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Thermally stable oxadiazole-containing polyacetylenes: Relationship between molecular structure and nonlinear optical properties

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Expermental

Materials

Bis(triphenylphosphine) palladium(II) chloride [$PdCl_2(PPh_3)_2$], norbornadienerhodium (I) chloride dimer ([$Rh(nbd)Cl]_2$), tungsten(VI) chloride (WCl_6), $MoCl_5$, tetraphenyltin (Ph_4Sn), and 2-methyl-3-butyn-2-ol were all purchased from Aldrich and used as received without further purification. 4-Bromobenzoic acid, triphenylphosphine, methyl-4-hydroxybenzoate, phosphorus oxychloride, surfurous oxychloride, 1-bromobutane, 1-bromooctane, and 1-bromodecane were purchased from Shanghai Chemical Reagent Co. and used as received without further purification. Dioxane, THF, and toluene were distilled from sodium benzophenone ketyl immediately prior to use. Triethylamine (Et_3N) and pyridine were distilled from potassium hydroxide prior to use. *N*, *N*- dimethylformamide (DMF) was purified by distillation over CaH_2 prior to utilization. Technical grade methanol was used to precipitate the polymers.

Instruments

The FTIR spectra were recorded as KBr pellets on a Nicolet 170sx spectrometer. The ^{1}HNMR spectra were collected on a Bruker Avance/DMX 300-MHz NMR spectrometer with chloroform-*d* ($CDCl_3$-*d*) or dimethyl sulfoxide-d_6 (DMSO-d_6) as solvents and tetramethylsilane as reference. Weight-average (Mw) and number-average (M_n) molecular weights and polydispersity index (PDI, M_w/M_n) were determined by a Waters 515 gel permeation chromatograph (GPC). THF was used as the eluent at a flow rate of 1.0 mL/min. A set of monodisperse polystyrene standards (Waters) was used for calibration. UV spectra were recorded on a Shimadzu UV-265 spectrometer with a 1-cm^2 quartz cell. Thermogravimetric analyses (TGAs) of the polymers were performed on a Perkin-Elmer TGA 7 under nitrogen at a heating rate of 10 °C /min.

The NLO property of the sample measured by *Z*-scan technique was performed with a Q-swithed ns/ps Nd:YAG laser system continuum with pulse width of 13 ns at 1 Hz repetition rate and 532 nm wavelength. The input energy was 100 μJ. The experiment was set up as ref.[1]. The relationship between the normalized transmittance *T*(z) and *z* position was obtained by moving the samples along the axis of the incident beam (*z* direction) with respect to the focal point. The incident and transmitted energies were detected simultaneously by an energy meter (Laser Precision Corporation Rjp-735).

The optical limiting (OL) properties in THF solutions were performed with a frequency-doubled, Q-switched, mode-locked continuum ns/ps Nd:YAG laser, which provided linearly polarized 4-ns optical pulses at a 532-nm wavelength with a repetition of 1 Hz. The experimental arrangement was similar to that in the literature.[2] The transverse mode of the laser pulses was nearly Gaussian. The input laser pulses were split into two beams by an attenuator (Newport). One was employed as a reference to monitor the incident laser energy, and the other was focused on the sample cell with a lens with a 30-cm focal length. The sample was positioned at the focus and housed in quartz cells with a thickness of 2 mm. The incident and transmitted laser pulses were monitored with two energy detectors, D1 and D2 (Rjp-735 energy probes, Laser Precision).

Monomer syntheses and polymerization

As shown in Scheme 1, the monomers were synthesized by a multistep reaction route with a Sonogashira cross-coupling and polymers were obtained by using $[Rh(nbd)Cl]_2$-Et_3N as catalyst. All the monomers were synthesized and polymerized according to the methods in ref.[3]. The structure of the intermediates, the monomers and polymers were confirmed.

Methyl 4-decyloxylbenzoate (1a)

A pale yellow solid, yield: 80 %. FTIR (KBr), ν (cm^{-1}): 3060 (Ar-H stretching), 2921, 2853 (aliphatic C-H stretching), 1724(C=O stretching), 1608, 1455(aromatic C=C stretching), 1022 (C-O, stretching), 850 (aromatic ring, *p*-subst.). ^{1}HNMR (300MHz, $CDCl_3$): δ 0.87 (t, 3H, CH_3), 1.23-1.47 (14H, $(CH_2)_7$ CH_3), 1.79 (m, 2H, OCH_2CH_2), 3.89 (s, 3H, OCH_3), 4.01 (t, 2H, OCH_2), 6.98 (d, 2H, *J* = 8.8 Hz, Ar-*H*), 7.98 (d, 2H, *J* = 8.8Hz, Ar-*H*).

Methyl 4-butyloxylbenzoate (1b)

FTIR (KBr), ν (cm^{-1}): 3058 (aromatic C-H stretching), 2960, 2853 (aliphatic C-H stretching), 1721 (C=O stretching), 1611, 1489 (aromatic C=C stretching), 1011 (C-O, stretching), 844 (aromatic ring, *p*-subst.). ^{1}HNMR (300MHz, $CDCl_3$): δ 0.94 (t, 3H, CH_3), 1.45 (2H, CH_2CH_3), 1.73 (m, 2H, OCH_2CH_2), 3.98(t, 2H, OCH_2), 3.86 (s, 3H, OCH_3), 6.96 (d, 2H, *J* = 8.8 Hz, Ar-*H*), 7.87 (d, 2H, *J* = 8.8 Hz, Ar-*H*).

4-Decyloxylbenzoyl hydrazine (2a)

A white acicular crystal, yield: 86%. FTIR (KBr), ν (cm^{-1}): 3333, 3177 (N-H, stretching), 2918, 2862 (aliphatic C-H stretching), 1648 (C=O stretching), 1612, 1471 (aromatic C=C stretching), 1020(C-O, stretching), 829 (aromatic ring, *p*-subst.). ^{1}H NMR (300MHz, DMSO-d_6): δ 0.85 (t, 3H, CH_3), 1.21- 1.45 (m, 14H, $(CH_2)_7$ CH_3), 1.71(m, 2H, OCH_2CH_2), 4.01 (t, OCH_2), 4.33 (s, 2H, NH_2), 6.95 (d, 2H, *J* = 8.8Hz, Ar-*H*), 7.77(d, 2H, *J* = 8.8Hz, Ar-*H*), 9.68 (s, 1H, $NHNH_2$).

4-Butyloxylbenzoyl hydrazine (2b)

FTIR (KBr), ν (cm^{-1}): 3317 (N-H, stretching), 2961, 2859 (aliphatic C-H stretching), 1721 (C=O stretching), 1611, 1456 (aromatic C=C stretching), 1021(C-O, stretching), 844 (aromatic ring, *p*-subst.). ^{1}H NMR (300MHz, DMSO-d_6): δ 0.96 (t, 3H, CH_3), 1.44 (m, 2H, CH_2 CH_3), 1.70(m, 2H, OCH_2CH_2), 4.03 (t, OCH_2), 6.95 (d, 2H, *J* = 8.7 Hz, Ar-*H*), 7.76 (d, 2H, *J* =8.7Hz, Ar-*H*), 9.60 (s, 1H, $NHNH_2$).

N-(4-bromobenzoyl)-n-(4-decyloxylbenzoyl) hydrazine (3a)

The yield was 82 %. FTIR (KBr), ν (cm^{-1}): 3217 (N-H, stretching), 2921, 2852 (aliphatic C-H stretching), 1643 (C=O), 1602-1461 (aromatic C=C stretching), 1012(C-O, stretching), 842 (aromatic ring, *p*-subst.). ^{1}HNMR (300MHz, DMSO-d_6): δ 0.86 (t, 3H, -CH_3), 1.20-1.46 (m, 14H, $(CH_2)_7$ CH_3), 1.86 (m, 2H, OCH_2CH_2), 3.98 (t, 2H, OCH_2), 6.98-7.01 (d, 2H, *J*= 8.7 Hz, Ar-*H*), 7.68-7.72 (d, 2H, *J* = 8.7 Hz, Ar-*H*), 7.80-7.90 (m, 4H, *J* = 8.0 Hz, Ar-*H*), 10.30 (s, 1H, N-*H*), 10.46 (s, 1H, N-*H*).

N-(4-bromobenzoyl)-N-(4-butyloxylbenzoyl) hydrazine (3b)

FTIR (KBr), ν (cm^{-1}): 3321, 3246 (N-H, stretching), 2957, 2871 (aliphatic C-H stretching), 1686, 1653 (C=O), 1606, 1476 (aromatic C=C stretching), 1012(C-O, stretching), 845 (aromatic ring, *p*-subst.). ^{1}HNMR (300MHz, DMSO-d_6): δ 0.94 (t, 3H, CH_3), 1.46 (m, 2H, CH_2CH_3), 1.72 (m, 2H, OCH_2CH_2), 4.05 (t, 2H, OCH_2), 7.06 (d, 2H, Ar-*H*, *J=9.0* Hz, Ar-*H*), 7.76 (d, 2H, *J=8.4* Hz, Ar-*H*), 7.84 (d, 2H, *J=8.4* Hz, Ar-*H*), 7.90 (d, 2H, *J=8.7* Hz, Ar-*H*), 10.25 (s, 1H，N-*H*), 10.43 (s, 1H, N-*H*).

2-(4-Bromophenyl)-5-(4-decyloxyphenyl)-1, 3, 4-oxadiazole (4a)

The yield was 85 %. FTIR (KBr), ν (cm^{-1}): 3060 (aromatic C-H stretching), 2921, 2853 (aliphatic C-H strtching), 1608, 1499 (aromatic C=c stretching), 1011(C-O stretching), 854 (aromatic ring, *p*-subst.). ^{1}HNMR (300MHz, $CDCl_3$) : δ 0.89(t, 3H, CH_3), 1.28-1.45 (m, 14H, $(CH_2)_7CH_3$), 1.85 (m, 2H, OCH_2CH_2), 4.04(t, 2H, OCH_2), 7.02 (d, 2H, *J* = 8.8 Hz, Ar-*H*), 7.67 (d, 2H, Ar-*H*, *J* = 8.5 Hz), 8.00 (d, 2H, *J*= 8.5 Hz, Ar-*H*), 8.04 (d, 2H, *J* = 8.8 Hz, Ar-*H*).

2-(4-Bromophenyl)-5-(4-butyloxyphenyl)-1, 3, 4-oxadiazole (4b)

FTIR (KBr), ν (cm^{-1}): 3071 (aromatic C-H stretching), 2958, 2872 (aliphatic C-H strtching), 1615, 1477(aromatic C=C stretching), 1005(C-O stretching), 835(aromatic ring, *p*-subst.). ^{1}HNMR (300MHz, $CDCl_3$) : δ 0.99(t, 3H, C H_3), 1.50 (m, 2H,CH_2CH_3), 1.81 (m, 2H, OCH_2CH_2), 4.05(t, 2H, OCH_2), 7.00 (d, 2H, *J*=8.7 Hz, Ar-*H*), 7.68 (d, 2H, *J*=8.4Hz, Ar-*H*), 8.01 (d, 2H, *J*= 8.4 Hz, Ar-*H*), 8.07(d, 2H, *J*=9.0 Hz, Ar-*H*).

4-[4-[5-(4-Decyloxyphenyl)-1,3,4-oxadiazol-2-yl]phenyl]-2-methyl-but-3-yn-2-ol (5a)

The yield was 74 %. FTIR (KBr), ν (cm^{-1}): 3416 (O-H stretching), 2924, 2852 (aliphatic C-H stretching), 1613, 1459 (aromatic C=C stretching), 1012 (C-O stretching), 838 (aromatic ring, *p*-subst.). ^{1}HNMR (300MHz, $CDCl_3$): δ 0.89 (t, 3H, CH_3), 1.29- 1.43 (m, 14H, $(CH_2)_7CH_3$), 1.75 (s, 6H, $C(CH_3)_2$) 1.83 (m, 2H, OCH_2CH_2), 4.04 (t, 2H, OCH_2), 7.03(d, 2H, *J* =8.7 Hz, Ar-*H*), 7.57 (d, 2H, *J* =8.4 Hz, Ar-*H*), 8.06 (m, 4H, Ar-*H*).

4-[4-[5-(4-Butyloxyphenyl)-1,3,4-oxadiazol-2-yl]phenyl]-2-methyl-but-3-yn-2-ol (5b)

FTIR (KBr), ν (cm^{-1}): 3416 (O-H stretching), 2958, 2871 (aliphatic C-H stretching), 1609, 1463 (aromatic C=C stretching), 1012 (C-O stretching), 850 (aromatic ring, *p*-subst.). ^{1}HNMR (300MHz, $CDCl_3$): δ 0.98 (t, 3H, CH_2CH_3), 1.51 (m, 2H, CH_2CH_3), 1.67 (s, 6H, $C(CH_3)_2$), 1.81 (m, 2H, OCH_2CH_2), 4.04 (t, 2H, OCH_2), 7.02(d, 2H, *J* =8.7 Hz, Ar-*H*), 7.57 (d, 2H, *J* =8.4 Hz, Ar-*H,*), 8.05 (d, 2H, Ar-*H*), 8.09 (d, 2H, Ar-*H*).

2-(4-Decyloxyphenyl)-5-(4-ethynylphenyl)-1, 3, 4-oxadiazole (6a)

The yield was 57.6 %. FTIR (KBr), ν (cm^{-1}): 3273 (≡C-H stretching), 2920, 2851 (aliphatic C-H stretching), 2100 (C≡C), 1611, 1456 (aromatic C=C stretching), 1016(C-O stretching), 843 (aromatic ring, *p*-subst.). ^{1}HNMR (300MHz, $CDCl_3$): δ 0.87 (t, 3H, CH_3), 1.25-1.48 (m, 14H, $(CH_2)_7CH_3$), 1.83 (m, 2H, OCH_2CH_2), 3.25 (s, 1H, ≡C-H), 4.04 (t, 2H, OCH_2), 7.02 (d, 2H, *J* =8.9 Hz,, Ar-*H*), 7.64 (d, 2H, *J* = 8.5 Hz, Ar-*H*), 8.08 (m, 4H, Ar-*H*).

2-(4-Butyloxyphenyl)-5-(4-ethynylphenyl)-1, 3, 4-oxadiazole (6b)

FTIR (KBr), ν (cm^{-1}): 3280 (≡C-H stretching), 2952, 2879 (aliphatic C-H stretching), 2100 (C≡C), 1612, 1495 (aromatic C=C stretching), 1006(C-O stretching), 842 (aromatic ring, *p*-subst.). ^{1}HNMR (300 MHz, $CDCl_3$): δ 0.87 (t, 3H, CH_3), 1.48 (m, 2H, CH_2CH_3), 1.84 (m, 2H, OCH_2CH_2), 3.24 (s, 1H, ≡C-*H*), 4.05 (t, 2H, OCH_2), 7.02 (d, 2H, *J*=8.8 Hz, Ar-*H*), 7.64 (d, 2H, *J*=8.3 Hz, Ar-*H*), 8.05 (d, 2H, *J*=8.9 Hz, Ar-*H*) , 8.09 (d, 2H, *J*=8.4Hz, Ar-*H*).

Poly[2-(4-decyloxyphenyl)-5-(4-ethynylphenyl)-1, 3, 4-oxadiazole] (P1)

Yellow black solid, yield 98%, $M_w = 2.54\times10^4$, $M_w/M_n = 1.71$ (GPC, Table 1, no2). FTIR (KBr), ν (cm^{-1}): 3046, 2926, 2855, 1611, 1496, 838. ^{1}HNMR (300 MHz, $CDCl_3$): δ 0.87 (br, 3H, CH_3), 1.26 (br, 14H, $(CH_2)_7CH_3$), 1.70 (br, 2H, OCH_2CH_2), 3.83 (br, 2H, OCH_2), 5.92(br, 1H, *cis* =C-*H*), 6.68 (br, Ar-*H* and *trans* =C-*H*), 6.93 (br, 2H, Ar-*H*), 7.69 (br, 4H, Ar-*H*).

Poly[2-(4-butyloxyphenyl)-5-(4-ethynylphenyl)-1, 3, 4-oxadiazole] (P2)

Yellow solid, yield 92%, $M_w = 2.93\times10^4$, $M_w/M_n = 1.36$ (GPC, Table 3, no.2). FTIR (KBr), ν (cm^{-1}): 3045, 2925, 2857, 1613, 1496, 837. ^{1}HNMR (300 MHz, $CDCl_3$): δ 0.96 (br, 3H, CH_3), 1.45 (br, 2H, CH_2CH_3), 1.90 (br, 2H, OCH_2CH_2), 3.82 (br, 2H, OCH_2), 5.92(br, 1H, *cis* =C-*H*), 6.67(br, Ar-*H* and *trans* =C-*H*), 6.91 (br, 2H, Ar-*H*), 7.67 (br, 4H, Ar-*H*).

Polymerization with Mo, W and Ta catalysts

The other catalysts were tried for polymerization of both monomers. The procedure was similar to the polymerization with $[Rh(nbd)Cl]_2$ catalyst as described above. There was a small quantity of polymer to be lower yielded by WCl_6-Ph_4Sn as a catalyst. However, there were only trace precipitate to be given by $TaCl_5$-Ph_4Sn, $MoCl_5$, WCl_6, and $MoCl_5$-Ph_4Sn.

References

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