Colourless Nonlinear Optical D-π-A Polymers with Sulphones as Electron Acceptors

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Novel colourless side-chain methacrylate copolymers exhibiting relatively narrow charge-transfer bands at 335 nm and second-order optical nonlinearities up to d_{33} = 4.3 pm V^{-1} (at 1064 nm) have been synthesized and characterized.

Recently, poled polymers with high second-order nonlinearities (χ^2) have raised much interest as promising candidates for electro-optic switching and second-harmonic generation (SHG).[1,2] The theory of molecular contributions (β) to nonlinear optical properties shows that high values of β occur for molecules with low-lying transitions involving a large oscillator strength and a large difference in dipole moment of ground and excited states.[3,4] This explains the preference for strongly absorbing charge-transfer (C-T) molecules in nonlinear optical (NLO) polymers. Various studies have appeared on polymers in which the coloured C-T molecules are dissolved,[5] covalently attached,[6] or incorporated in network matrices.[7]

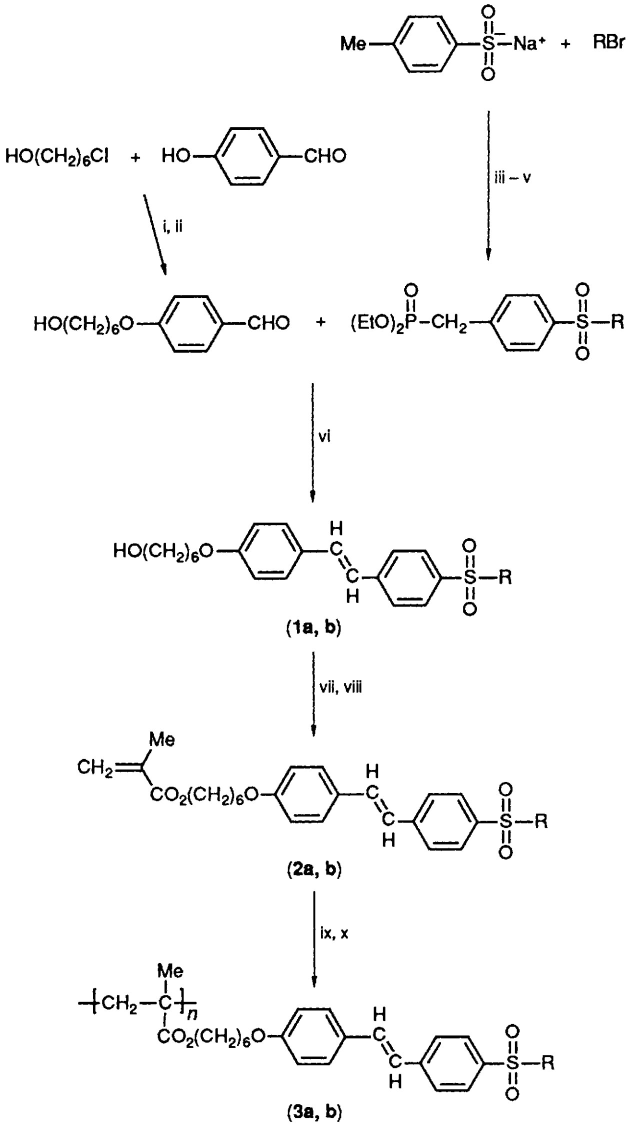
A drawback for SHG application stems from the fact that CT bands are generally rather broad.[8] The residual absorption of the second harmonic in the tail of such a broad band, which often leads to photodegradation, limits the attainable increase of χ^2 by resonant enhancement in SHG polymers.

For this reason, well known molecules in nonlinear optics such as DANS (*N,N*-dimethylamino-*p*-nitrostilbene, $\lambda_{max.}$ = 438 nm) cannot be used to double the frequency of light of a solid-state laser (from about 800 to 400 nm). A polymer bearing NLO-active groups with narrower C-T absorption bands would, therefore, be very valuable. The width of the C-T bands in the usual molecules with electron accepting and donating groups of mainly resonant character is partly due to the condition of the Franck–Condon excited state far from equilibrium geometry. For inductive donors and acceptors the geometries of ground and excited state are much more alike. Hence, such substituents could lead to narrower C-T absorption bands.

We now report on novel colourless NLO polymers with C-T groups in their side chains having sulphone groups as strong inductive[9] electron acceptors. The sulphone group as an acceptor in NLO polymers has been independently disclosed by Ulman *et al.*[10] in that the synthetic use of sulphones was stressed.

The synthesis of the polymers used in this study is given in Scheme 1. Homopolymers (**3a,b**) as well as copolymers of methyl methacrylate (MMA) and a methacrylate substituted with a 4-alkoxy-4′-alkylsulphone stilbene unit (**2a,b**) are synthesized by thermal radical polymerization, using benzoyl peroxide or azoisobutyronitrile (AIBN) as initiator. Semi-dilute solutions are required to avoid crosslinking.[11] The key step in the converging synthesis of the substituted monomer consists of the Wittig reaction, in which the donor side and the acceptor side are linked together, enabling both the length of the spacer between the main chain and acceptor, and the alkyl group linked to the sulphone to be varied independently.‡

Homopolymers (**3a,b**) are semi-crystalline, which is not acceptable for NLO applications because of light scattering. Amorphous materials are obtained by copolymerization with MMA at contents of (**2a,b**) below 50 wt% (**2a**) or 25 wt% (**2b**), respectively. The molar mass (M_w) of all polymers, as determined by GPC [tetrahydrofuran eluent, poly methyl methacrylate (PMMA) standards], was in the range of 1.5 ×



(**a**) R = Me
(**b**) R = $(CH_2)_5Me$

Scheme 1. *Reagents and conditions*: i, NaI-EtOH; ii, KOH-H_2O; iii, NaI-MeOH; iv, NBS-CCl_4; v, $P(OEt)_3$; vi, NaH; vii, CH_2=CMe-C(:O)Cl; viii, $C_6H_6NMe_2$-CH_2Cl_2; ix, AIBN–toluene; x, benzoylperoxide.

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‡ Yields (**1a, 1b**) 48%; (**2a**) 90%; (**2b**) 32%.

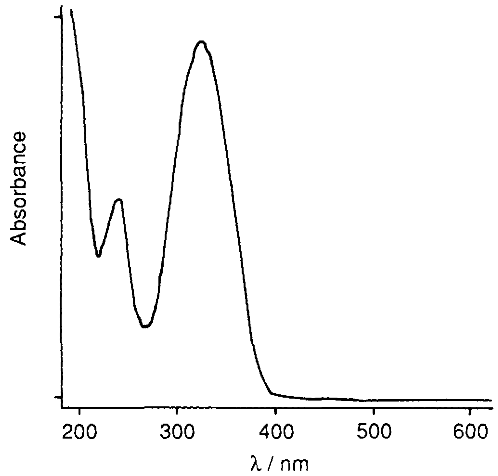

Figure 1. UV-VIS absorption spectrum of (**3b**), showing the narrow absorption C-T band in the near UV and transparency in the visible region.

10^4—3×10^4 g mol^{-1}. Spectroscopic data of monomers (**2a,b**) and of (co)polymers agree with the structures assigned.§

The UV-VIS absorption spectra of (co)polymers with (**2a,b**) (Figure 1) show rather narrow bands, with a negligible absorption around 400 nm ($\varepsilon < 10^{-4}\ \varepsilon_{\text{max.}}$). Electric field induced second harmonic generation (EFISH) measurements at 1064 nm on (**1a**) yield a value of $\beta = 10 \times 10^{-30}$ esu, assuming parallelism of dipole and transition moments. The actual value will be larger, as it can be easily seen that the dipole moment of the ground state, mainly located on the $-SO_2-$ unit, makes an appreciable angle (*ca.* 45°) with the molecular axis, along which the transition moment will be directed. Measurement of SHG at 1064 nm on corona-poled layers of copolymers give d_{33} values of 1.2, 1.4, and 4.3 pm V^{-1} for compositions containing 25 wt% (**2b**), 25 and 50 wt% (**2a**), respectively. Detailed optical and NLO data will be published presently.

We may conclude that these novel polymers, owing to their relatively narrow absorption bands, offer great possibilities for use as frequency doubling devices by means of SHG. In view of the cut-off wavelength around 400 nm, they can in principle be used to double the frequency of a solid-state laser ($\lambda = 820$ nm $\rightarrow \lambda = 410$ nm). Their efficiency can probably be increased significantly by substitutions that turn the ground-state dipole moment in the direction of the molecular axis. Experiments with that aim are in progress.

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§ *Experimental data*: (**2a**): IR (KBr) 1150, 1300, 1580, 1620, 1720, 2800 cm^{-1}. (**2b**): ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.8—1.8 (br, m), 1.9 (s), 3.1 (t), 4.1 (m), 5.5 (s, t), 6.1 (s), 6.8—8.0 (br, m); ^{13}C NMR (80 MHz, $CDCl_3$) δ 14, 18, 23, 24, 26, 28, 29, 30, 32, 57, 65, 68, 115, 125, 126, 127, 129, 130, 133, 137, 138, 143, 160, 167; UV-VIS (chloroform) 335 nm (ε 24 100 dm^3 mol^{-1} cm^{-1}); DSC m.p. 100 °C. (**3a**): IR (KBr) 1150, 1300, 1600, 1680, 2800 cm^{-1}. (**3b**): ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.6—2.2 (br, b), 3.1 (t), 4.0 (br, m), 6.6—8.0 (br, m); UV-VIS (chloroform) 335 nm (ε 24 100 dm^3 mol^{-1} cm^{-1}); DSC T_g 124 °C.