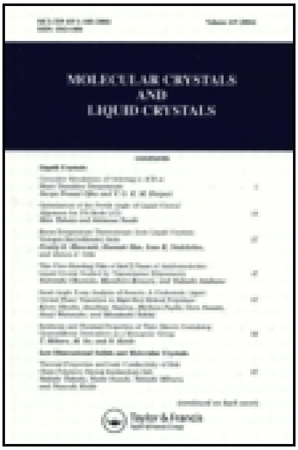

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electro-Absorption Spectroscopy on Poly(Arylene Vinylene)s

O. M. Gelsen [a] , D. A. Halliday [a] , D. D. C. Bradley [a] , P. L. Burn [b] , A. B. Holmes [b] , H. Murata [c] , T. Tsutsui [c] & S. Saito [c]

[a] Cavendish Laboratory, Madingley Road, Cambridge, CB3 OHE, U. K.

[b] University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U. K.

[c] Dept. Materials Science and Technology, Kyushu Univ., Fukuoka, 816, Japan

Version of record first published: 24 Sep 2006.

To cite this article: O. M. Gelsen , D. A. Halliday , D. D. C. Bradley , P. L. Burn , A. B. Holmes , H. Murata , T. Tsutsui & S. Saito (1992): Electro-Absorption Spectroscopy on Poly(Arylene Vinylene)s, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 216:1, 117-121

To link to this article: http://dx.doi.org/10.1080/10587259208028759

Mol. Cryst. Liq. Cryst. 1992, Vol. 216, pp. 117–121
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

ELECTRO-ABSORPTION SPECTROSCOPY ON POLY(ARYLENE VINYLENE)S

O. M. GELSEN, D.A. HALLIDAY and D. D. C. BRADLEY
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K.
P.L. BURN and A.B. HOLMES
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.
H. MURATA, T.TSUTSUI and S.SAITO
Dept. Materials Science and Technology, Kyushu Univ., Fukuoka, 816 Japan

Abstract

We report spectrally resolved electroabsorption (EA) measurements on poly(arylene vinylene)s. The materials poly(thienylene vinylene), PTV, and poly(*p*-phenylene vinylene), PPV, are particularly attactive as they can be prepared from soluble precursors which allow ready fabrication of films. The subsequent thermal conversion of the precursor yields samples with good optical and mechanical properties and environmental stability. Both materials give a strong electro-optic response, an induced change in the optical absorption leading to a refractive index change of order 10^{-4} for applied electric fields between 25 and 100 kV/cm. The EA signal scales quadratically with applied field and shows an anisotropy of 2.3 with respect to the polarisation of the incident light at the main peak.

INTRODUCTION

Recently conjugated polymers have attracted considerable interest, both from the viewpoint of understanding fundamental electronic processes and for practical applications in electronical, electro-optical, electro-luminescent and all-optical devices, for example polymer based FETs[1], MIS-devices[1,2] and photoluminescent diodes[3,4]. Electro-modulation spectroscopy has proved to be a useful tool in obtaining fundamental information about the effect of an external electric field on semiconducting materials [5,6] as well as providing data on field induced nonlinear susceptibilities[7]. We have previously reported electro-absorption measurements on several thiophene-derived polymers[8], a detailed analysis of electro-optic coefficients[9] and the photo-refractive effect[10] in PTV. In this paper we present data on PPV and PTV, and especially want to emphasise how an improvement in the material synthesis can effect the optical absorption and the electro-optic properties.

MATERIALS

Samples between 40 and 150 nm thickness were prepared via precursor routes.

The PTV precursor polymer was dip-coated from THF solution onto spectrosil substrates, and thermally converted under acid-containing flowing nitrogen at 200 °C [11].

We compare measurements on two batches of PPV: Sample A was prepared by the conventional sulphonium route[12] and exhibits material showing a sharp π–π^* absorption peak with several shoulders, that have been assigned to coupling of the excited state to different vibrational levels. Sample B was prepared by a method as described in [12], which yealds highly ordered material with well pronounced vibrational structure. Samples of both PPVs were spin coated.

Aluminium electrodes were subsequently evaporated on top of the films. Contacts were made using 'silver-dag'.

EXPERIMENTAL DETAILS

Our EA apparatus consists of a thermal light source (150W tungsten lamp), grating monochromator and detector (S20 photomultiplier tube or Si photodiode). Samples are held in a liquid nitrogen "cold finger" cryostat at temperatures down to 77K in a dynamic vacuum of about 10^{-4} mbar.

The pre-monochromated light (spectral resolution 2nm) transmitted by the polymer film is modulated with an AC high voltage of frequency, f, (typically 5 to 10 kHz) and detected using a lock-in amplifier set at 2f. Applying peak voltages between 500V and 2000 V across a gap of 0.2mm between the electrodes we obtain electric fields ranging from 25 to 100 kV/cm. The EA data are synchronously normalised by using a second lock-in and chopping the light beam at low frequency (15 - 20Hz).

RESULTS

Figure 1a displays the linear optical data of PTV. The data were obtained by nearly normal incidence reflection and absorption measurements and subsequent iterative Kramers-Kronig analysis[13].The imaginary part k features a broad maximum in the visible region with a peak at about 2.28 eV, the corresponding real part peaks at an energy of 1.84 eV.

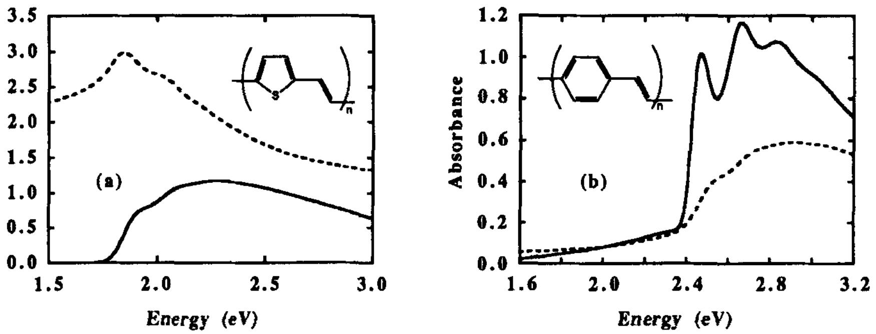

FIGURE 1 (a) Real part n (dotted line) and imaginary part k (solid line) of the complex refractive index of PTV,
(b) absorbance of PPV samples A (dotted line) and B (solid line)

Figure 1b compares the optical absorbance of PPV prepared by the two different synthetic methods. Sample B exhibits sharp peaks at 2.45, 2.65 and 2.85 eV with a shoulder at about 3.05 eV. These features cannot be observed in sample A.

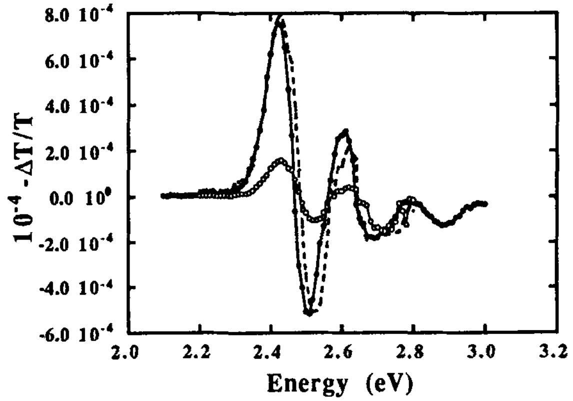

FIGURE 2: EA spectra of PPV sample A (open circles) and sample B (full circles); the solid line is a guide to the eye, the dotted line shows the EA spectrum of sample A scaled to the height of B

Figure 2 shows EA spectra of PPV samples A and B. Both curves show similar line shapes as can be seen from the scaled spectrum of sample A . However, sample B shows an increase by a factor of about 5, having taken the sample thicknesses in account. The EA signal scales quadratically with applied electric field and shows an anisotropy of 2.3 with respect to polarisation of the incident light.

For negligible reflectivity the relative change in transmission T is directly related to the induced change in the absorption coefficient, α [7]:

$$\Delta T/T = -\Delta\alpha\ d,$$

where d is the sample thickness. Using

$$\alpha = \frac{4\pi k}{\lambda},$$

where λ is the wavelength, and the Kramers-Kronig relationship

$$\Delta n = \frac{2E}{\pi}\int_0^\infty \frac{\Delta k}{E'^2 - E^2}\,dE',$$

one obtains the field induced change in the real part of the refractive index, Δn, from the change in imaginary part, Δk.

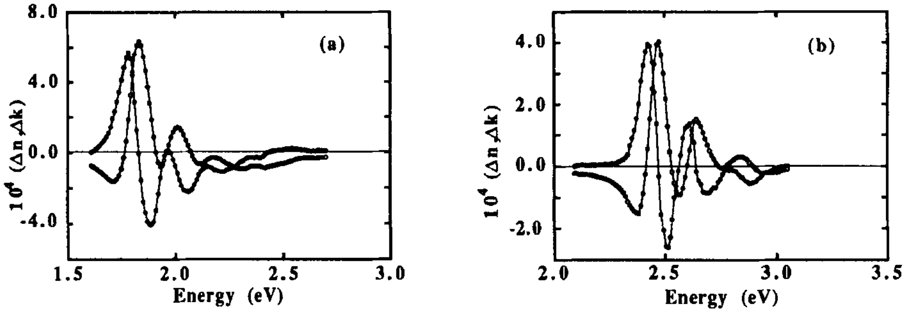

FIGURE 3: (a) Field induced change in real part (open circles) and imaginary part (full circles) of PTV at 120 K with an electric field of 100 kV/cm,
(b) field induced change in real part (open circles) and imaginary part (full circles) of PPV sample B at 80 K with an electric field of 50 kV/cm.

Figure 3 illustrates the field induced changes in the complex refractive index of PTV and PPV sample B. Both materials show an induced change of order 10^{-4}, which represents a substantial electro-optic nonlinearity. Combining the linear optical data from figure 1a and 3a we have calculated[9] the nonlinear susceptiblity $\chi^{(3)}(-\omega;\omega,0,0)$ with a peak of 7.5 10^{-8} esu.

CONCLUSIONS

Conjugated polymers which have been prepared from soluble precursors, represented here by the materials PTV and PPV, hold large nonlinear electro-optical coefficients. However, there is still potential to increase these properties by modifying the chemical synthesis to obtain better and more ordered material.

ACKNOWLEDGEMENTS:

We gratefully thank the New Energy and Industrial Technology Development Organisation of Japan [NEDO], Toshiba Corporation, and the Air Force Office of Scientific Research (Grant AFOSR-90-0213) for partial support of this work.

REFERENCES:

1. J.H. Burroughes, C.A. Jones, R.H. Friend, Nature, 355, 137, (1988)
2. K.E. Ziemalis, A.T. Hussain, D.D.C. Bradley, R.H. Friend, J. Rühe, G. Wegner, Physical Review Letters, 66, 2231, (1991)
3. J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burn, A.B. Holmes, Nature, 347, 539, (1990)
4. A.R. Brown, P.L. Burn, D.D.C. Bradley, R.H. Friend, A. Kraft, A.B. Holmes, *these proceedings*
5. M. Cardona, Modulation Spectroscopy, Academic Press, New York and London (1969)
6. L. Sebastian, G. Weiser, Phys.Rev.Lett., 46 (1981), 1156
7. S.D. Phillips, R. Worland, G. Yu, T. Hagler, R. Freedman, Y. Cao, V. Yoon, J. Chiang, W.C. Walker and A.J. Heeger, Phys.Rev.B40, 9751, (1989)
8. O.M. Gelsen, D.D.C. Bradley, H. Murata, N. Takada, T.Tsutsui, S. Saito, G. Leising, Proceedings IWEPP '91, *in press*
9. O.M. Gelsen, D.D.C. Bradley, H. Murata, T. Tsutsui, S. Saito, J. Ruehe, G. Wegner, Proceedings ICSM '90, Synth. Met., 41-43 ,875, (1991)
10. D.D.C. Bradley, O.M. Gelsen, Physical Review Letters Comment, *in press*
11. H. Murata, S. Tokito, T. Tsotsui and S. Saito, Synth.Met.36, 95, (1990)
12. P.L. Burn et al., Proceedings IWEPP '91, *in press*
13. P.O. Nilsson, Appl.Opt.7 (3), 435, (1968)