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Radical as well as anionic polymerisation mechanisms in the synthesis of poly(*p*-arylene vinylene) precursors

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Abstract

Experiments have been performed to clarify the polymerisation mechanism of chloromethyl-4-(*n*-butylsulfinyl)methylbenzene **1a** and 4-chloromethyl-4′-(*n*-butylsulfinyl)methylbiphenyl **1b** in NMP. Addition of TEMPO and water to the polymerisation mixture led to the conclusion that radical as well as anionic mechanisms occur which lead to the formation of a high and a low molecular weight polymer fraction, respectively. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymerisation mechanism; *p*-quinodimethane systems; Poly(*p*-arylene vinylene) precursors

Poly-(*p*-phenylene vinylene) (PPV) and its derivatives remain the most investigated class of conjugated polymers for use as active layer in polymer based Light Emitting Diodes (LED's). To obtain the desired polymer several synthetic methods have been developed and most of them are based on similar chemistry. The Gilch route [1], the Wessling route [2], the xanthate route [3,4] and the sulfinyl route [5,6] differ from each other only in the type of leaving (L) and polariser (P) groups [7] used. Because of the similarity in the chemistry used they can all be described by a general scheme (Fig. 1). A base induced 1,6-elimination from a *p*-xylene derivative **1** leads to the in situ formation of a *p*-quinodimethane system **2**. In a second step this intermediate polymerises spontaneously and rapidly to yield high molecular weight PPV precursor polymers **3**. The conjugated structure **4** is obtained directly or after thermal treatment depending on the specific chemical structure of the starting monomer and the polymerisation conditions.

Our sulfinyl route differs from the other routes in that a chemical differentiation is introduced between a leaving group and a so called "polariser". As leaving group a halide is used. At the other benzylic position a sulfinyl group is placed which has a threefold function: preferential stabilisation of the anion formed in the first step of the process, polarisation of the *p*-quinodimethane system in such a way that regular head to tail addition results, and third it provides the specific chemistry to allow the formation of a double bond.

In the past the nature of the underlying mechanism of this type of *p*-quinodimethane based polymerisations was unclear; both anionic [8–10] and radical [2,11,12] mechanisms have been proposed. Discussion of the polymerisation mechanism has recently been reinitiated by the work of Hsieh et al. [13–16] in which experimental proof is claimed to support the hypothesis of an anionic mechanism for the Gilch route. At the same time Cho et al. [17] and our group [18,19] published experimental results that point to radical processes taking place in the Wessling route and our sulfinyl route respectively. Also the earlier observation within our research group that GPC analyses of PPV precursor polymers synthesised in dipolar, aprotic solvents like DMF, NMP and DMSO show a bimodal molecular weight distribution [20], whereas corresponding polymers synthesised in protic solvents like MMF show a monomodal distribution [18,19], prompted further investigation into the polymerisation mechanism. Therefore we reinvestigated the synthesis of the precursor polymers poly{[1,4-phenylene]-[1-(*n*-butylsulfinyl)ethylene]} and poly{[4,4′-biphenylene]-[1-(*n*-butylsulfinyl)ethylene]} via our sulfinyl route in NMP.

In this article we present some of our recent results that reveal new insights in the mechanism of *p*-quinodimethane based polymerisations and which point to an alternative interpretation of the events occurring in the Gilch route.

In earlier work we proved that PPV precursor polymers are formed via a radical polymerisation mechanism when

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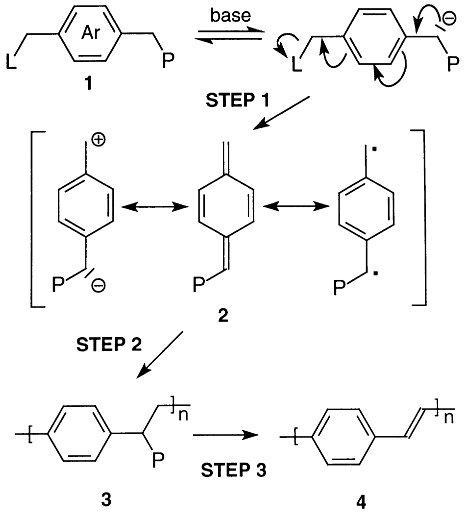

Wessling route : L = P = $^+SR_2X^-$
Gilch route : L = P = Cl
Xanthate route : L = P = SCSOEt
Sulfinyl route : L = Cl ; P = S(O)R

1a : Ar = phenylene ; L = Cl ; P = S(O)*n*Bu
1b : Ar = biphenylene ; L = Cl ; P = S(O)*n*Bu

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

our route was performed in a polar, protic solvent like MMF [18,19]. One of the experimental results that led to this conclusion was the effect of a radical inhibitor, 2,2,6,6-tetramethylpiperinoxyl (TEMPO), on the reaction. Addition of a small amount (0.01 eq.) results in a decrease in yield and molecular weight, whereas addition of 0.5 eq. TEMPO totally inhibits the polymerisation reaction.

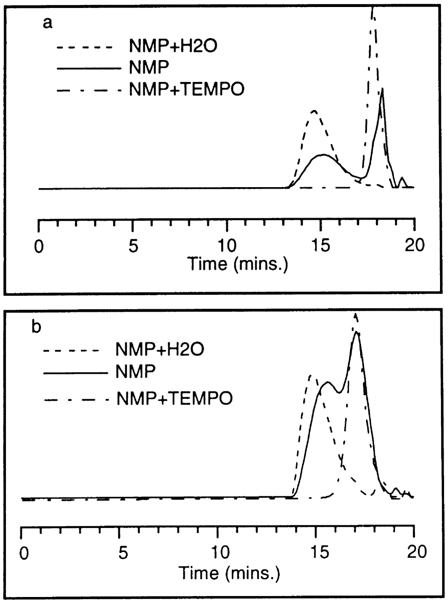

Fig. 2. Overlay of GPC$^{(i)}$-chromatograms before and after addition of TEMPO or water to the standard polymerisation mixture of (a) **1a** and (b) **1b**. (i) 2 PLgel 10 µm mixed-B columns, DMF, 70°C.

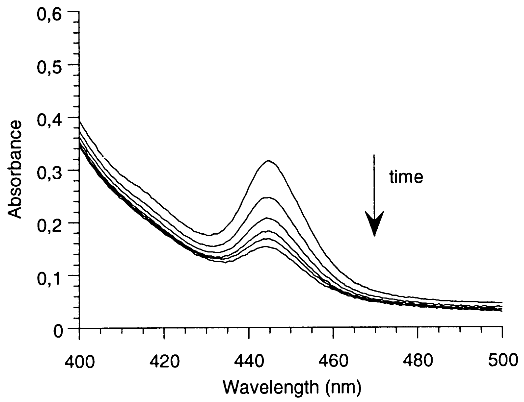

Fig. 3. UV–vis spectrum: formation and decrease of a signal around 445 nm which is assigned to the *p*-quinodimethane system of **1b**.

A standard polymerisation [19] of chloromethyl-4-(*n*-butylsulfinyl)methylbenzene **1a** in NMP yields a precursor polymer that shows a bimodal molecular weight distribution according to GPC analysis (Fig. 2(a)). In contrast with the results obtained in MMF, addition of 0.5 eq. TEMPO in NMP does not block all polymer formation. GPC measurements show a monomodal distribution on the low molecular weight side of the chromatogram ($\overline{M}_w = 3\ 000$ g/mol; PD = 1.1) at the same elution volume as the second peak of the standard bimodal distribution (Fig. 2(a)). It seems that addition of TEMPO only inhibits the formation of the high molecular weight polymer. This points to the occurrence of a radical mechanism which is responsible for the formation of the high molecular weight polymer in NMP. From this experiment the origin of the low molecular weight polymer is not clear, but the results seem to point to a non-radical mechanism for its formation. When we take the nature of the solvent into account, an anionic mechanism seems to be probable. Indeed NMP belongs to the class of dipolar, aprotic solvents which specifically solvate cations very efficiently and enhance the reactivity of the anions. Hence if an anionic mechanism is postulated for this kind of *p*-quinodimethane based polymerisations it is most probable to take place in this class of solvents. To check if such polymerisation mechanism does take place in NMP, 5 vol% of water is added to the standard reaction mixture. The result is consistent with our expectations: GPC-analysis shows that the higher molecular weight polymer ($\overline{M}_w = 61\ 000$ g/mol; PD = 1.7) is still present, but the formation of low molecular weight polymer is blocked (Fig. 2(a)). Whether this anionic mechanism is of a chain- or step-growth nature, will be the subject of further work. ^{1}H-NMR studies show that in both cases a polymer with a similar structure is formed.

A second example comprises the polymerisation in NMP of 4-chloromethyl-4′-(*n*-butylsulfinyl)methylbiphenyl **1b** which also shows a bimodal molecular weight distribution in GPC analysis (Fig. 2(b)). As the resonance energy to be broken on formation of the *p*-quinodimethane system is expected to be quite high, we first investigated the formation

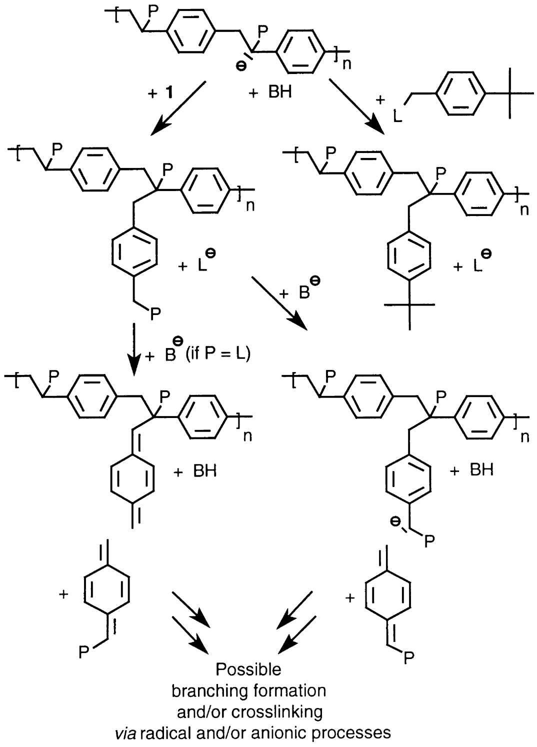

Fig. 4. A tentative reaction scheme for branching formation and the possible influence of 4-*t*-butylbenzylchloride.

of such species with UV–vis spectroscopy. On addition of a base (Na$^+$tBuO$^-$) to a solution of the monomer **1b** in NMP instantaneously a new signal around 445 nm is observed which quickly diminishes in time (Fig. 3). This peak at 445 nm probably corresponds to the absorption of the appropriate *p*-quinodimethane system [21,22]. Addition of 0.5 eq. TEMPO or 5 vol% water gives rise to a monomodal distribution of a low molecular weight ($\overline{M}_w = 8\,000$ g/mol; PD = 1.1) or a high molecular weight ($\overline{M}_w = 40\,000$ g/mol; PD = 1.5) polymer. An overlay of the corresponding GPC-chromatograms is shown in Fig. 2(b).

From these two examples it becomes clear that an anionic process yields even in a solvent well suited for this kind of polymerisation a low molecular weight material ($\overline{M}_w < 10\,000$ g/mol). Within this context we want to propose an alternative interpretation of the results obtained by Hsieh [13–16]. We consider that the backbone of the polymer, that is obtained in a standard reaction, is formed via a radical mechanism, which can explain the high molecular weight. In the same conditions an anionic polymerisation mechanism leads to the formation of low molecular weight polymer and, in our view, anionic attack on the backbone can be the cause of branching and even crosslinking. The acidic additive 4-*t*-butylbenzylchloride used by Hsieh, possibly acts as a terminator for this anionic process and prevents gelation. A proposed rationalisation for this reaction is shown in Fig. 4. The chemical differentiation between a leaving group and a polariser in our route may explain why this crosslinking does not occur. However further experiments are planned to investigate the branching and crosslinking processes in more detail.

These experimental results in NMP combined with earlier observations lead to the conclusion that two different mechanisms can take place in this type of *p*-quinodimethane based polymerisation. Addition of a radical inhibitor or water shows that a high molecular weight polymer is formed via a radical mechanism while an anionic polymerisation mechanism is responsible for the formation of a lower molecular weight polymer. However, the extent to which these processes occur is largely controlled by the nature of the solvent.

References

[1] Gilch HG, Wheelwright WL. J Pol Sci: A-1 1966;4:1337–1349.
[2] Wessling RA. J Pol Sci, Pol Symp 1985;72:55–66.
[3] Son S, Lovinger AJ, Galvin ME. Polym Mat Sci Engng 1995;72:567–568.
[4] Son S, Dodabalapur A, Lovinger AJ, Galvin ME. Science 1995;269:376–378.
[5] Vanderzande DJ, Issaris AC, Van Der Borght MJ, van Breemen AJ, de Kok MM, Gelan JM. Macromol Symp 1997;125:189–203.
[6] Vanderzande DJ, Issaris AC, Van Der Borght MJ, van Breemen AJ, de Kok MM, Gelan JM. Polym Preprints 1997;38(1):321–322.
[7] Louwet F, Vanderzande D, Gelan J. Synth Met 1992;52:125–130.
[8] Lahti PM, Modarelli DA, Denton III FR, Lenz RW, Karasz FE. J Am Chem Soc 1988;110:7258–7259.
[9] Garay R, Lenz RW. Makromol Chem 1989;5(Suppl.):1–7.
[10] Cho BR, Han MS, Suh YS, Oh KJ, Jeon SJ. J Chem Soc, Chem Commun 1993:564–566.
[11] Denton III FR, Lahti PM, Karasz FE. J Pol Sci A: Pol Chem 1992;30:2223–2231.
[12] Li I, Howell BA. Polym Preprints 1996;37(2):517–518.
[13] Hsieh BR, Yu Y, VanLaeken AC, Lee H. Macromolecules 1997;30:8094–8095.
[14] Hsieh BR, Yu Y, Forsythe EW, Schaaf GM, Feld WA. J Am Chem Soc 1998;120:231–232.
[15] Yu Y, VanLaeken AC, Lee H, Hsieh BR. Polym Preprints 1998;1:161–162.
[16] Hsieh BR, Wan WC, Yu Y, Gao Y, Goodwin TE, Gonzalez SA, Feld WA. Macromolecules 1998;31:631–636.
[17] Cho BR, Kim YK, Han MS. Macromolecules 1998;31:2098–2106.
[18] Issaris A, Vanderzande D, Gelan J. Polymer 1997;38(10):2571–2574.
[19] Issaris A, Vanderzande D, Adriaensens P, Gelan J. Macromolecules 1998;31(14):4426–4431.
[20] Louwet F, Vanderzande D, Gelan J. Synth Met 1995;69:509–510.
[21] Pearson JM, Six HA, Williams DJ, Levy M. J Am Chem Soc 1971;93(20):5034–5035.
[22] Williams DH, Fleming I. Spectroscopic methods in organic chemistry. 4. New York: McGraw-Hill, 1989 p. 26.