the EO coefficient (r_{33}) were carried out at two different wavelengths, and the results are reported in Table 1.

Thin films for EO measurements were prepared as described previously,[32] starting from solutions of the NLO polycarbonates at 10−15 wt % in cyclopentanone. The r_{33} values, reported in Table 1, were measured using a Teng−Man simple reflection technique.[33]

For the **PC-Z-DR1** and **PC-AF-DR1** polymers, containing 29 and 20 wt % of **DR1** chromophore, r_{33} values of 22 and 16 pm/V (at 830 nm) were measured, respectively. It has been reported that the r_{33} values for FTC-based guest−host systems increase up to 55 pm/V upon chromophore loading, but decrease again when more than ~25 wt % is added.[9,34] For **PC-Z-FTC**, containing 36 wt % of the highly active **FTC-OH** dye, an EO coefficient of 26 pm/V (at 1300 nm) was recorded. This can be attributed to the detrimental aggregation effects between the highly polar chromophores, which decreases the EO response at high chromophore loading levels. This hypothesis is in part supported by the fact that the highest r_{33} value, being 38 pm/V, was obtained for **PC-AF-FTC** containing only 24 wt % of chromophore. A similar behavior has been observed for other polymer systems containing highly active dyes.[3,35]

This problem may be avoided by incorporation of bulky structures into the polymer backbone or directly into the chromophore that can ensure site isolation, consequently avoiding chromophore aggregation at high loading densities.[9,36,37]

In conclusion, a versatile, generally applicable synthetic methodology for side-chain NLO polycarbonates was developed. This represents the first example of covalent incorporation of NLO chromophores to a prepolymerized polycarbonate backbone. This methodology allows to adjust the polymer backbone structure and to vary the chromophore loading level in order to fine-tune the physical properties of the resulting material. The resulting NLO polycarbonates possess a high thermal stability, good solubility and can be easily processed into films of excellent quality. In spite of the high chromophore concentrations, fairly high glass transition temperatures were obtained (T_{g}s as high as 202 °C). Moreover, when a **FTC** type of chromophore was incorporated EO coefficients as high as 38 pm/V (at 1300 nm) were achieved. The combination of these properties provides a great promise for the development of EO devices based on NLO polymers.

Acknowledgment. This research was supported by the Dutch Technology Foundation STW, Applied Science Division of NWO, and carried out within the framework of the project TOE 6067 “Broadband and wavelength selective modulators for optical communication based on electro-optic polymers”.

Supporting Information Available: Detailed synthetic procedures and characterization data for the monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA801875W