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Polymerization of a *p*-quinodimethane derivative to a precursor of poly(*p*-phenylene vinylene)—indications for a free radical mechanism

A. Issaris, D. Vanderzande* and J. Gelan

Laboratory for Organic and Polymer Chemistry, Limburg University, Institute for Material Research, Division Chemistry, Universitaire Campus, B-3590 Diepenbeek, Belgium
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A new synthetic route to high molecular weight poly(*p*-phenylene vinylene) derivatives—via a *p*-quinodimethane intermediate—has been investigated. Whether the polymerization is ionic or free radical has been under discussion for a long time. Strong indications for a self-initiating free radical mechanism for the polymerization are presented. © 1997 Elsevier Science Ltd.

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Introduction

Because highly conjugated polymers are mostly insoluble and infusible, their major problem regards applications is the difficulty in processing them. A possibility for avoiding this problem is working with precursor polymers, which can be transformed into the conjugated polymer. The Wessling precursor route[1] is the best known route for preparing poly(*p*-phenylene vinylene) (PPV) and derivatives, in which bis(sulfonium halide) salts of *p*-xylene are treated with an alkali base in water. Whether this polymerization is ionic or free radical has been under discussion for several years[1–3]. Molecular weight and molecular weight distribution determinations of the ionic precursor are very difficult due to irreversible interactions between the precursor and the gel permeation chromatography (g.p.c.) columns[3]. Another disadvantage is the instability of this precursor polymer: the sulfonium groups are good leaving groups, which results in unfavourable substitutions by the solvent and the counter ion.

Recently, our research group[4–6] has established a generalized novel route to non-ionic precursor polymers which are at ambient temperature and soluble in organic solvents. Because of the latter, characterization of the polymer and the determination of molecular weight and molecular weight distribution can be performed in a straightforward way. This opens new perspectives on the study of the reaction mechanism.

In this communication, we report indications for a free radical mechanism for the polymerization of 1-sulfinyl substituted *p*-quinodimethane systems.

Results and discussion

In a previous paper[4] we presented a general scheme for the base induced polymerization of α,α'-functionalized *p*-xylene derivatives. Two requirements have to be fulfilled (*Figure 1*): (i) in the α-position of the *p*-xylene premonomer (**1**) a polarizer is necessary, which can stabilize the anion (**2**) formed in the first step of the process; and (ii) a leaving group is needed in the

α'-position to obtain the *p*-quinodimethane intermediate (**3**), which is the actual monomer of the polymerization. The quinoid structure (**3**) will polymerize into the precursor polymer (**4**), which, in a next step, can be converted—depending on the polarizer—into the conjugated polymer (**5**) by thermal treatment.

We have already shown[4] that the polymerization described above, with a sulfone group instead of sulfoxide group as polarizer in tetrahydrofuran (THF) as medium, resulted in low molecular weight polymers (oligomers). This was probably due to precipitation of the polymer. However, when the solvent was changed into a more polar aprotic solvent [N,N-dimethylformamide (DMF) or 1-methyl-2-pyrrolidinone], the molecular weight increased significantly ($M_w = 3 \times 10^6$, according to g.p.c. measurements using polystyrene standards); g.p.c. indicates a bimodal molecular weight distribution.

First, we report the polymerization of α-chloro-α'-sulfinyl-*p*-xylene via this generalized route in polar protic solvents like *N*-methylformamide (MMF) at 20°C resulting in a *monomodal* molecular weight distribution (*Figure 2*). As a result of the low pK_s of MMF (autoprotolyseconstant $K_s = 10^{-10.5}$)[7] the base we use (sodium t-butoxide) will dissociate and form t-butanol and the MMF anion. The latter will act as the actual base, finally resulting in the quinoid structure (**3**) (*Figure 1*).

In this generalized route one should make a clear distinction between the two parts in the process (*Figure 1*, I and II): first, the formation of the *p*-quinodimethane system (**3**) and secondly the polymerization itself. However, in practice, it is difficult to investigate these two steps separately because the *p*-quinodimethane system (**3**) is not stable; thus cannot be isolated. So, it is not possible to distinguish between effects on the quinoid formation and effects on the polymerization itself.

Investigating the mechanism of the polymerization of the *p*-quinodimethane derivatives, we found several indications for a free radical mechanism and against an anionic mechanism, based on the following experiments.

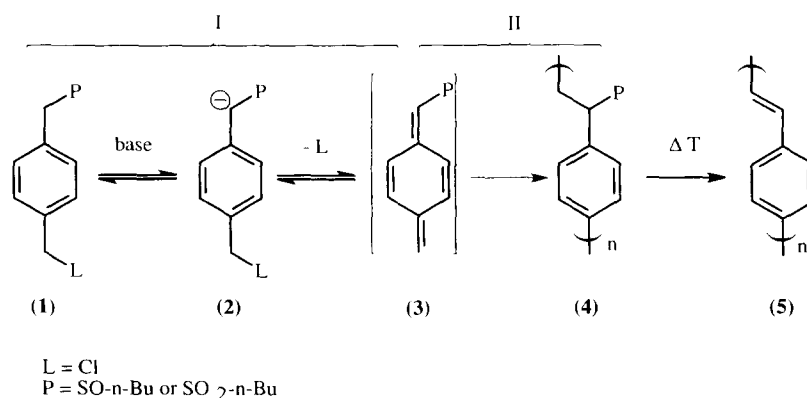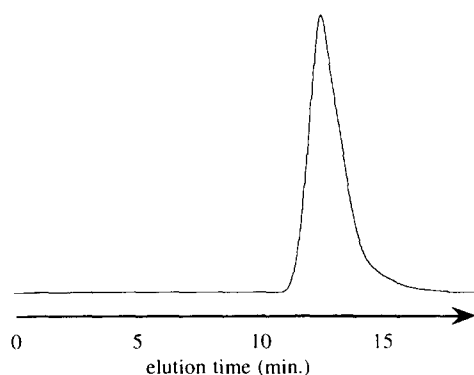---

* To whom correspondence should be addressed

L = Cl
P = SO-n-Bu or SO $_2$-n-Bu

Figure 1 General scheme of the polymerization reaction

Figure 2 G.p.c. chromatogram of the polymerization of (1) in MMF at 20°C with Na t-BuO during 1 h (M_w = 800 000; yield = 25%)

Table 1 Polymer characteristics for the polymerization in polar protic medium

Polymerization medium	$\bar{M}_p{}^a$	Yield (%)	M_w/M_n
N-Methylformamide	803 000	26	2.7
N-Methylformamide + 10% water	502 000	21	3.2

^{a} The polymerization took place at 20°C under nitrogen atmosphere with sodium t-butoxide as base. The polymer was precipitated in diethyl ether and the yield was calculated against the equivalents of monomer. The g.p.c. measurements were made against polystyrene standards at 70°C with flow rates of 1.0 ml min^{-1} in DMF

Table 2 Polymer characteristics for the polymerization in the presence of a radical trapper

Amount of radical trapper (equiv)	$\bar{M}_p{}^a$	Yield (%)
0.0	1 400 000	24
0.01 TEMPO	400 000	10
0.1 TEMPO	200 000	<1
0.5 TEMPO	No polymer	
0.05 DPPH	1 733 000	<1
0.15 DPPH	444 000	<1

^{a} See footnote to Table 1

It is known from the literature[8] that for an anionic polymerization any moisture present in the reaction mixture definitely terminates propagating carbanions by proton transfer. Water has an especially negative effect on an anionic polymerization, since it is an active chain-transfer agent. In general, most anionic polymerizations are carried out in an inert atmosphere in an aprotic solvent like dioxane, THF, etc.

Nevertheless, in our case the polymerization is carried out in a polar protic solvent (MMF) and even an addition of a large amount of water (10%) had a rather small effect on the polymerization (*Table 1*). This implies that the polymerization of α-leaving group α'-polarizer p-xylene (1) cannot be anionic.

The addition of known radical scavengers such as DPPH (2,2-diphenylpicrylhydrazyl) and TEMPO (2,2,6,6-tetramethylpiperidinooxy) to a polymerizing system will stop polymerization if it is a radical reaction. Ionic polymerizations will be unaffected by such additions.

Adding TEMPO and DPPH as a radical trapper to the reaction system in different amounts leads to the results depicted in *Table 2*. Both experiments show that these effective radical trappers almost stop the polymerization reaction, which indicates the radical character of the polymerization of the p-quinodimethane system (3).

As depicted in *Table 2*, the addition of 0.5 equiv TEMPO stops the polymerization completely. The residual reaction mixture was thoroughly investigated by means of nuclear magnetic resonance, mass spectrometry and infra-red spectroscopy. The mixture consisted of three products from which one could be identified as unreacted monomer. The two other components (a) and (b) seem to be very interesting (*Figure 3*).

Component (a) is formed via a side reaction of the polymerization. The quinoid structure (3) (*Figure 1*) is attacked by the solvent, resulting in a substitution of the leaving group by the solvent. The resulting product (a) will not form a quinoid system under these circumstances, so
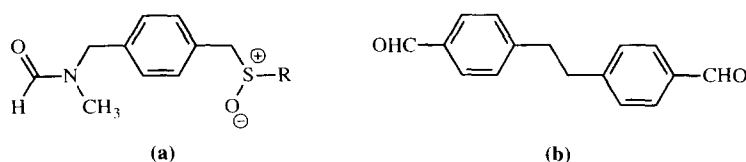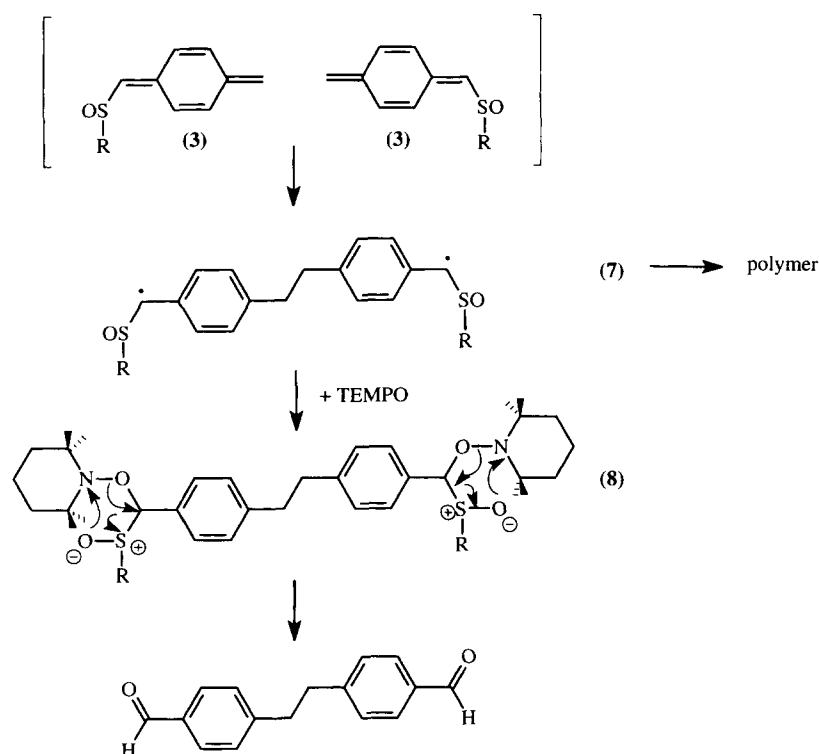

Figure 3 Residual reaction mixture

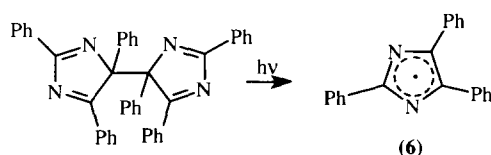**Figure 4** Proposed mechanism of the formation of the dialdehyde

Figure 5 Formation of the 2,4,5-triphenylimidazole radical

Table 3 Polymer characteristics for the polymerization in the presence of initiator (6)

Amount of (6) (%)	$\bar{M}_p{}^a$	Yield (%)	M_w/M_n
1	1052000	23	3.4
10	217000	19	3.3
20	144000	18	2.4

^{a} See footnote to Table 1

Table 4 Polymer characteristics for the polymerization in the presence of transfer agent

Polymerization conditions	$\bar{M}_p{}^a$	Yield (%)	M_w/M_n
Standard polymerization	772000	25	2.9
+0.5 equiv (against monomer) CBr_4	216000	30	2.2

^{a} See footnote to Table 1

is not able to participate in the polymerization. As a result the polymer yield will decrease.

Compound (b) tells us a lot about the character of the polymerization. This dialdehyde can be formed (*Figure 4*) only by the coupling of two quinoid structures (3). The resulting biradical (7) will react with TEMPO when this trapper is added. The formed dinitroxide (8) is not stable and will lead to the depicted dialdehyde (*Figure 4*). The formation of this product can be explained by the rearrangement shown in *Figure 4*, though hydrolysis of (8) as a possible pathway cannot be excluded. The identified dialdehyde leads us immediately to the proposed initiating particle (7)—a biradical intermediate—of the polymerization of the *p*-xylylene derivative, providing us with strong evidence for the radical character of the polymerization of the *p*-quinodimethane derivative to a precursor of PPV.

Li *et al.*[9] also identified a dinitroxide pyrolysing *p*-cyclophane at 600°C and condensing the resulting *p*-xylylene vapour in toluene/TEMPO solution at −78°C. Upon warming the solution up, the dinitroxide was formed.

Photo-initiation occurs when radicals are produced by ultraviolet or visible light irradiation of a reaction system. When 2,4,5-triphenylimidazole dimer[10] is irradiated, relatively stable radicals are formed (6) (*Figure 5*). These radicals are able to alter the molecular weight of the precursor polymer (4) (*Table 3*). This

indicates again the radical character of the polymerization. The addition of the 2,4,5-triphenylimidazole dimer possibly causes additional initiation, which results in lower molecular weights. Another explanation for the decrease in molecular weight is the termination of the propagating chain by the stable radical (6).

Carbon tetrabromide is generally known as an excellent transfer agent for radical polymerizations because of the weak C–Br bond[8]. The addition of this agent results in a decrease in the molecular weight of the formed precursor polymer, consistent with the radical character of the polymerization reaction (*Table 4*). The polymerization yield did not really change under these circumstances.

Conclusions

In conclusion, the fact that the studied polymerization can occur in a protic medium, and the possibility of altering the molecular weight of the polymers by adding

transfer agents or suppressing the polymer formation by radical trappers, gives us strong arguments for the radical character of the polymerization. Additionally we could identify the initiating particle of the polymerization, strongly suggesting the self-initiation of the system.

Knowing the mechanism of the base-induced polymerization of the p-xylene derivative to the precursor of PPV, new methods to control the process are at hand. For example, transfer agents lead to the possibility of varying in a simple way the molecular weight of the precursor polymer and consequently the molecular weight of the conjugated polymer.

Denton et al.[3] did analogous studies on the Wessling Soluble Precursor Method[1]. They saw the effect of radical trappers on the Wessling polymerization and they therefore suggested a radical chain propagation sequence for the Wessling route. If the p-quinodimethane system is a common intermediate in their and our precursor routes, we propose that, in general, the polymerizations of these systems occur via a self-initiated radical chain mechanism.

Acknowledgements

References

1. Wessling, R. A., *J. Polym. Sci., Polym. Symp.*, 1985, **72**, 55.
2. Lahti, P. M., Modarelli, D. A., Denton, F. R., III, Lenz, R. W. and Karasz, F. E., *J. Am. Chem. Soc.*, 1988, **110**, 7258.
3. Denton, F. R., III, Lahti, P. M. and Karasz, F. E., *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 2223.
4. Louwet, F., Vanderzande, D., Gelan, J. and Mullens, J., *Macromolecules*, 1995, **28**, 1330.
5. Louwet, F., Vanderzande, D. and Gelan, J., *Synth. Met.*, 1992, **52**, 125.
6. Louwet, F., Vanderzande, D. and Gelan, J., *Synth. Met.*, 1995, **69**, 509.
7. Reichardt, C., *Solvents and Solvent Effects in Organic Chemistry*, 2nd edn. VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1990, p. 408.
8. Odian, G., *Principles of Polymerization*, 3rd edn. Wiley-Interscience, New York, 1991, p. 224.
9. Li, I., Howell, B. A., Koster, R. and Priddy, D. B., *Polym. Preprints*, 1996, **37**, 2, 517.
10. Harwood, L. M. and Moody, C. J., *Experimental Organic Chemistry (Principles & Practice)*, 1st edn. Blackwell, Oxford. 1989, p. 699.