Photostable nonlinear optical polycarbonates

Mirko Faccini,^{*a*} Muralidharan Balakrishnan,^{*b*} Mart B. J. Diemeer,^{*b*} Riccardo Torosantucci,^{*a*} Alfred Driessen,^{*b*} David N. Reinhoudt^{*a*} and Willem Verboom^{**a*}

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Highly thermal and photostable nonlinear optical polymers were obtained by covalently incorporating the tricyanovinylidenediphenylaminobenzene (TCVDPA) chromophore to a polycarbonate backbone. NLO polycarbonates with different chromophore attachment modes and flexibilities were synthesized. In spite of the high loading levels (ranging from 33.1 to 39.8 wt%), the polymers exhibit T_g s as high as 215 °C, representing a significant improvement of over 100 °C of the material T_g compared with that of the guest–host system containing the same chromophore at similar high loadings. EO coefficients up to 33 pm V⁻¹ at 830 nm were achieved, and a good temporal stability of the dipole alignment at 50 °C was observed.

Introduction

In the past decade, a large number of nonlinear optical (NLO) chromophores has been synthesized and incorporated as guests in a wide variety of host polymers.¹⁻¹² In particular, amorphous polycarbonate (APC) has been extensively investigated as a host polymer, due to its low crystallization tendency, good solubility in spin-casting solvents and high glass transition temperature ($T_g = 205 \text{ °C}$).^{13,14} Moreover, its compatibility with large $\mu\beta$ chromophores and its high dielectric constant allow a good poling efficiency.¹⁵

Although the T_g of APC polymers is high, the incorporation of a chromophore will induce plasticization, considerably lowering the T_g of the composite material, and therefore reducing the temporal stability of the poling induced alignment.¹⁶ Moreover, chromophores can sublimate out of the matrix at high processing temperatures, or could be dissolved by organic solvents used in fabrication of multilayer devices. One way to solve these problems is by covalently incorporating the chromophores into high- T_g polymers.¹⁷

Surprisingly, in spite of the exceptional properties of polycarbonates when employed as host, to the best of our knowledge there are no examples in the literature about the incorporation of chromophores as a side-chain in a polycarbonate backbone.

Recently, we have described a series of chromophores based on the highly thermal and photostable tricyanovinylidenediphenylaminobenzene (**TCVDPA**)^{18,19} which were incorporated as a guest at high loading in polysulfone.²⁰ Although the increase of the chromophore concentration led to higher electro-optical (EO) coefficients, it also resulted in a dramatic decrease of the T_g of the polymeric material, which might be detrimental for the long term efficiency of a device. To provide EO materials with improved stability, the TCVDPA chromophore (17) (Chart 1) is incorporated into a polycarbonate backbone, combining the good properties of polycarbonates with the improved temporal stability given by chromophore attachment. The synthesis and the properties of six novel thermally and photochemically stable NLO polycarbonates in which the TCVDPA chromophore (17) is either "donor-embedded" into the polymer backbone or linked to it through flexible spacers is described. Moreover, the effects of the attachment mode and the flexibility on the poling efficiency and alignment stability are studied, together with a comparison with a guest–host system incorporating the same chromophore.

Results and discussion

Synthesis

The synthesis of the necessary dihydroxy-functionalized monomers 3 and 9 containing the triphenyl amine donor group is given in Scheme 1. Monomer 3, having flexible alkyl chains, was synthesized by reaction of bisphenol 1 with 2-bromo-1-propanol (2) under Finkelstein conditions. The synthesis of bisphenol monomer 9 starts with the demethylation of 4-methoxy-triphenylamine (4) with BBr₃ to give 4-hydroxy-triphenylamine 5. Saponification of the ester in diarylmethane derivative 6 with KOH gave 7 having a free valeric acid moiety, which was then reacted with 4-hydroxy-triphenylamine 5 under DCC coupling conditions to afford ester 8. Cleavage of the benzyl ether bonds by Pd/C catalyzed reduction with hydrogen gave bisphenol monomer 9.

The general synthesis route for the NLO active polymers is depicted in Scheme 2. Condensation polymerization of equimolar amounts of the dihydroxy-functionalized triphenyl amine group containing monomers (1, 3, or 9) with the corresponding bisphenol (A or Z) bis(chloroformate) (10-A or 10-Z) in solution using pyridine as a base, afforded the donor containing polycarbonates. Subsequent post-tricyanovinylation by treatment with tetracyanoethylene (TCNE) gave the corresponding NLO active polymers. The tricyanovinyl (TCV) groups were introduced in the last stage of the polymer preparation to

^aLaboratories of Molecular Nanofabrication, University of Twente, MESA+ Research Institute for Nanotechnology, P.O. Box 217, 7500 AE Enschede, The Netherlands. E-mail: w.verboom@utwente.nl ^bIntegrated Optical Microsystems, University of Twente, MESA+

^oIntegrated Optical Microsystems, University of Twente, MESA+ Research Institute for Nanotechnology, P.O. Box 217, 7500 AE Enschede, The Netherlands







Scheme 1 Synthesis of monomers 3 and 9. *Reagents and conditions*: (a) K_2CO_3 , KI, THF, reflux; (b) BBr₃, CH₂Cl₂, rt; (c) KOH, ethanol, water, reflux; (d) dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridinium-4-toluenesulfonate (DPTS), CH₂Cl₂, rt; (e) H₂, Pd/C, Na₂CO₃, THF, rt.



Scheme 2 Synthesis of NLO polycarbonates. Reagents and conditions: (a) pyridine, THF, CH₂Cl₂, rt; (b) TCNE, DMF, 90 °C.

prevent the exposure of the chromophores to the harsh reaction conditions.

To prove the introduction of the TCV group, the IR spectra of the **12-Z** and **15-Z** polymers are shown in Fig. 1 for comparison. In the latter case a strong -CN stretching band is visible at 2218 cm⁻¹. Upon tricyanovinylation, in the ¹H NMR spectra the aromatic protons *meta* to the amino group shift from about 7.2 in **12-Z** to about 7.9 ppm (doublet) as result of the strong electron-withdrawing effect of the TCV group. The degree of



post-functionalization was determined from the peak area of the protons *ortho* to the TCV moiety (marked with (a) in Chart 1) and the peak areas of the methyl protons of the bisphenol A moieties (b) or the methylene protons of the bisphenol Z units (c). For the donor embedded **14-A** and **14-Z** polymers functionalization proceeded for 73 and 75%, respectively. For the **15-A** and **15-Z** polymers, having a three-carbon spacer connecting the triphenylamine donor unit to the polycarbonate backbone, over 80% tricyanovinylation was obtained. However, for the **16-A** and **16-Z** polymers, having the donor attached as a side chain, the highest degrees of functionalization were obtained, namely 92 and 88%, respectively.

Thermal analysis

The thermal properties of the NLO polymers (Chart 1) are reported in Table 1. The decomposition temperature (T_d) of all chromophore-containing polycarbonates is in the range between 329 and 380 °C, the donor-embedded polycarbonates **14-A** and **14-Z** being the most stable structures. Due to their more rigid structure, these two polymers, in spite of the high chromophore loading of over 38 wt%, possess the highest T_gs of the whole series, 206 and 215 °C, respectively. This result represents a significant improvement of over 100 °C of the material T_g compared with that of a guest–host system incorporating the TCVDPA chromophore (**17**) at similar high loadings, as reported previously.²⁰

Table 1 Summary of the thermal, physical, and optical properties of the NLO polycarbonates^a

	λ_{\max}^{b}/nm	$T_{\rm d}{}^c/{}^{\circ}{\rm C}$	$T_{\rm g}/^{\circ}{\rm C}$	$M_{ m w}$	$M_{\rm w}/M_{\rm n}$	Chrom. content (wt%)	$r_{33}^{d}/\text{pm V}^{-1}$
TCVDPA (17)	531	360	85 ^{ce}			35 in PS ^e	12
14-A	523	371	206	12700	2.3	39.8	15
14-Z	523	380	215	14600	1.9	38.6	15
15-A	524	351	166	12400	1.7	37.0	33
15-Z	524	359	172	8300	1.9	36.2	31
16-A	526	329	178	12400	1.8	35.3	13
16-Z	526	341	184	10900	1.8	33.1	12

^{*a*} For structures see Chart 1. ^{*b*} λ_{max} was measured in CH₂Cl₂. ^{*c*} The onset temperature of degradation (T_d onset) can be calculated from the intersection of the tangent to the slope of the curve corresponding to the first weight loss event. ^{*d*} Measured at 830 nm. ^{*e*} As guest in polysulfone host (data taken from ref. 20).

While the introduction of flexible alkyl chromophore-polymer tethers can enhance the chromophore mobility, facilitating the poling process, it is known that it will reduce the T_g of the material.²¹ For the **16-A** and **16-Z** polycarbonates, having the chromophore anchored as a side-chain through a valeric acid tether, the T_g drops to 178 and 184 °C, respectively. However, this drop is even more pronounced when three-carbon spacers are introduced between the chromophore and the bisphenol moieties, leading to a T_g of 166 °C for polymer **15-A** and 172 °C for polymer **15-Z**. The higher intrinsic structural rigidity induced by the cyclohexyl group²² in the bisphenol Z monomer generally results in polymers with substantially higher T_gs (6 to 9 °C increment) with respect to those containing a bisphenol A monomer, having two methyl groups instead.

Linear optical properties

UV spectra of the NLO polymers were recorded in CH₂Cl₂ and the λ_{max} values are reported in Table 1. All NLO polycarbonates studied have a strong charge-transfer band (450–650 nm) in the visible region of the spectrum, with λ_{max} lying between 523 and 526 nm. A typical spectrum is shown in Fig. 2. In general a small but consistent blue shift (5–8 nm) compared with that of the TCVDPA chromophore (17) is noticeable for all polymers. This can be attributed to the fact that, in the polymer, the chromophore is more closely surrounded by a low dielectric constant environment. Moreover, all derivatives have a minimum in the absorption spectra (around 400 nm) between the charge-transfer band and the higher-energy aromatic electronic transitions.

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Fig. 2 Absorption spectra of the TCVDPA chromophore (17) and the 14-A polymer in CH₂Cl₂.

Photobleaching test

To obtain an estimation of the photostability of the NLO polycarbonates, the straightforward and low-cost qualitative method described in ref. 20 was used. It concerns the monitoring of the decrease in absorbance during irradiation of oxygen-saturated solutions of chromophore-containing polymers in $CDCl_3$ with visible white light.

Photobleaching tests were carried out for the chromophorecontaining 14-A, 15-A, polymethylmethacrylate-DR1 (PMMA-DR1), and polyurethane-DANS (PU-DANS) polymers (Chart 2). From Fig. 3 it can be seen that the 14-A and 15-A polycarbonates, containing the highly photostable TCVDPA chromophore, have exceptional stability under the experimental condition used. In fact, only 5% decay of the original absorbance was noticed after irradiation for 130 min. There is no significant difference in the photobleaching behavior between the two polycarbonate polymers, indicating the minor influence of the polycarbonate backbone on the photobleaching process. In comparison, the PMMA-DR1 (18) and PU-DANS (19) polymers, containing stilbene-based and azo-based chromophores, show significantly faster degradation rates. This trend reflects the behavior obtained for the monomeric chromophores reported previously²⁰ suggesting that, for solution experiments, there is little or negligible influence of the nature of the polymeric structure on the chromophore degradation rate. This parameter is known to play a fundamental role in photostability experiments conducted on thin films.²³ From these results it can be concluded that the described NLO polycarbonates are among the most photostable structures ever reported.



Chart 2 Structures of PMMA-DR1 (18) and PU-DANS (19) polymers.



Fig. 3 Photobleaching curves of the **14-A**, **15-A**, PMMA-DR1 (**18**), and PU-DANS (**19**) polymers in CDCl₃. *A* is the absorbance at time *t* and A_0 is the initial absorbance. Photolyses were carried out in 10 mm quartz cuvettes with light from a 75 W halogen lamp. The samples were irradiated at a distance of 10 cm from the light source and were shielded from daylight.

Electric field poling and EO property measurements

All polymers described have good solubility in common organic solvents, such as THF and CH₂Cl₂. Thin films for EO measurements were prepared as described previously,²⁰ 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 at a wavelength of 830 nm.²⁴

As an example, Fig. 4 shows the poling curve of the **14-A** polymer. The poling curves of all polycarbonates show as a general trend the strong dependence of the EO coefficient on the poling temperature. The measured r_{33} value increases linearly with the poling temperature, reaching a maximum at 10–15 °C below the T_g of the material. After this point, no further increase or even a decrease of the EO coefficient is observed. Therefore these temperatures were chosen as the poling temperatures.

The 14-A and 14-Z polymers, having the highest chromophore loading density of the series (39.8 and 38.6 wt%, respectively), have an r_{33} value of 15 pm V⁻¹. In comparison, the 15-A and 15-Z polymers exhibit a more efficient poling, with r_{33} values of 33 and 31 pm V⁻¹, respectively. This probably reflects the intrinsically lower T_g values, caused by the higher degree of chain flexibility, enabling the chromophore a higher degree of freedom to reorient under the electric field. These high EO coefficients significantly outperform that of the 17–polysulfone guest–host system (12 pm V⁻¹ at 35 wt%), as reported previously.²⁰ This result can possibly be explained by a combination of the good poling efficiency provided by the polycarbonate and the improved shielding of chromophores by the attached polymer backbone.

For the **16-A** and **16-Z** polymers a higher EO response was expected, due to a possibly higher poling efficiency provided by the chromophore-to-polymer tethers. However, disappointing r_{33} values of 13 and 12 pm V⁻¹, respectively, were recorded. From other studies it is known that the degree of dipolar ordering within a covalently attached chromophore–host matrix heavily depends on subtle differences in architectural design, including polymer backbone rigidity, degree of branching, free volume, chromophore binding mode, and chromophore electrostatic interactions.²⁵⁻²⁸

To study the effect of the chromophore-to-polymer binding mode and the attachment flexibility on the temporal stability of the dipole alignment, the decay of the EO coefficient at 50 °C was followed over time for poled samples of the 14-A, 15-A, and 16-A polycarbonates. From Fig. 5 it is clear that 14-A and 15-A have the highest temporal stability, retaining over 90% of their original EO response after 300 h. Differently, for 16-A a faster decay was observed, retaining only 74% of the starting value. These trends might be understood considering the two factors that contribute to the decay: (i) the $T_{\rm g}$ of the polymer, that is related to the energy needed for the whole backbone to increase its mobility, and (ii) the chromophore binding mode, that is related to its degree of freedom and therefore to the energy needed for the single chromophore to reorient. While the first factor is predominant at high temperatures (less than 50 °C to the T_{g}), the latter has a large influence at lower temperatures. Since all polycarbonates in this study have a $T_{\rm g}$ higher than 160 °C it is







Fig. 5 Comparison of the thermal decay curves at 50 °C for different EO polymer systems.

assumed that at 50 $^{\circ}$ C the observed decay is due to differences in the chromophore binding mode.

In case of the **14-A** and **15-A** polymers the chromophore is part of the polymer main-chain being covalently bound at two positions. Therefore it requires more energy to relax back to the centrosymmetric state. However, in case of **16-A** the NLO chromophore is attached as a side appendage to the backbone, giving to it a greater degree of freedom to reorient independently, without requiring the additional energy needed for the polycarbonate structure to move with it.

Furthermore, a temporal stability experiment at the same temperature was conducted with a poled sample of the chromophore 7 at 25 wt% as guest in polysulfone, resulting in a material with a T_g of 110 °C. A much steeper decay was observed during the first 24 h after poling, after which a constant but slow decrease took place, resulting in a loss of 32% of the original EO signal after 250 h.

From these results it can be concluded that the stability of the dipole alignment increases with the number of chromophoreto-polymer attachment points. Moreover, direct incorporation of the TCVDPA chromophore into the polymer backbone gives a higher temporal stability than being attached through a tether.

Conclusions

NLO polycarbonates incorporating the TCVDPA chromophore (17) with different attachment modes and flexibility show interesting properties. Chemical bonding of the chromophore to the backbone allowed high loading levels (ranging from 33.1 to 39.8 wt%) without any plasticization effect. T_g values as high as 215 °C were obtained, representing a significant improvement of over 100 °C of the material $T_{\rm g}$ compared with that of the guesthost system containing the same chromophore at similar high loadings reported previously.²⁰ Higher poling efficiencies were achieved when a larger degree of chain flexibility was introduced, with EO coefficients (up to 33 pm V^{-1} at 830 nm) that significantly outperform that of the 17-polysulfone guest-host system. The temporal stability at 50 °C increases with the number of chromophore-to-polymer attachment points, retaining up to 92% of the original r_{33} value after 300 h of isothermal heating. Thanks to their excellent photostabilities, combined with their thermal stabilities up to 380 °C, these NLO polycarbonates could represent a step forward toward long-lifetime device-quality materials.

Experimental

General procedures

All chemicals were obtained from commercial sources and used without further purification. THF was freshly distilled from Na/ benzophenone, and CH₂Cl₂ from CaCl₂. All chromatography associated with product purification was performed by flash column techniques using Merck Kieselgel 600 (230–400 mesh). All reactions were carried out under an inert argon atmosphere. Melting points (uncorrected) of all compounds were obtained with a Reichert melting point apparatus and a Kofler stage. ¹H and ¹³C NMR spectra were recorded on a Varian Unity 300 using tetramethylsilane (TMS) or the corresponding residual solvent signal as internal standard. FAB-MS spectra were recorded on

a Finningan MAT 90 spectrometer with *m*-nitrobenzyl alcohol (NBA) as a matrix. Thermogravimetric (TGA) analyses were conducted using a Perkin-Elmer TGA-7 thermogravimetric analyzer (heating rate: 20 °C min⁻¹). Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7 instrument at a heating rate of 20 °C min⁻¹. The molecular weights and polydispersities (relative to polystyrene standards) were determined using a PL-GPC-120 (gel permeation chromatograph (GPC) using THF as eluent. Infrared spectra were taken on a Perkin-Elmer BX FT-IR spectrometer by incorporating samples in KBr disks. UV-Vis measurements were carried out on a Varian Cary 3E UV-spectrophotometer.

Compounds 1^{20} 6^{29} and DPTS³⁰ were prepared according to literature procedures.

4,4'-Bis[(3-propanoyl)oxy]triphenylamine (3). A suspension of 1 (300 mg, 1.08 mmol), KI (718 mg, 3.25 mmol), K₂CO₃ (598 mg, 3.25 mmol) in dry THF (20 mL) was stirred for 10 min. Subsequently, 2-bromo-1-propanol (2) (0.211 mL, 2.6 mmol) was added and the mixture was refluxed over night. After cooling to rt, water was added (50 mL). The mixture was extracted with CHCl₃ (3 × 50 mL) and then purified with column chromatography: hexane–ethyl acetate (2 : 8) to give **3** as a grey solid (60%): mp 63–65 °C; ¹H NMR (CDCl₃) δ 1.78–1.97 (m, 4H, CH₂), 3.67–3.78 (m, 4H, OCH₂), 3.98–4.02 (m, 4H, OCH₂), 6.70–6.85 (m, 7H, ar-H), 6.94 (d, *J* = 8.7 Hz, 4H, ar-H), 7.06 (t, *J* = 7.7 Hz, 2H, ar-H); ¹³C NMR (CDCl₃) δ 32.3, 60.8, 66.3, 115.5, 120.9, 121.4, 126.5, 129.1, 141.6, 148.9, 155.0; MS MALDI-ESI *m*/*z* 393.1 ([M⁺], calcd for C₂₄H₂₇NO₄ 393.4). Elem. anal. calcd: C, 73.26; H, 6.92; N, 3.56; found: C, 73.38; H, 6.80; N, 3.76%.

4-Hydroxytriphenylamine (5). BBr₃ (98.4 mL of a 1 M solution in CH₂Cl₂) was added dropwise to a solution of 4-methoxytriphenylamine (4) (7.5 g, 24.6 mmol) in dry chloroform (100 mL) at 0 °C. After stirring for 1 h at this temperature, the mixture was allowed to warm to rt and stirred for 5 h. The reaction was carefully quenched with methanol using an ice bath. The solvent was evaporated and the residue dissolved in ethyl acetate (150 mL). The resulting solution was washed with a saturated solution of NaHCO₃ (2×50 mL) and water (2×50 mL), dried over MgSO₄, and evaporated to give 5 as a green solid in a quantitative yield: mp 108 °C; ¹H NMR (CDCl₃) δ 6.77-6.89 (m, 2H, ar-H), 6.90-7.06 (m, 8H, ar-H), 7.13-7.35 (m, 4H, ar-H); ¹³C NMR (CDCl₃) δ 117.4, 125.8, 127.1, 130.3, 133.7, 139.4, 146.7, 153.5; MS MALDI-ESI m/z 261.1 ([M⁺]), 262.1 ([M + H⁺]), calcd for C₁₈H₁₅NO 261.11. Elem. anal. calcd: C, 82.73; H, 5.79; N, 5.36; found: C, 82.61; H, 6.06; N, 5.18%.

4,4-Bis[4'-(benzyloxy)phenyl]valeric acid (7). A mixture of compound **6** (9.71 g, 17.46 mmol) and potassium hydroxide (5.4 g) in a mixture of ethanol (26 mL) and water (8 mL) was heated at refluxed for 24 h, cooled, and concentrated. Water (400 mL) was added to the residue and the mixture acidified with glacial acetic acid and then extracted with CH₂Cl₂ (6 × 100 mL). The combined extracts were dried with MgSO₄ and evaporated to dryness to give **7** as a white-yellow powder (70%): mp 80–82 °C; ¹H NMR (CDCl₃) δ 1.61 (s, 3H, CH₃), 2.18 (t, *J* = 7.8 Hz, 2H, CH₂), 2.45 (t, *J* = 7.8 Hz, 2H, CH₂), 5.05 (s, 4H, OCH₂), 6.92 (d, *J* = 7.9 Hz, 4H, ar-H), 7.14 (d, *J* = 7.95 Hz, 4H, ar-H),

7.32–7.47 (m, 10 H, ar-H); ¹³C NMR (CDCl₃) δ 28.1, 30.7, 36.7, 44.7, 70.2, 114.6, 127.2, 127.7, 128.8, 133.9, 137.4, 141.3, 157.1, 179.9; MS MALDI-ESI *m*/*z* 466.5 ([M⁺]), 489.4 ([M + Na⁺]), 505.4 ([M + K⁺]), calcd for C₃₁H₃₀O₄ 466.2. Elem. anal. calcd: C, 79.80; H, 6.48; found: C, 79.63; H, 6.27%.

4,4-Bis[4'-(benzyloxy)phenyl]-1-[4-(triphenylamine)] valerate (8). To a solution of 7 (1.96 g, 4.21 mmol) in dry CH₂Cl₂ (25 mL) was added 5 (1.0 g, 3.83 mmol), followed by DPTS (250 mg, 4.21 mmol), and the mixture was stirred at rt for 15 min. DCC (888 mg, 4.21 mmol) was then added and the mixture was stirred for 12 h. The reaction mixture was filtered, and the filtrate was evaporated to dryness under reduced pressure. The crude product was purified by flash chromatography eluting with 7:3 CH₂Cl₂-hexane, to give 8 as a white solid (70%): mp 90–93 °C; ¹H NMR (CDCl₃) δ 1.71 (s, 3H, CH₃), 2.43 (t, J = 7.8 Hz, 2H, CH_2), 2.61 (t, J = 7.8 Hz, 2H, CH_2), 5.09 (s, 4H, OCH_2), 6.98 (d, J = 8.8 Hz, 6H, ar-H), 7.03–7.15 (m, 8 H, ar-H), 7.22 (d, J = 8.6 Hz, 4H, ar-H), 7.26–7.50 (m, 14H, ar-H); ¹³C NMR (CDCl₃) δ 28.1, 30.7, 36.7, 44.7, 70.2, 114.6, 122.3, 123.0, 124.3, 125.0, 127.2, 127.7, 128.7, 129.5, 133.9, 137.4, 141.3, 145.7, 145.9, 157.1, 173.8; MS MALDI-ESI m/z 709.3 ([M⁺]), 732.3 ([M + Na⁺]), 748.3 ([M + K⁺]), calcd for C₄₉H₄₃NO₄ 709.32. Elem. anal. calcd: C, 82.91; H, 6.11; N, 1.97; found: C, 83.22; H, 5.85; N, 2.25%.

4,4-Bis(4'-hydroxyphenyl)-1-[4-(triphenylamine)] valerate (9). A mixture of **8** (1.0 g, 1.4 mmol), 10% Pd/C (100 mg), and sodium carbonate (86 mg) in dry THF (8.6 mL) was vigorously stirred under an atmosphere of hydrogen until the theoretical amount of hydrogen was consumed. The reaction mixture was then filtered and evaporated to dryness, to give **9** as a white solid in quantitative yield: mp 92–94 °C; ¹H NMR (CDCl₃) δ 1.60 (s, 3H, CH₃), 2.35 (t, J = 7.7 Hz, 2H, CH₂), 2.51 (t, J = 7.7 Hz, 2H, CH₂), 6.77 (d, J = 8.5 Hz, 4H, ar-H), 6.91 (d, J = 8.8 Hz, 2H, ar-H), 6.88–7.08 (m, 12H, ar-H), 7.23 (t, J = 7.9 Hz, 4H, ar-H); ¹³C NMR (CDCl₃) δ 28.1, 30.7, 36.7, 44.8, 115.2, 122.3, 123.0, 124.3, 125.0, 128.7, 129.5, 141.2, 145.7, 145.9, 147.9, 153.8, 173.4; MS MALDI-ESI *m*/*z* 530.2 ([M]⁺), 531.2 ([M + H⁺]), 570.2 ([M + K⁺]), calcd for C₃₅H₃₁NO₄ 529.63. Elem. anal. calcd: C, 79.37; H, 5.90; N, 2.64; found: C, 79.14; H, 5.97; N, 2.89%.

Polycarbonate 11-A. To a mixture of 1 (2.0 g, 7.21 mmol) and bisphenol A bis(chloroformate) (10-A) (2.55 g, 7.21 mmol) in a mixture of dry CH₂Cl₂ (20 mL) and dry THF (15 mL) was added dropwise a solution of pyridine (1.23 mL, 15.14 mmol) in dry THF (5 mL) at 0 °C. Subsequently, the polymer was stirred overnight at rt. The mixture was precipitated in methanol (350 mL), filtered and washed with methanol. Drying at 60 °C for 24 h yielded **11-A** as a white solid (81%): ¹H NMR (CDCl₃) δ 1.69 (s, 6H, CH₃); 6.95–7.07 (m, 1H, ar-H), 7.09–7.17 (m, 14H, ar-H), 7.19–7.26 (m, 6H, ar-H); IR $\bar{\nu}$ 1774 (s, C=O), 1225 and 1189 (s, C–O).

Polycarbonate 12-A. This compound was prepared in a similar way from **3** and bisphenol A bis(chloroformate) (**10-A**) as a white solid (76%): ¹H NMR (CDCl₃) δ 1.65 (s, 6H, CH₃), 2.13 (m, 4H, CH₂), 3.96–4.21 (m, 4H, OCH₂), 4.44 (t, *J* = 6.1 Hz, 4H, OCH₂), 6.77–6.87 (m, 4H, ar-H), 7.06 (d, *J* = 8.7 Hz, 5H, ar-H), 7.16–7.24 (m, 12 H, ar-H); IR $\bar{\nu}$ 1165 (s, C–O), 1596 (s, C=C

aromatic), 1760 (s, O-COO), 2920 (s, C-H), 3043 (s, C-H, aromatic).

Polycarbonate 13-A. This compound was prepared in a similar way from **9** and bisphenol A bis(chloroformate) (**10-A**) as a white solid (75%): ¹H NMR (CDCl₃) δ 1.64 (s, 3H, CH₃), 1.68 (s, 6H, CH₃), 2.32–2.37 (m, 2H, CH₂), 2.53 (t, J = 8.6, 2H, CH₂), 6.77 (d, J = 9.1 Hz, 2H, ar-H), 6,91 (d, J = 8.7 Hz, 2H, ar-H), 6.97–7.08 (m, 6H, ar-H), 7.15–7.23 (m, 20H, ar-H); IR $\bar{\nu}$ 1162 (s, C–O), 1365 (s, C–H), 1590 (s, C=C aromatic), 1775 (s, O–COO broad), 2976 (s, C–H), 3038 (s, C–H, aromatic).

Polycarbonate 11-Z. This compound was prepared in a similar way from **1** and bisphenol Z bis(chloroformate) (**10-Z**) as a white solid (82%): ¹H NMR (CDCl₃) δ 1.55 (s, 6H, CH₂), 2.27 (s, 4H, CH₂), 7.03 (br, 1H, ar-H), 7.08–7.17 (m, 14H, ar-H), 7.23–7.29 (br, m, 6H, ar-H); IR $\bar{\nu}$ 1774 (s, C=O), 1225 and 1189 (s, C=O).

Polycarbonate 12-Z. This compound was prepared in a similar way from **3** and bisphenol Z bis(chloroformate) (**10-Z**) as a white solid (78%): ¹H NMR (CDCl₃) δ 1.43 (s, 6H, CH₂), 2.12–2.42 (m, 8H, CH₂), 3.96–4.20 (m, 4H, OCH₂), 4.38–4.53 (m, 4H, OCH₂), 7.10 (d, *J* = 8.5 Hz, 5H, ar-H), 7.16–7.24 (m, 12H, ar-H); IR $\bar{\nu}$ 1164 (s, C–O), 1597 (s, C=C aromatic), 1760 (s, O–COO), 2923 (s, C–H), 3043 (s, C–H aromatic).

Polycarbonate 13-Z. This compound was prepared in a similar way from **9** and bisphenol Z bis(chloroformate) (**10-Z**) as a white solid (75%): ¹H NMR (CDCl₃) δ 1.39–1.67 (m, 9H, CH₂), 2.21–2.36 (m, 6H, CH₂), 2.52–2.58 (m, 2H, CH₂), 6.91 (d, *J* = 8.8 Hz, 2H, ar-H), 6.96–7.30 (m, 28H, ar-H); IR $\bar{\nu}$ 1181 (s, C–O), 1590 (s, C=C aromatic), 1775 (s, O–COO broad), 2936 (s, C–H), 3040 (s, C–H, aromatic).

Polycarbonate 14-A. A solution of **11-A** (3.0 g) and TCNE (11.7 g, 91.3 mmol) in DMF (10 mL) was heated at 90 °C for 4 h. After cooling, the polymer was precipitated in methanol (400 mL). The precipitate was filtered off and washed with methanol. Drying yielded **14-A** as a purple solid (90%): ¹H NMR (CDCl₃) δ 1.62 (s, 6H, CH₂), 6.92 (d, 2H, ar-H), 7.11 (d, 4H, ar-H), 7.14–7.29 (m, 12H, ar-H), 7.89 (d, 2H, ar-H); IR $\bar{\nu}$ 2219 (s, C=N), 1774 (s, C=O), 1654 (w, C=C), 1185 (s, C–O).

Polycarbonate 15-A. This compound was prepared in a similar way from **12-A** and TCNE as a purple solid (83%): ¹H NMR (CDCl₃) δ 1.65 (s, 6H, CH₃), 2.02–2.32 (m, 4H, CH₂), 3.97–4.21 (m, 4H, OCH₂), 4.38–4.53 (m, 4H, OCH₂), 6.83 (d, J = 8.7 Hz, 2H, ar-H), 6.94 (d, J = 8.3 Hz, 4H, ar-H), 7.05–7.23 (m, 12H, ar-H), 7.92 (d, J = 9.4 Hz, 2H, ar-H); IR $\bar{\nu}$ 1165 (s, C=O), 1596 (s, C=C aromatic), 1760 (s, O–COO), 2218 (s, C=N), 2920 (s, C–H), 3043 (s, C–H, aromatic).

Polycarbonate 16-A. This compound was prepared in a similar way from **13-A** and TCNE as a purple solid (80%): ¹H NMR (CDCl₃) δ 1.59 (s, 3H, CH₃), 1.68 (s, 6H, CH₃), 2.33–2.45 (m, 2H, CH₂), 2.50–2.63 (m, 2H, CH₂), 6.95 (d, *J* = 9.1 Hz, 2H, ar-H), 7.07–7.41 (m, 25H, ar-H), 7.96 (d, *J* = 9.3 Hz, 2H, ar-H); IR $\bar{\nu}$ 1162 (s, C–O), 1365 (s, C–H), 1590 (s, C=C aromatic), 1776

(s, O–COO broad), 2220 (s, C≡N) 2977 (s, C–H), 3038 (s, C–H, aromatic).

Polycarbonate 14-Z. This compound was prepared in a similar way from **11-Z** and TCNE as a purple solid (85%): ¹H NMR (CDCl₃) δ 1.55 (s, 6H, CH₂), 2.27 (s, 4H, CH₂), 6.98 (d, 2H, ar-H), 7.17 (d, 4H, ar-H), 7.35–7.21 (m, 12H, ar-H), 7.95 (d, 2H, ar-H); IR $\bar{\nu}$ 2219 (s, C \equiv N), 1774 (s, C \equiv O), 1654 (w, C \equiv C), 1156 (s, C–O).

Polycarbonate 15-Z. This compound was prepared in a similar way from **12-Z** and TCNE as a purple solid (90%): ¹H NMR (CDCl₃) δ 1.43 (s, 6H, CH₃), 2.03–2.20 (m, 8H, CH₂), 3.96–4.20 (m, 4H, OCH₂), 4.38 (t, J = 6.0 Hz, 4H, OCH₂), 6.80 (d, J = 8.7 Hz, 2H, ar-H), 6.91 (d, J = 8.3 Hz, 4H, ar-H), 7.23 (m, 12 H, ar-H), 7.93 (d, J = 9.4 Hz, 2H, ar-H); IR $\bar{\nu}$ 1165 (s, C–O), 1596 (s, C=C, aromatic), 1760 (s, O–COO), 2219 (s, C=N), 2920 (s, C–H), 3043 (s, C–H, aromatic).

Polycarbonate 16-Z. This compound was prepared in a similar way from **13-Z** and TCNE as a purple solid (82%): ¹H NMR (CDCl₃) δ 1.42–1.69 (m, 9H, CH₂), 2.17–2.31 (m, 4H, CH₂), 2.33–2.43 (m, 2H, CH₂), 2.48–2.61 (m, 2H, CH₂), 6.96 (d, *J* = 9.0 Hz, 2H, ar-H), 7.01–7.48 (m, 25H, ar-H), 7.94 (d, *J* = 8.4 Hz, 2H, ar-H); IR $\bar{\nu}$ 1181 (s, C–O), 1591 (s, C=C aromatic), 1775 (s, O–COO, broad), 2220 (s, C=N), 2936 (s, C–H), 3040 (s, C–H, aromatic).

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