

New Method for preparing Poly(benzo[*c*]thiophene) Thin Films by Photopolymerization

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Conducting poly(benzo[*c*]thiophene) thin films may be prepared by photopolymerization of the monomer, benzo[*c*]thiophene.

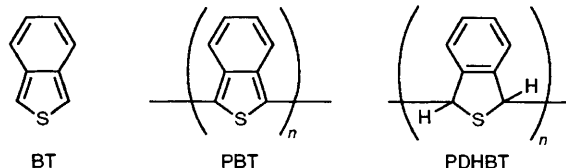
Recently poly(benzo[*c*]thiophene) (PBT) which has a small bandgap (1.1 eV) and whose conducting doped state is transparent in the visible region has attracted particular attention.^{1,2} Its properties may be explained by the large quinoid character of the polymer backbone geometry or its electronic structure.³ PBT has so far been prepared by either electrochemical or chemical polymerization⁴ of its monomer, benzo[*c*]thiophene (BT). Here, we report a new preparative method for thin films of PBT by photopolymerization of BT.

BT was synthesized by Cava's method.⁵ Typically, photopolymerization was carried out by irradiation of a MeCN solution containing BT ($7.5 \times 10^{-2} \text{ mol dm}^{-3}$), CCl_4 ($7.5 \times 10^{-2} \text{ mol dm}^{-3}$) as an electron acceptor and tetrabutylammonium bromide (TBABr; $1.0 \times 10^{-2} \text{ mol dm}^{-3}$) as a salt with a 500 W Xe lamp through a monochromator.

A homogeneous bluish thin film was obtained on the entrance glass window of the cell. Prolonged irradiation

caused the film to grow to several μm thick, with formation of a bluish black precipitate. The film and the precipitate were identified as PBT by visible absorption and IR spectroscopy, and elemental analysis, in comparison with authentic PBT.[†] The film conductivity ($3 \times 10^{-4} \text{ S cm}^{-1}$) was not as high as the values reported (10^{-2} – $10^{-1} \text{ S cm}^{-1}$),⁴ probably because of its partly doped state.[†] Films which had been prepared on conducting Sn-doped In_2O_3 glass were electrochemically active with a redox potential of 0.4 V vs. SCE (saturated calomel electrode), and showed electrochromic behaviour characteristic of PBT. Interestingly, the PBT film was easily converted to poly(1,3-dihydrobenzo[*c*]thiophene) (PDHBT),

[†] Authentic PBT was prepared by the electropolymerization of BT in MeCN containing 0.1 mol dm^{-3} TBABr at 0.6 V vs. SCE or by the chemical polymerization of BT with H_2SO_4 (ref. 4). Spectral data: $\nu_{\text{C}=\text{S}}$ 1150 cm^{-1} , $\nu_{\text{C}=\text{C}}$ of thiophene ring 980 cm^{-1} , λ_{max} 750 nm. The PBT ($\text{C}_8\text{H}_4\text{S}$) film contained a small amount of PDHBT ($\text{C}_8\text{H}_6\text{S}$; 9%), as shown by the IR spectrum ($\nu_{\text{C}-\text{H}}$ of dihydrothiophene ring 1420 and 2500 cm^{-1}). elemental analysis: calc. for $(\text{C}_8\text{H}_4\text{S})_{0.921}(\text{C}_8\text{H}_6\text{S})_{0.099}\text{Br}_{0.015}(\text{H}_2\text{O})_{0.307}$: C, 68.5; H, 3.4; S, 22.85; Br, 0.85; found: C, 68.5; H, 3.4; S, 22.7; Br, 0.86%. The film had 0.016 equiv. of Br^- dopant per BT unit, which corresponded to a doping ratio of 60% on the basis of the electrochromic behaviour of authentic PBT.



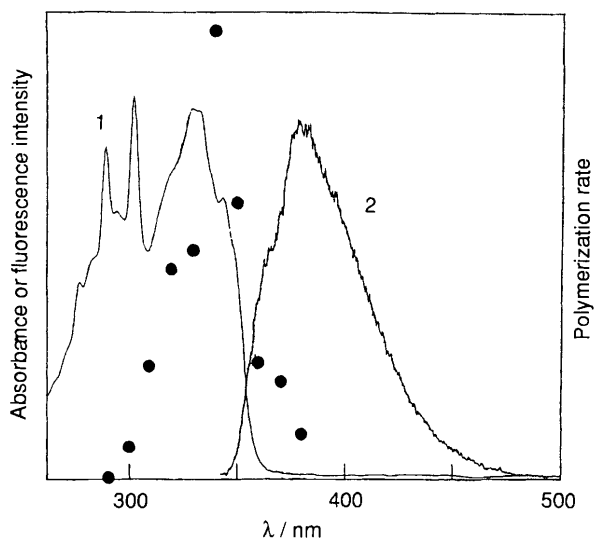


Fig. 1 Action spectrum (●) of the PBT film growth rate in the photopolymerization. The MeCN solution, containing $7.5 \times 10^{-2} \text{ mol dm}^{-3}$ BT, $7.5 \times 10^{-2} \text{ mol dm}^{-3}$ CCl_4 and $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ TBABr, was irradiated by monochromatic light. The UV absorption spectrum (1) and the fluorescence spectrum (2) of BT in MeCN are also shown.

highly soluble in tetrahydrofuran (THF) and CH_2Cl_2 , by electrolysis of the film on an Sb-doped SnO_2 glass in THF containing 0.1 mol dm^{-3} HCl at -1.0 V .[‡] The GPC profile of the resulting PDHBT suggested that the original PBT had a number-averaged molecular weight of 1.2×10^4 and a weight-averaged molecular weight of 1.3×10^4 , corresponding to a degree of polymerization of *ca.* 300.

No product was obtained in deaerated solutions without an electron acceptor; oxygen could act as an electron acceptor. A yellowish brown PDHBT film was obtained either in the absence of TBABr or on using tetrabutylammonium tetrafluoroborate as a salt. The products, PBT, PDHBT, or their mixture, depended on the anion of the added salt. A similar dependence of the products on the anion was encountered in the electropolymerization of BT using various supporting

[‡] This new method is useful for analysis of PBT; details will be reported elsewhere. The converted PDHBT was identified by NMR spectroscopy: ^{13}C NMR δ (CDCl_3), 59.5, 124.6, 127.2 and 142.6.

electrolytes, although this is not understood mechanistically. We discuss now the primary process in the photopolymerization giving the PBT film in the presence of TBABr, without further consideration of the anion dependence.

The action spectrum of the growth rate of the primary film agreed with the absorption spectrum of BT (Fig. 1). The quantum yield of the film growth was $>0.1\%$ at $334 \pm 3 \text{ nm}$.[§] BT had a strong fluorescence at 380 nm, whose excitation spectrum agreed with the absorption spectrum. The fluorescence was quenched at a diffusion-controlled rate by CCl_4 with a reduction potential of -1.4 V . The excited BT has strong reducing power (-2.83 V), evaluated from the oxidation potential (0.52 V) and the excitation energy (3.35 eV) of BT. Quenching experiments and the energetics suggested that the photopolymerization in the first stage is driven by electron transfer from the excited BT to CCl_4 and by coupling of the resulting BT cation radicals.

The present photopolymerization should provide a basis for photochemical micro-fabrication of PBT-based conducting polymer thin films.

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[§] The incident photon flux at $334 \pm 3 \text{ nm}$ was $2.1 \times 10^{17} \text{ quanta cm}^{-2} \text{ s}^{-1}$ evaluated by chemical actinometry using iron(III) trioxalate. Some oligomers, up to the heptamer, were present in the reaction solution after the photopolymerization. These MeCN-soluble products were not considered in the estimation of quantum yields.