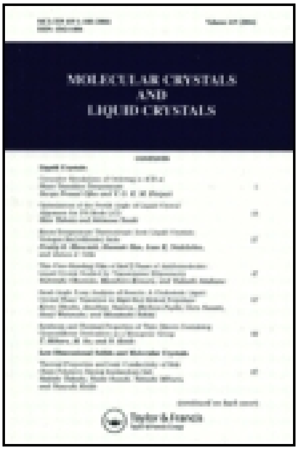

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: D. Albagli , G. Bazan , R. R. Schrock & M. S. Wrighton (1992): Electrochemistry of Well-Defined Redox Active Block Polymers Prepared by Ring-Opening Metathesis Polymerization, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 216:1, 123-128

To link to this article: http://dx.doi.org/10.1080/10587259208028760

Mol. Cryst. Liq. Cryst. 1992, Vol. 216, pp. 123–128
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Printed in the United States of America

ELECTROCHEMISTRY OF WELL-DEFINED REDOX ACTIVE BLOCK POLYMERS PREPARED BY RING-OPENING METATHESIS POLYMERIZATION

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Abstract The preparation and electrochemistry of well-defined redox active polymers and block polymers is presented. Polymers were prepared in a living polymerization by ring-opening metathesis of norbornene derivatives using Mo alkylidene compounds as the catalyst. Redox active monomers were synthesized and used to prepare a series of polymers and block polymers. The polymers were characterized by NMR, GPC, and DSC. The solution electrochemistry was studied by cyclic voltammetry and normal pulse voltammetry. Unique redox molecules could be incorporated at the starting end or the terminating end group, or at both. Putting a redox group into the starting end group required synthesis of the appropriate Mo alkylidene compound. This unique redox group serves as an internal standard of redox equivalents. The average composition of these redox active polymers could be determined by electrochemical techniques, confirming the integrity of and the control over the polymerization process.

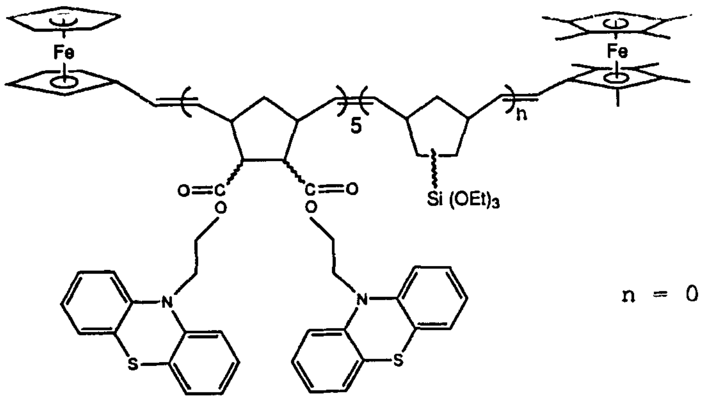
INTRODUCTION

Studies of electroactive polymers have focused more on the electrochemical properties than on polymer structure. But the ability to control the structure of an electroactive polymer, such as the sequence of subunits or the conformation and morphology, may offer a means to improve or tailor the desired electrochemical behavior. Such a high level of control over the structure is not practically attained with traditional polymerization methods. With living polymerization techniques however one has the ability to control the length and nature of blocks and to introduce unique end groups, while producing a polymer that has a low polydispersity. Ring-opening metathesis polymerization (ROMP) was used as the living polymerization method to prepare a series of such well-defined multifunctional redox active polymers based on ferrocene and phenothiazine. We wish to present the electrochemical behavior of these redox active polymers prepared by ROMP to demonstrate the control over the polymer structure afforded by this synthetic approach.

RESULTS AND DISCUSSION

The polymers were prepared by ring-opening metathesis polymerization of norbornene derivatives using an initiator of the type Mo(=CR)(NAr)(O-t-Bu)$_2$.[1] Such Mo compounds have been shown to catalyze living polymerizations in a well-behaved manner. Further, these Mo compounds are tolerant of a wide range of functional groups. To make polymers with a redox active starting end group, the Mo compound with R=ferrocenyl was prepared by a metathesis reaction between vinyl ferrocene and the Mo compound where R=t-butyl.[2] Using Mo(=C(ferrocenyl)) to initiate polymerization yields polymers with a unique ferrocenyl end group. At the other end, the living polymerization is terminated in a Wittig-like reaction between an aldehyde and the living chain.

To demonstrate the control over the primary structure that can be achieved using this system, as applied to the preparation of redox-active polymers, the following were made:



n = 0,2

The polymers will be abbreviated as Fc-$(Phz)_5$-OMFc and Fc-$(Phz)_5$-$(Si)_2$-OMFc. Also, Fc-$(Phz)_5$-t-Bu was prepared using pivaldehyde in the termination reaction. The subscripts indicate the number of equivalents of monomer relative to the amount of initiator. All three polymers were made from the same living intermediate. The batch was divided into three parts after formation of the phenothiazine block, Fc-(Phz)~. Two were capped immediately, and to the third a new monomer, triethoxysilylnorbornene, was added to produce the block polymer, and then capped. Short polymers were made so that the end groups are clearly evident in the electrochemistry.

The homopolymers were characterized by GPC and DSC, the block polymer was not because of the reactivity of the alkoxysilyl group. The polydispersity index determined was 1.22, quite good for such a short chain length. Longer polymers prepared with this monomer have lower PDI values of ~1.10. The average molecular weight determined by GPC shows the polymer composition is roughly consistent with that expected, but differences between the flow properties of the sample and the calibrant prevent a more quantitative assessment. DSC shows that this material has a glass transition, T_g=81°C. This is only 7°C lower than the limiting T_g found for such homopolymers.[2] ^{1}H NMR spectra of the three polymers show the presence of the expected functional groups, but because of peak overlap the integrals can not be used to establish the composition.

Electrochemical experiments both resolve the various portions of the polymer, and permit a more quantitative analysis of the polymer composition. A cyclic voltammogram of Fc-$(Phz)_5$-OMFc is shown in Figure 1. Three separate waves are observed at +0.05 V (octamethylferrocenyl), +0.40 (ferrocenyl) and +0.75 V (phenothiazine). The redox waves observed for the end groups are characteristic of one-electron, reversible, solution couples. Comparison of the peak currents in each of these waves shows the ratio of initiator end group to terminator end group is ~1.06. The redox wave for phenothiazine, marked by the reductive spike,

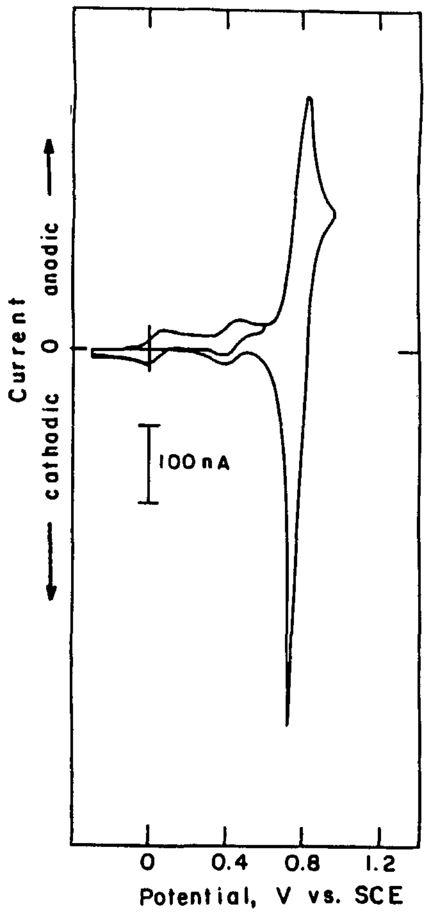


FIGURE 1. Cyclic voltammograms of Fc-(Phz)$_5$-OMFc in CH_2Cl_2/0.1 M [n-Bu_4N]AsF_6, 50 mV/s, at a 500 mm Pt disk electrode. In the first cycle the potential sweep was reversed at +0.50 V, and in the second cycle at 1.00 V.

indicates that upon oxidation some material is deposited on the electrode surface but then the accumulated polymer is reductively desorbed. In separate experiments, it was found that repetitive cycling does not lead to deposition on the electrode. Thus the polymer is completely desorbed upon reduction, probably owing to the small size of the polymer.

For this reason normal pulse voltammetry could be used to overcome the problems of oxidative deposition and allow a more quantitative study.[3] The ratio of the limiting currents for each couple indicates the ratio of the redox components. The ratios found were 1.0:1.08:10.4 for Fc-(Phz)$_5$-OMFc, and 1.0:10.2 for Fc-(Phz)$_5$-t-Bu. The NPV results establish that the average composition of the polymer is the same as the stoichiometry of the reagents used in the synthesis.

The triethoxysilyl groups in the block polymer enable the covalent attachment of the polymer to an appropriately pretreated electrode surface.[4] Only two equivalents of the monomer were added so as to try to maximize the number of polymer chains that had access to bond to the electrode by keeping the number of siloxane bonds per chain to a minimum. However, adding only two equivalents means some chains will not acquire an (Si) block. The polymers mentioned above strictly lacking a (Si) block though, act as a control to clearly illustrate the effect of this block. Figure 2 shows the scan rate dependence for the cyclic voltammetry of a Pt electrode soaked in a solution of Fc-(Phz)$_5$(Si)$_2$-OMFc for 14 h. Whereas the analogous polymer lacking the (Si) block did not persistently adhere to the electrode, the voltammograms observed here have waveshapes characteristic of a surface bound redox couple, and are persistent, indicating that the (Si) block was successfully incorporated into the polymer and covalently linked the polymer to the electrode.

SUMMARY

Ring opening metathesis polymerization using Mo(=CR)(NAr)(O-t-Bu)$_2$ type initiators can be used to prepare redox active polymers with as well defined a primary structure as can be expected. Normal pulse voltammetry quantitatively shows the result of the polymerization process through the redox activity of the unique redox groups in each of components; initiator end group, backbone, and terminator end group. Incorporating alkoxysilyl groups in a block in the polymer

determines a unique point of covalent attachment within the polymer to the electrode surface.

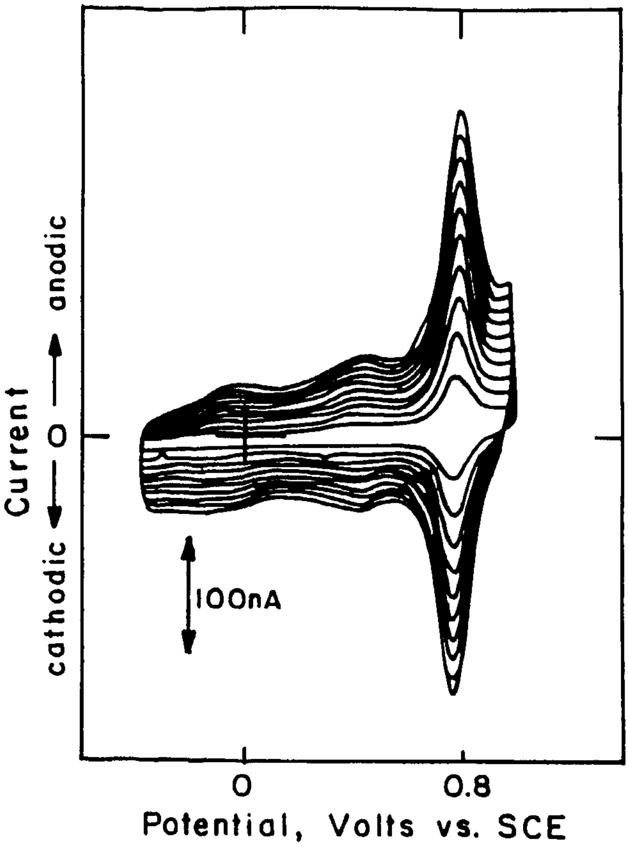


FIGURE 2. Scan rate dependence of the cyclic voltammetry for a Pt electrode derivatized with Fc-(Phz)$_5$(Si)$_2$-OMFc, in CH_2Cl_2/0.1 M [n-Bu_4N]PF_6 from 100 to 1000 mV/s in 100 mV/s increments. The coverage of phenothiazine groups is 3 x 10^{-10} mol/cm^2 and of the polymer is 3.x 10^{-11} mol/cm^2.

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