ELSEVIER

Polymer 42 (2001) 5793–5796

polymer

www.elsevier.nl/locate/polymer

Polymer Communication

The Gilch polymerisation towards OC_1C_{10}-PPV: indications for a radical mechanism

L. Hontis, V. Vrindts, L. Lutsen, D. Vanderzande*, J. Gelan

Laboratory for Organic and Polymer Chemistry, Limburg University Centre, Institute for Material Research, Division Chemistry, University Campus, B-3590 Diepenbeek, Belgium

Received 5 December 2000; received in revised form 12 January 2001; accepted 25 January 2001

Abstract

Although *p*-quinodimethane based polymerisations have been investigated by a number of research groups, the nature of the underlying polymerisation mechanism — radical or anionic — is still under discussion. The effect of different types of additives on the Gilch polymerisation was examined and experimental results of this study are presented in this paper. We can not completely exclude anionic processes, but taken as a whole the results obtained, are a strong indication that the main polymerisation mechanism operating in the Gilch route is of radical nature and yields high molecular weight polymers. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: OC_1C_{10}-PPV; Gilch polymerisation; Polymerisation mechanism

1. Introduction

Poly(*p*-phenylene vinylenes) (PPVs) are known to be interesting materials for use as the active layer in optoelectronic applications, such as polymer light-emitting diodes (PLEDs) [1]. The derivative known as OC_1C_{10}-PPV exhibits very good properties (e.g. luminescence efficiency). To synthesise this type of conjugated polymers various routes were developed including: the Wessling–Zimmerman [2], Gilch [3] and Sulfinyl [4,5] routes. These routes are based on similar chemistry and involve the in situ formation and polymerisation of *p*-quinodimethane systems. A general scheme consisting of three steps is represented in Fig. 1. The Gilch polymerisation route is recently the most common used.

The mechanism of the second step of this type of *p*-quinodimethane based polymerisation routes is still under discussion. It's not easy to study, because of the carbanion chemistry involved in the first step. Additives meant to affect anionic polymerisation could also interfere with the *p*-quinodimethane formation. One should therefore be very careful in interpreting the effects of these additives. The complexity of the chemistry involved in the whole polymer synthesis makes the nature of the polymerisation mechanism, anionic or radical, uncertain.

Recent reports retain this ambiguity. Results of H–D exchange, kinetic, and product studies reveal a radical polymerisation mechanism for the Wessling route [6]. Previous mechanistic studies on the Sulfinyl route showed that apparently both types of mechanism can occur simultaneously, strongly dependent on the type of ring substituents and solvent used [7]. Even in solvents that enhance the reactivity of anions, experiments with the radical scavenger TEMPO show that the main pathway occurs via radicals [8]. In contrast, for the Gilch route, addition of the 'acidic' additive 4-*tert*butylbenzyl chloride [9] and the nucleophile 4-methoxyphenol [10] resulted in an inverse relationship between amount of additive and molecular weight, indicating an anionic polymerisation mechanism.

In an attempt to further elucidate the mechanism of the Gilch polymerisation several experiments with different types of additives (Fig. 2) were performed. The polymerisation procedure was kept constant for all experiments. The effects of the additives on the molecular weight of the polymer were evaluated by size exclusion chromatography (SEC).

2. Experimental

2.1. Materials

All reagents were purchased from Aldrich, unless stated otherwise. Dioxane was dried over sodium and distilled

---

* Corresponding author. Tel: +32-11-268321; fax: +32-11-268301.
E-mail address: Dirk.Vanderzande@luc.ac.be (D. Vanderzande).

PII: S0032-3861(01)00076-3

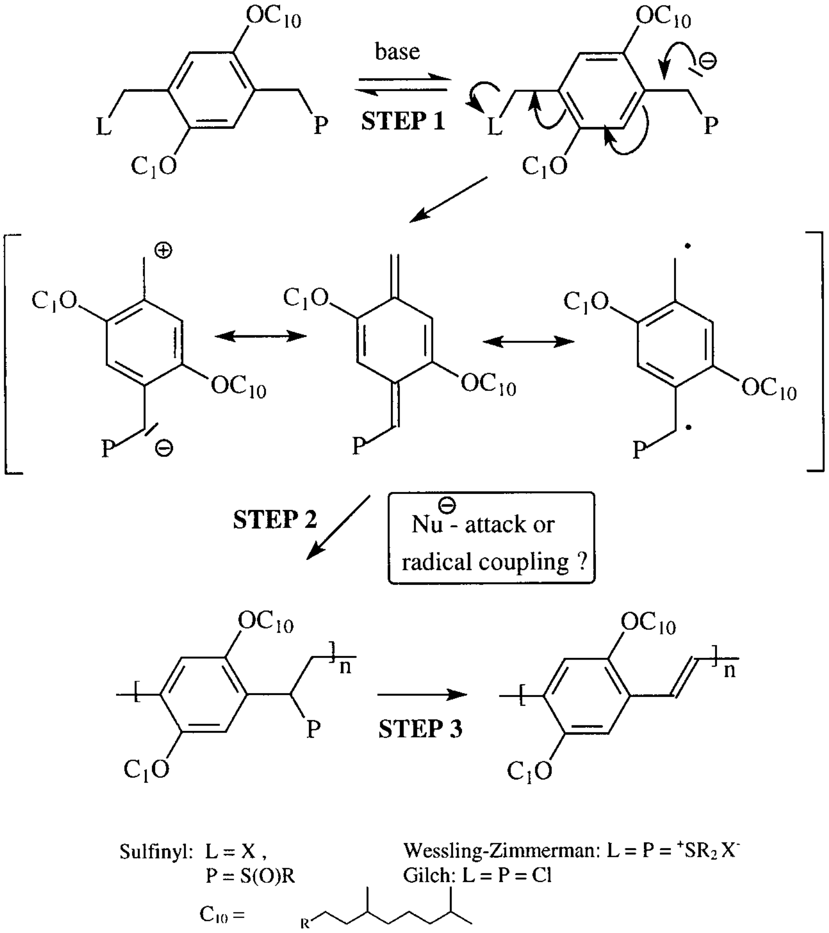

Fig. 1. General scheme for *p*-quinodimethane based polymerisations.

prior to use. The monomer 2,5-bis(chloromethyl)-1-(3,7-dimethyl-octyloxy)-4-methoxybenzene was obtained from Covion Organic Semiconductors.

2.2. General polymerisation procedure — preparation of Poly[2-(3,7-dimethyloctyloxy)-5-methoxy-p-phenylene vinylene] (=OC$_1$C$_{10}$-PPV)

All the glassware was dried overnight in a drying oven prior to use. A 100 ml three-neck flask with Teflon stirrer, reflux condenser and elbow to add solid base was flushed with N_2. The reactor at room temperature was then charged with 21 ml of dry dioxane, and passing N_2 through it for about 15 min degassed the solvent. With about 4 ml of dry dioxane 0.18 g (0.5 mmol) of solid 2,5-bis(chloromethyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene was rinsed in. All additives were added in an amount of 0.5 eqiv to the monomer solution. Polymerisation was initiated by a first addition of 1.3 eqiv of solid potassium *tert*-butoxide. In most cases the viscosity increased significantly while the reaction mixture turned from colourless to yellow/orange. After 10 min 3.3 eqiv of solid potassium *tert*-butoxide was added and the reaction mixture became a deep orange. Stirring was continued for 2 h and afterwards the reaction mixture was heated to 96–98°C until a homogeneous solution was obtained (2–12 h). For work-up the solution was cooled to 30°C and during vigorous stirring 25 ml of water was added slowly. Also 3.5 ml 1.0 M aqueous hydrochloric acid and 2.5 ml methanol were added, and the precipitated polymer was recovered by filtration. It was washed with methanol and dried under reduced pressure at room temperature.

2.3. General purification procedure

The polymers were purified using a similar procedure to that described in Ref. [11]. The polymer was dissolved in

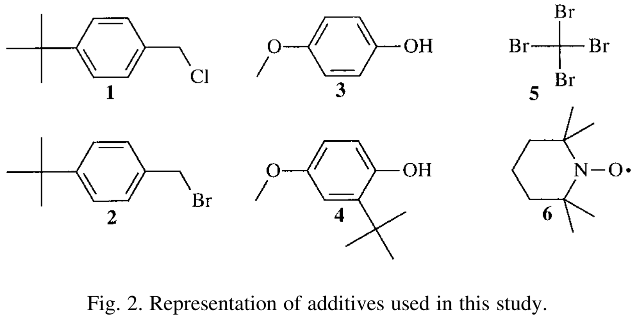

Fig. 2. Representation of additives used in this study.

Table 1
SEC results after purification and polymer yields (Last column: between brackets: yield before purification)

Experiment	M_w (g/mole)	PD	Yield (%)
standard (1)	754 000	8.0	78 (85)
standard (2)	797 000	7.3	74 (78)
standard (3)	650 000	7.0	85 (86)
$\text{tBu}\phi\text{CH}_2\text{Cl}$ (1)	581 500	9.7	76 (77)
$\text{tBu}\phi\text{CH}_2\text{Cl}$ (2)	720 000	9.9	80 (83)
$\text{tBu}\phi\text{CH}_2\text{Br}$ (1)	533 000	5.9	80 (83)
$\text{tBu}\phi\text{CH}_2\text{Br}$ (2)	655 000	6.7	80 (83)
CBr_4 (1)	73 000	3.8	75 (100)
CBr_4 (2)	85 000	2.9	83 (100)
TEMPO (1)	179 000	4.5	21 (33)
TEMPO (2)	227 000	4.3	26 (38)
MeOPhOH (1)	1513 400	17.4	12 (30)
MeOPhOH (2)	16 300	2.6	3 (22)
MeOPhOH (3)	679 000	14.2	10 (39)
tBuMeOPhOH (1)	479 200	9.7	8 (14)
tBuMeOPhOH (2)	58 000	3.8	2 (20)
tBuMeOPhOH (3)	189 500	9.5	3 (40)

20 ml of THF and heated to 68°C. The solution was cooled to 40°C and a dropwise addition of methanol caused the polymer to precipitate. The precipitated polymer was recovered by filtration, washed with methanol and dried under reduced pressure at room temperature.

2.4. SEC measurements

SEC measurements were performed in HPLC grade tetrahydrofuran at 40°C relative to polystyrene standards with a narrow polydispersity. The flow rate was kept constant at 1 ml/min and toluene was used as flow rate marker. Separation to hydrodynamic volume was obtained using two 10 μm mixed-B Polymer Labs columns (30 cm × 7.5 mm). The detector was a SpectraSYSTEM RI-150 Refractive Index.

3. Results and discussion

A common way to investigate a polymerisation mechanism is to look at the influence of additives on the reaction and its products. There are different kinds of additives: some affect anionic processes, while others exhibit an effect on radical processes. For this study the six additives depicted in Fig. 2 were used.

This combination of additives was chosen to distinguish between anionic and radical polymerisation mechanisms. Because of recent reports by Hsieh [9] and Ferraris [10] the additives 4-*tert*butylbenzyl chloride **1**, 4-*tert*butylbenzyl bromide **2** and 4-methoxyphenol **3** were expected to act as anionic initiators/terminators. Previous mechanistic studies proved TEMPO **6**, a radical inhibitor, and carbon tetrabromine **5**, a chain transfer agent, were good indicators for a radical mechanism [8]. The additive 2-*tert*butyl-4-methoxyphenol **4** was added to our study to clarify the effect of the non-butylated derivative **3**.

All experiments were done in duplicate,except for the experiments with the additives **3** and **4**, which were done in triplicate. For all experiments the amount of additive was set at 0.5 eqiv, to enhance the visibility of effects. The results obtained show that this polymerisation procedure has reasonable reproducibility. SEC results after purification and polymerisation yields are listed in Table 1. According to TLC and 1H-NMR analysis the residual fractions seem to be rather complex and will be subject of future study.

The standard polymerisation procedure leads to polymer with a molecular weight from 700 to 800 kD in a yield of over 70%. Addition of 4-*tert*butylbenzyl chloride or bromide did not affect the polymer yield and resulted in a small decrease in molecular weight. It can be concluded that these additives do not exhibit the effect experienced by Hsieh and do not act as anionic initiators for the polymerisation. The additive carbon tetrabromine resulted in a serious decrease in molecular weight and a lowering of polydispersity, while the yield was not affected; which is consistent with it acting as a chain transfer agent. The effect of TEMPO on the polymerisation is consistent with inhibition of a radical polymerisation mechanism; the yield of polymer decreased by a factor 4 and the molecular weight decreased.

The effects of the additives 4-methoxyphenol and 2-*tert*-butyl-4-methoxyphenol are more complex. Reproducibility of molecular weight is poor, whereas the yield after purification is somewhat more consistent. Before purification the resulting polymer is a wet, sticky substance — probably because side products are entrapped — which makes the separation difficult, leading to a spread in the yields. Apparently for these reactions the molecular weight of the resulting polymer is very sensitive to reaction conditions, leading to a spread in molecular weights. The yields were decreased to a low level indicating a huge influence of these additives on the reactions occurring during synthesis. But because the additive 2-*tert*butyl-4-methoxyphenol, which has much less nucleophilic properties, seems to exhibit a similar effect on the yield as additive **3**, these results do not support the hypothesis of anionic initiation. While, for the present, we can not exclude any anionic interference of these two additives on the successive reaction steps, in combination with the other results reported here, we conclude that their main effect is probably a strong radical inhibiting one, as described previously for the case of quinones [12].

4. Conclusions

This study was undertaken in an attempt to elucidate the nature of the polymerisation mechanism — anionic or radical — of *p*-quinodimethane based polymerisations. A reproducible polymerisation procedure to synthesise OC_1C_{10}-PPV via the Gilch route in dioxane at RT was developed, based on the Covion procedure, and used to investigate the influence of different types of additives. It is not our objective to claim a full understanding of the processes occurring during polymer synthesis, because the involved chemistry is extremely complex. However, the results obtained do require a re-examination and reinterpretation of previous results [9,10], which lead to the conclusion of a non-radical polymerisation mechanism. We are not able to definitively exclude anionic processes but, as a whole, the results obtained are a strong indication that the main polymerisation mechanism of the Gilch route is radical in nature and yields high molecular weight polymer.

Acknowledgements

We thank the Inter University Attraction Pole (IUAP) of the Belgian Government for the financial support. And we especially like to acknowledge Dr H. Becker and Dr W. Kreuder from Covion Organic Semiconductors for the valuable discussions and for putting the essential monomer at our disposal.

References

[1] Burroughes J, Bradley D, Brown A, Marks R, Mackay K, Friend R, et al. Nature 1990;347:539.
[2] Wessling RAJ. Pol Sci, Pol Symp 1985;72:55.
[3] Gilch HG, Wheelwright WL. J Pol Sci : A-1 1966;4:1337.
[4] Vanderzande DJ, Issaris AC, Van Der Borght MJ, van Breemen AJ, de Kok MM, Gelan JM. Macromol Symp 1997;125:189.
[5] Vanderzande DJ, Issaris AC, Van Der Borght MJ, van Breemen AJ, de Kok MM, Gelan JM. Polym Preprints 1997;38(1):321.
[6] Cho BR, Kim YK, Han MS. Macromolecules 1998;31:2098.
[7] Adriaensens P, Van Der Borght M, Hontis L, Vanderzande D. Gelan J Polym 2000;41(19):7003.
[8] Hontis L, Van Der Borght M, Vanderzande D. Gelan J Polym 1999;40:6615.
[9] Hsieh BR, Yu Y, VanLaeken AC, Lee H. Macromolecules 1997;30:8094.
[10] Neef CJ, Ferraris JP. Macromolecules 2000;33:2311.
[11] Becker H, Spreitzer H, Ibrom K, Kreuder W. Macromolecules 1999;32:4925.
[12] Finley KT. In: Patai ES, editor. Chemistry of quinonoid compounds. New York: Wiley, 1974. p. 339.