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SYNTHESIS AND KINETIC ANALYSIS OF POLY(2,2’-DYMETHOXY-4,4’-BIPHENYLENEVINYLENE
A novel conducting polymer

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Abstract

The title polymer was obtained electrochemically by the reduction of 4,4’-bis(dibromomethyl)-2,2’-dimethoxybiphenyl under very smooth conditions. The DSC and TG/DTG curves registered at four different heating rates showed that the polymer is stable in air up to 150°C, where smooth degradation starts. Above 300°C, decomposition is fast and exothermic ($\Delta H=-323$ J g^{-1}). The activation energy (116±4 kJ mol^{-1}) was determined by Ozawa’s method.

Keywords: conducting polymer, DSC, kinetic analysis, PPV, TG

Introduction

Poly(*p*-phenylenevinylene) (PPV) and related derivatives, formed essentially by functionalization of the phenylene or vinylene units, constitute a very attractive family of conjugated polymers for electroluminescent devices [1, 2].

We have recently described the synthesis and characterization of a variety of poly(arylenevinylene)s by the cathodic reduction of substituted $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*p*-xylenes [3–5], as well as some poly(*p*-xylylene)s [6, 7], whose thermal decomposition in a non-oxidizing atmosphere is known to produce PPVs [8].

Various types of thermal analysis techniques have been applied to almost all fields, including materials chemistry and more particularly conducting polymers. Dynamic thermogravimetry, in which the change in mass of a sample heated at constant rate is recorded and plotted *vs*. temperature, is an effective method of studying thermal stability and the kinetics of thermal decomposition reactions [9].

The kinetic investigation of the random degradation of high polymers can be achieved from thermogravimetric data by the application of Ozawa’s method [10], in which the slope of plots of log heating rate *vs*. $1/T$ gives the activation energy (E_a) of the process.

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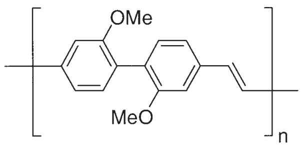


(I)

Fig. 1 Structure of poly(2,2'-dimethoxy-4,4'-biphenylenevinylene)

In this paper, we report the synthesis, thermal behaviour and kinetic analysis of a new conjugated polymer(I), which involves 2,2'-methoxy-substituted biphenylene units attached to vinylene units, as shown in Fig. 1.

Experimental

Materials

2-Iodo-5-methylanisole(II) was obtained as described in the literature [11].

Preparation of 4,4'-dimethyl-2,2'-dimethoxybiphenyl(III)

2-Iodo-5-methylanisole(II) (2.00 g; 8.06 mmol) and freshly activated copper bronze (3.08 g; 48,5 mmol) were sealed in a glass tube and heated for 4 h at 220°C. After extraction with acetone in a Soxhlet apparatus for 12 h, the solvent was removed and the solid was recrystallized (methanol) to give yellow crystals, yield 0.828 g (3.42 mmol; 85%). M_p: 118–120°C (Lit. [12]: 122°C). ^{1}H NMR (δ, $CDCl_3$/TMS): 2.39 (6H, s, CH_3); 3.75 (6H, s, OCH_3); 6.79 (2H, s, 3,3'-Ar-H); 6.81 (2H, d, J=8 Hz, 6,6'-Ar-H); 7.12 (2H, d, J=8 Hz, 5,5'-Ar-H). FTIR (cm^{-1}, KBr): 3054 ($\nu_{arom.}$ C–H); 2960, 2938, 2916 and 2860 ($\nu_{sat.}$ C–H); 1607 and 1496 (benzene ring); 1467 ($\delta_{sat.}$ C–H); 1254 and 1038 (νC–O–C); 867 and 810 (1,2,4-trisubstituted benzene ring).

Preparation of 4,4'-bis(dibromomethyl)-2,2'-dimethoxybiphenyl(IV)

4,4'-Dimethyl-2,2'-dimethoxybiphenyl(III) 0.351 g; 1.45 mmol), N-bromosuccinimide (1.19 g; 6.68 mmol) and dibenzoyl peroxide (2.5 mg) were added to dry carbon tetrachloride (5 ml), and the mixture was heated to reflux for 4 h under VIS illumination (300 W halogen bulb) and then cooled to room temperature. The insoluble succinimide was filtered off and washed with chloroform. The combined filtrate was shaken with aqueous sodium chloride and then with water. After drying over anhydrous magnesium sulfate and solvent evaporation, the solid was recrystallized (CCl_4/$CHCl_3$) to give yellow crystals, yield 0.497 g (0.891 mmol; 61%). M_p: 179–181°C. ^{1}H NMR (δ, $CDCl_3$/TMS): 3.83 (6H, s, OCH_3); 6.68 (2H, s, $CHBr_2$); 7.13 and 7.15 (2H, dd, J=1 Hz; 5 Hz, 5,5'-Ar-H); 7.19 (2H, d, J=5 Hz, 6,6'-Ar-H); 7.22 (2H, d, J=1 Hz, 3,3'-Ar-H). FTIR (cm^{-1}, KBr): 3034 ($\nu_{arom.}$ C–H); 2968, 2939, 2913 and 2870 ($\nu_{sat.}$ C–H); 1601 (benzene ring); 1463 ($\delta_{sat.}$ C–H); 1254 and 1032 (νC–O–C); 877 and 818 (1,2,4-trisubstituted benzene ring);

681 (νC–Br). Elemental analysis gave (calc.): C 34.31 (34.41)%, H 2.53 (2.51)%. Cyclic voltammetry: –1.8 V *vs*. Ag/AgBr.

Preparation of poly(2,2'-dimethoxy-4,4'-biphenylenevinylene)(I)

Compound IV (0.789 g; 1.41 mmol) was electrolyzed at a controlled potential of –1.8 V (*vs*. Ag/AgBr) in a conventional cell equipped with a magnetically stirred mercury pool cathode, an Ag/AgBr reference electrode, a graphite anode and a microporous divider. The solvent was DMF containing 0.1 mol l^{-1} Et_4NBr as supporting electrolyte. The cathode compartment was continually flushed with a slow stream of dry nitrogen. After ca. 4.2 F mol^{-1} had passed, the cell current dropped close to the background value and the electrolysis was stopped. Water was added to the catholyte and the polymer was filtered off, washed and dried. Yield: 201 mg (0.843 mmol; 60%). ^{1}H NMR (δ, $CDCl_3$/TMS): 3.76 (6H, s, OCH_3); 6.79 (2H, m, 3,3'-Ar-H); 7.11–7.21 (6H, m, Ar-H and vinylic hydrogens). FTIR: 2997, 2934 and 2856 ($\nu_{sat.}$ C–H); 1605 and 1492 (benzene ring); 1462 ($\delta_{sat.}$ C–H); 1252 and 1039 (νC–O–C); 964 ($\delta_{trans.}$ H–C=C–H); 853 and 813 (1,2,4-trisubstituted benzene ring). $\overline{M}_n$=6275 [5]. Electrical conductivity after doping with iodine vapor: $2{\cdot}10^{-5}$ S cm^{-1} [5].

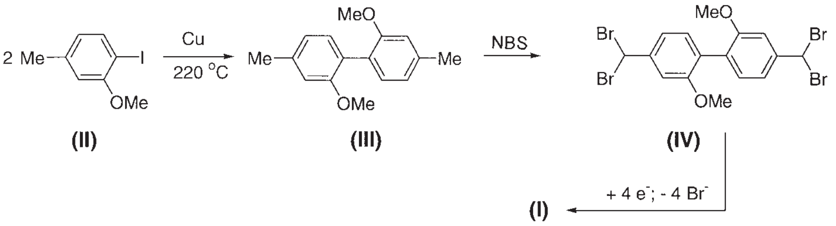
Thermal analysis

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were obtained with a thermobalance model TG-50 (Shimadzu), using platinum crucibles with ca 3 mg of sample, under a dynamic air atmosphere (50 ml min^{-1}), at different heating rates (5, 10, 20 and 40°C min^{-1}).

Differential scanning calorimetry (DSC) curves were obtained with a DSC-50 (Shimadzu) cell, using an aluminum crucible with ca. 2 mg of sample, in a dynamic nitrogen atmosphere (50 ml min^{-1}), at a heating rate of 10°C min^{-1}.

Results and discussion

Polymer (I) was prepared electrochemically by cathodic reduction of compound IV, which was obtained by Ullmann condensation of 2-iodo-5-methylanisole (II), followed by benzylic bromination of the resulting biphenyl (III), as shown in Scheme 1. All compounds were spectroscopically characterized and although the ^{1}H NMR



Scheme 1 Synthetic route to polymer I

peaks of polymer(I) were somewhat broadened, the chemical shifts and integrations were as expected for these oligomers. The IR absorption at 964 cm^{-1} confirmed the *trans*-alkene structure.

The TG/DTG curves at the four chosen heating rates (Fig. 2) reveal that polymer is thermally stable up to approximately 150°C. Thermal decomposition occurs in two main steps when the heating rate is low (5 or 10°C min^{-1}), but in three steps at higher rates (20 or 40°C min^{-1}). In all cases, the decomposition is complete and no residue is left above 700°C.

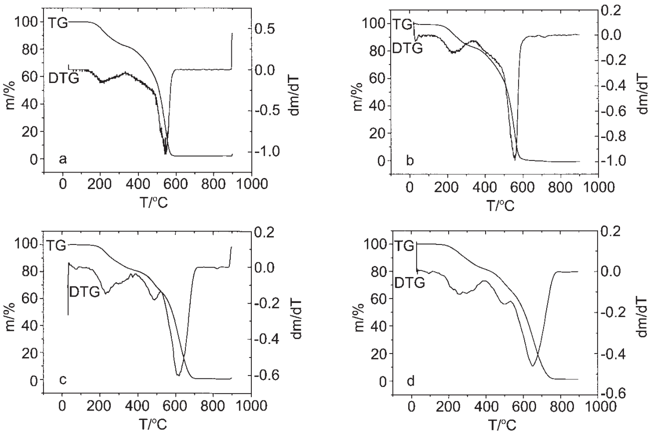


Fig. 2 TG/DTG curves for polymer(I) at different heating rates: a – 5°C min^{-1}; b – 10°C min^{-1}; c – 20°C min^{-1}; d – 40°C min^{-1}

The DSC curve (Fig. 3) indicates no significant enthalpic changes up to 330°C. There are two overlapping exothermic events at 384 and 463°C (ΔH=–323 J g^{-1}),

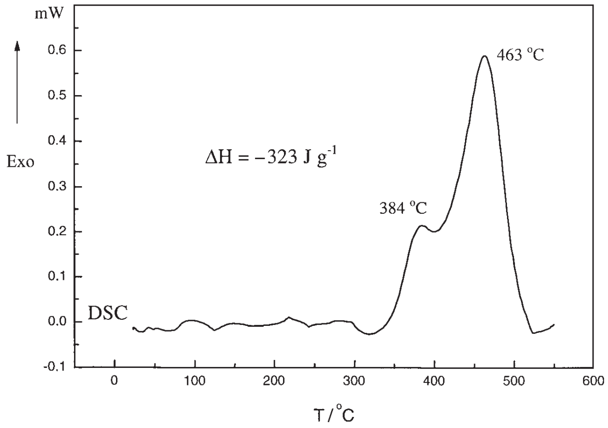


Fig. 3 DSC curve for polymer I

which suggest that the thermal decomposition is spontaneous, even in an inert atmosphere. These events are in agreement with those observed in the TG/DTG curves.

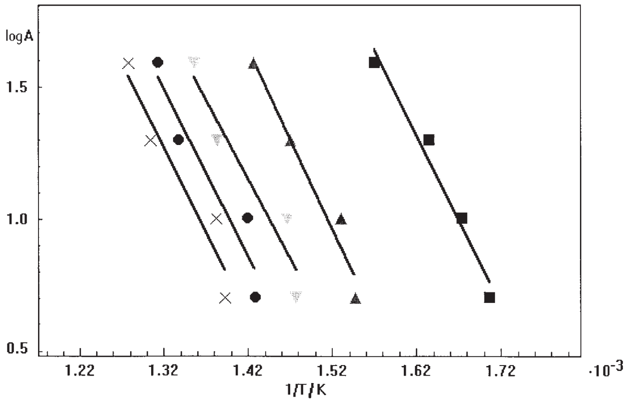


Fig. 4 Ozawa's plots for polymer I

The data from the four TG curves were applied in Ozawa's method in order to determine the activation energy for the beginning of the main decomposition step at around 300 to 500°C. Figure 4 presents the obtained plots, which demonstrate a fairly good correlation at the four heating rates (A). Thus, the value obtained for E_a is 116±4 kJ mol^{-1}.

Conclusions

The conjugated polymer poly(2,2'-dimethoxy-4,4'-biphenylenevinylene) was prepared electrochemically at room temperature. The TG curves at four different heating rates indicated that this new material is stable up to 150°C. Above 350°C, degradation is fast, and Ozawa's method of kinetic analysis resulted in an activation energy of 116±4 kJ mol^{-1} for this process.

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