KINETIC MODELLING OF THE FORMATION AND POLYMERIZATION OF PARA-QUINODIMETHANE DERIVATIVES FOR THE SYNTHESIS OF POLY(PARA-PHENYLENE VINYLENE) PRECURSORS

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Summary

An intrinsic kinetic model is developed to describe the synthesis of poly(para-phenylene vinylenes) (PPV) homo- and copolymer precursors. In the sulfinyl precursor route, the competition between the anionic and radical initiation is modeled as a function of reaction time and concentrations of premonomer and base. The competition between byproduct formation and radical polymerization was analyzed in terms of elementary reaction rates. In the dithiocarbamate precursor route, the copolymer composition is modeled accounting for the sterical hindrance of the base. The model describes the dependence of the copolymer composition on the monomer formation from the premonomer and on the (cross-)propagation.

Keywords

Novel functional materials, materials for energy applications, high value-added products, free radical polymerization, poly(para-phenylene vinylenes)

Introduction

Since the manufacturing [1] of a Light Emitting Diode (LED) with poly(para-phenylene vinylenes) (PPV) layers as the active material, interest for conjugated polymers is growing. PPVs are now used in solar cells, LEDs, Thin Film Transistors (TFT), Field Effect Transistors (FET) and biosensors. Despite the large potential of these materials and a pressing need for tuned polymer properties, available kinetic models[2, 3] are scarce.

Reaction scheme

A base solution is mixed with a para-xylene derivate solution, forming the actual monomer (a para-quinodimethane derivate) via a base induced 1,6-elimination.
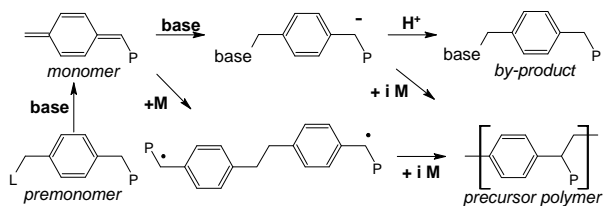

Figure 1: L = leaving group = Cl (sulfinyl) or R$_2$NC(S)S (dithiocarbamate), P = polarizer = SOC$_8$ (sulfinyl) or R$_2$NC(S)S (dithiocarbamate), M = monomer.

The monomer can either dimerize and form a biradical initiator[4] or can undergo a nucleophilic addition reaction with the base forming an anionic initiator. The radical initiator can propagate and form macrobiradicals, occasionally recombining to form longer macrobiradicals[5]. Depending on the proton activity, the anionic initiator can propagate or terminate via proton transfer forming an ether byproduct. In general, the precursor polymer can be formed via two distinct polymerization mechanisms.

Methodology

Rate equations were derived based on the elementary reactions. A semi-batch model was used to describe the time needed to feed the base. The resulting model equations were solved via the method of moments.

Results and discussion

Homopolymerization (sulfinyl route)

Characteristic of the sulfinyl[4] route is a chemical differentiation between the leaving group L and the polarizer P of the premonomer (Fig. 1). Only one benzylic hydrogen of the premonomer is acidic, leading to a single monomer type. At low premonomer concentrations, the monomer is consumed via anionic initiation and terminated before propagation occurs. This can be tracked by UV-vis spectroscopy. The time at which the absorbance of the solution is maximal (see Fig. 2) serves as a comparison with the simulated concentration profiles.

The rate of anionic initiation (first order in monomer concentration) greatly exceeds the rate of monomer dimerization (second order in monomer concentration). At higher premonomer concentrations, the picture radically changes: dimerization of monomers occurs in competition with the ether byproduct formation. A fast radical polymerization takes place (Fig. 3). Both experimental and simulation data show a maximum in final polymerization yield with increasing base concentration (in sBuOH), caused by an increase in the rate of formation of the byproduct (Fig. 4).
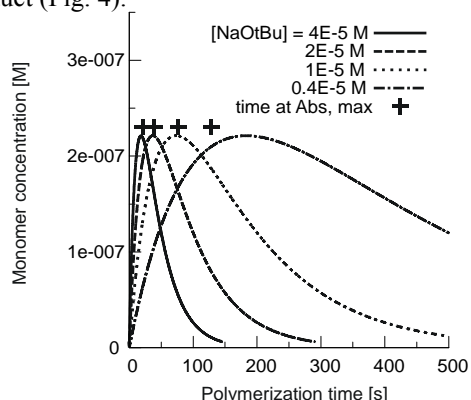

Figure 2: Monomer concentration as a function of reaction time, [premonomer] = 1E-6M, parameter = base concentration. Solvent = sBuOH.
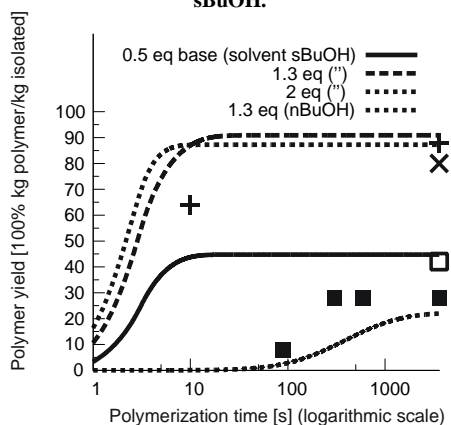

Figure 3: Polymer yield as a function of reaction time, [premonomer] = 0.2M, parameter = base concentration. Solvent = sBuOH and nBuOH.
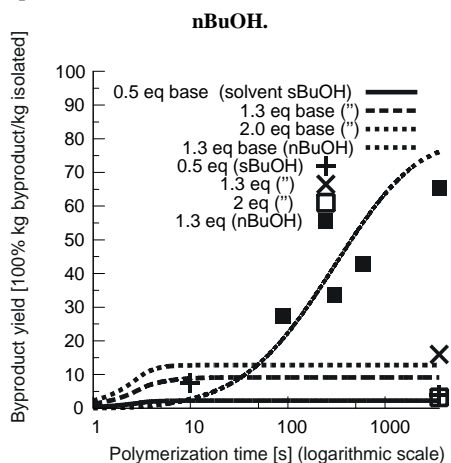

Figure 4: Byproduct yield as a function of reaction time, [premonomer] = 0.2M, parameter = base concentration. Solvent = sBuOH and nBuOH.

Copolymerization (dithiocarbamate route)

In the dithiocarbamate[6] route both the leaving group L and the polarizer P are chemically identical. In contrast to the sulfinyl route, where only one benzylic hydrogen is acidic and homopolymerization occurs, the two types of benzylic hydrogens are acidic resulting in two isomeric monomers and thus leading to the occurrence of copolymerization. The composition of the resulting copolymer can be determined by ^{1}H NMR, where 4 types of triads can be distinguished[6]. The triad composition of the copolymer was modeled by accounting for 10 macrobiradical types and their propagation reactions. Depending on sterical hindrance of the base used, one type of benzylic proton can be abstracted preferentially. This leads to one monomer type being more abundant.

Triad type	Exp. 1 LHMDS	Sim. 1 $k_A=3k_B$	Exp. 2 KOtBu	Sim. 2 $k_A=k_B$
A	20	18.75	22	25
B	17	18.75	25	25
C	47	43.75	27	25
D	16	18.75	26	25

Table 1: ^{1}H NMR determined abundance of triads for two different bases[6], compared with simulation results.

Assuming all (cross-)propagation coefficients to be equal, we found that ratios of 1,6-elimination reaction rates (k_A/k_B) equal to 1 and 3 described the NMR data (See Table 1). Tuning regioregularity is interesting for designing specific morphology in (blends of) polymeric materials.

Conclusions and acknowledgements

The competition between radical and anionic initiation mechanisms was modeled for synthesis of PPV precursors, taking into account the molecular structure of the premonomer, leading to either homo- or copolymerization.

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