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Cationic Polymerization of 1,3-dioxolane Using Sacrificial Anodes

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The electroinitiated polymerization of 1,3-dioxolane is carried out with metallic cationic initiators generated electrochemically V, Hg, Cr, Al

Key Words: Electrochemical polymerization, Electrolyse, Conductivity.

INTRODUCTION

The electrolysis of 1,3-dioxolane in solution in a dioxane medium containing lithium perchlorate leads to the formation of a polymer[1]. The potential difference in bounds of the two electrodes is huge, 510 V for a current of about 50 μA. This polymer develops only in the anodic compartment (R = 50%); there is an induction period during which electrolysis stops inducing a break of polymerization. Then, this can continue even without flow of current; it seems that the monomer is oxidized when the reaction takes place in dichloroethane[2]. Polymerization starts with the electrolysis but reaches an equilibrium that depends on the past charge, on temperature and on the monomer concentration. Polymerization of 1,3-dioxolane can also be driven in a pure environment containing one electrolyte such as $LiAsF_6$,[3] then one gets a conductor polymer containing lithium ion, probably by oxidization of dioxolane. We undertook a study of the polymerization of this monomer first because it polymerizes in a cationic way as we have reported, then because the gotten polymer can be used in replacement of the poly(ethylene oxide) (PEO) in systems of all solid energy storage such as the one made by the set lithium/electrolyte conductor polymer by Li^+/insert compound. The poly (dioxolane) waited of formula $(—CH_2CH_2OCH_2O—)_n$ contains indeed the C—C—O sequence of the PEO and can therefore complex the alkaline cations.

EXPERIMENTAL

The electrochemical apparatus has been described recently[4]. All the electrolyses are carried out in a cell with three compartments separated by fritted glass.

The reference electrode SCE (saturated calomel electrode) is connected to the

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cell by a bridge containing the organic electrolytic solution. The residual concentration of metals in the polymers was determined by arc excitation emission spectrography and the infrared spectra were recorded on a Perkin-Elmer 1600 FTIR.

Metals were supplied by Alpha Products, Karlsruhe, Germany. The purities are as follows: Al: 99.99%; V: 99.7%; Cr: 99.99%; Hg: 99.99%. Anodes were chemically polished before each electrolysis, according to Tegart[5].

Supporting electrolyte: The $(n\text{-Bu})_4NClO_4$ is obtained from reaction of $(nBu)_4NBr$ (Fluka) and $HClO_4$ (Prolabo). The precipitate was recrystallized in water until bromide or hydroxide ion was no more detected and then dried at 80°C under reduced pressure.

The purification of dichloromethane and nitromethane has been described previously[4]. 2,6-Di-*tert*-butyl-4-methylpyridine (DTBMP) was purified by sublimation under reduced pressure at 40°C. Monomer: 1,3-dioxolane (Fluka purum) was distilled over CaH_2.

Molecular weight determination

Molecular weights were determined using high-pressure liquid chromatography (HPLC Waters 590 equipped with a differential refractometer Waters 410, using three Styragel columns of length = 30 cm, diameter = 0.78 cm) of nominal pore widths 50, 1000 and 10000 Å and tetrahydrofuran (THF) as eluant. Calibration curves are based on polystyrene standards.

RESULTS AND DISCUSSION

The oxidation potentials of the metals are measured by recording a voltamperometric curve I(E), on a piece of material dipped in nitromethane containing M/10 $(nBu)_4NClO_4$ as supporting electrolyte. All the metals are oxidizable at a potential below 1.4 V[6–7] (against standard calomel electrode) except titanium, but it is known that this material is quickly covered with a protective, but not conductive, oxide layer, then imposing a potential of less than 1.4 V leads to the dissolution of the anode alone with the formation of metallic cations. Indeed this value is too low. The oxidation of 1,3-dioxolane or of the anion of the supporting electrolyte is shown by the I(E) curves (Fig. 1, Table-1).

TABLE-1
OXIDIZATION POTENTIAL IN V/SCE OF ANODES IN NITROMETHANE AND DICHLOROMETHANE, CONTAINING 0.1 M $(n\text{-Bu})_4NClO_4$

Anode	Hg	Al	V	Cr
CH_3NO_2	0.8	0.2	0.95	1.3
CH_2Cl_2	0.9	0.2	0.9	1.1

Electroinitiated cationic polymerization of 1,3-Dioxolane

This work was limited to the study of the cation initiator influence while keeping tetrabutylammonium perchlorate as electrolyte support. Materials of Cr,

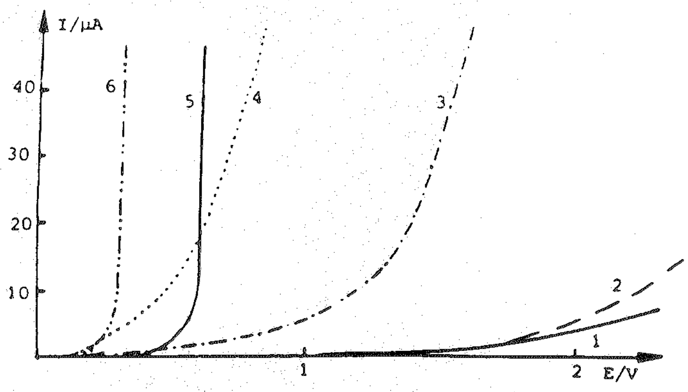

Fig. 1. Electrochemical behaviour of 1,3-dioxolane (concentration 10^{-2} M) on Pt (10 rps) and of metals in nitromethane containing 0.1 $M(nBu)_4NClO_4$: (1) residual current; (2) 1,3-dioxolane; (3) chromium; (4) vanadium; (5) mercury; (6) aluminum

Hg, Al and V anodes have been tested in nitromethane and dichloromethane medium. We note a few differences in the final results, whether monomer is added since the beginning of the electrolysis or at the end of this one, when the initiator cations have been generated. When the electrolysis is driven in solvent medium, we notice that polymerization appears during the first hour that follows the end of the flow of current.

The solution warms up and becomes more viscous, and then small white spots (heap of polymer) propagate progressively in the cell. As dioxolane makes the used salt supports soluble, we also achieve electrolyses in monomer medium; in these conditions the polymer fills the cell out. The gotten results are shown in Table-2.

TABLE-2
ELECTROCHEMICAL POLYMERIZATION OF 1,3-DIOXOLANE. INFLUENCE OF METAL AND SOLVENT. POLYMER ISOLATED WITHOUT ADDITION OF SODIUM ÉTHANOLATE. [dioxolane] = 4,77 M; t = 20°C; SUPPORTING ELECTROLYTE: $(n\text{-Bu})_4NClO_4$.

Anode	Solvent	[Initiator] × 10^2 M	V/SCE	Polymer yield (%)	M_w	M_n	$I = M_w/M_n$
Al	CH_3NO_2	1.60	1.0	18	5400	4060	1.32
Hg	CH_3NO_2	1.20	0.8	32	3370	2450	1.37
V	CH_3NO_2	0.17	1.4	15	850	840	1.00
Cr	CH_3NO_2	0.11	1.4	30	5400	4090	1.32
Cr	CH_2Cl_2	0.11	1.4	25	3200	2540	1.26
Al	Without	0.92	1.0	71	8500	5150	1.65
V	Without	0.34	1.4	45	4850	3420	1.41
Hg	Without	1.30	0.8	61	6200	4280	1.44

M_w: Weight-average molecular weight, based on polystyrene standard calibration.
M_n: Number-average molecular weight, based on polystyrene standard calibration.

Polymer weights (2500–5000) are rather lower than those gotten by the chemical way (5000 to 10000 for example with the benzyl hexafluoroantimonate at −15°C). It is the same thing in yields: 30% in solvent medium in our case against 70% chemically.

Without solvent the polymer development is promoted as well as the increase of its molecular weight.

The set of experiments quoted higher had a big defect. We did not add a termination agent before treating the polymer. In the following experiences (Table-3), sodium ethanolate has been added in the medium before extracting the polymer by the method described in Experimental part. One well finds that the polymer is living as show it the best gotten results, that is in agreement with observations of most authors. It is indeed likely that it is the physical treatment that follows the electrolysis (evaporation of solvent) that reduces yields and molecular weights of the polymer.

TABLE-3

ELECTROCHEMICAL POLYMERIZATION OF 1,3-DIOXOLANE; POLYMER ISOLATED AFTER ADDITION OF SODIUM ÉTHANOLATE; INFLUENCE OF THE INITIAL CONCENTRATION OF MONOMER. ANODE Al

t = 20°C; [initiator] = 10^{-2} M; SUPPORTING ELECTROLYTE: $(n\text{-Bu})_4NClO_4$ = 0.1 M

[1,3-Dioxolane]	Polymer yield in %	M_w	M_n	$I = M_w/M_n$
3.57	35	12100	9444	1.28
5.7	54	19250	14010	1.37
7.1	63	21780	11760	1.85
8.6	65	24950	15310	1.62
10.7	60	36850	18880	1.95
14.3	65	50200	27250	1.84

Influence of the initial monomer concentration: Aluminum gave the best results; this metal has been used in the experiment set that clearly shows the role of the initial monomer concentration[8].

The tetrabutylammonium perchlorate remains the salt support. In Table-3 we notice certain homogeneity of yields of the order of 60–65%. The living character of the polymer is clearly shown by the increase of its molecular weight when the monomer concentration grows.

Influence of the anode material: In this test the initiator concentration is constant, what is easily feasible while calculating the quantity of current to pass in the cell. As ClO_4^- was confirmed to be one of the most interesting anions in the case of donor monomers as well as in the case of lactones, we worked in $(n\text{-Bu})_4NClO_4$ M/10 medium (Table-4).

Chromium has a particular behaviour; polymerization is very quickly important: the solution becomes opaque and the current is blocked. It explains why we should have stopped the electrolysis when the concentration of the initiator was only 4×10^{-4} M, that is to say 10 times weaker than for the other experiments. Yields are more, of the order of 60%. We notice that even though the experimental conditions are very neighbors, one can find strong variations of certain characteristics of the polymer. For example, for aluminum the M_w and M_n molecular weights vary from the simple to double, from an experience to the other. In general, molecular weights and yields of the polymer are equivalent to those gotten during the classic chemical polymerization[9]. On the other hand, values that we got are always better than those measured during electrolysis with oxidization of the monomer[2, 3].

TABLE-4

ELECTROCHEMICAL POLYMERIZATION OF 1,3-DIOXOLANE; INFLUENCE OF METAL, WITHOUT SOLVENT; POLYMER ISOLATED AFTER ADDITION OF SODIUM ETHANOLATE; t = 20°C; SUPPORTING ELECTROLYTE: $(n\text{-Bu})_4NClO_4$ 0.1 M

Anode	[Initiator] × 10^3 M	V/SCE	Polymer yield (%)	M_w	M_n	$I = M_w/M_n$
Al	5.50	1.0	52	17400	8390	2.07
Hg	5.50	1.0	59	26040	14550	1.79
V	5.50	1.4	62	23710	13600	1.74
Cr	0.43	1.4	65	11820	5540	2.13
Cr*	0.43	1.4	33	—	—	—

*Electrolysis achieved in presence of DTBMP.

In all experiments the transfer is important. Let us take the case of chromium; one finds $\alpha R = 9.3 \times 10^4$ for a DP = 294. If the electrolysis is driven in presence of the cluttered basis 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), the yield decreases as in each of the experiments already quoted. The gotten polymer is then characterized mainly by a weaker polydispersity index ($I = M_w/M_n$): 1.1 for 1.65 without basis.

Polymer analysis: The NMR spectra of the polymer are identical to those of the monomer:

Monomer: $\delta = 3.8$ ppm (s, 4H), 4.8 ppm (s, 2H).

Polymer: $\delta = 3.7$ ppm (s, 4H), 4.7 ppm (s, 2H).

Polymer study: For a possible use of this polymer as conductor by lithium ion, we measured the conductivity of polymeric electrolyte prepared from our samples. The selected polymer has been prepared by using the vanadium anode ($M_w = 23700$; $M_n = 13600$). The polydioxolane and the lithium salt are dissolved in the acetonitrile, and then a thin disk was made by acetonitrile evaporation. The lithium salt used is the bis(trifluoromethanesulfone) imide lithium, $LiN(CF_3SO_2)_2$, whose weak crystalline energy confers to polymer (to the PEO for example) a plasticizer effect that makes the mixture morphous[10]. The following measures have been achieved for a mixture with a ratio of $O/Li^+ = 12$ (Fig. 2).

At 25°C one finds a conductivity of $77 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$, usual values for this type of polymer. Goulart *et al.*[11] mention conductivities between 10^{-6} and 10^{-5} $\Omega^{-1}\ cm^{-1}$ for this polymer when the O/Li^+ ratio varies from 8 to 16. Alamgir *et al.*[12] give conductivities included between $10^{-6}$and $4.34.3 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ when DOL/Li^+ varies from 4/1 to 16/1.

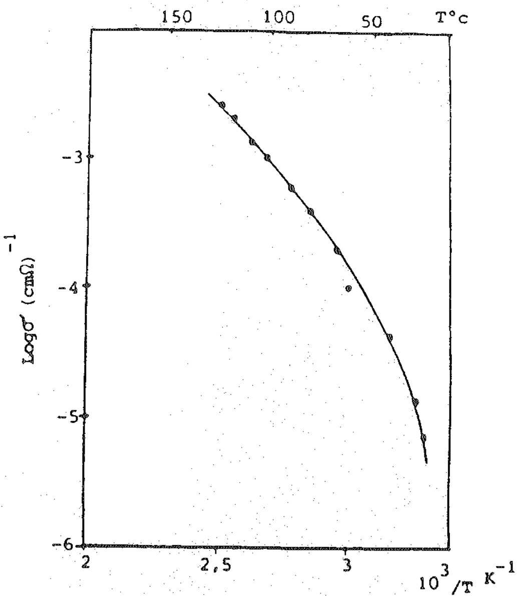

Fig. 2. Conductivity plot of the poly-DOL/LiTFSI system; n = 12 (n: O/Li$^+$ ratio in the polymeric electrolyte)

Conclusion

The gotten polymers are, in general, polydispersed and have weak molecular weight. The polydispersity index is near to 2 and the molecular weights exceed rarely ten thousand but remain within the limits usually quoted for this polymerization type, and without taking precaution to eliminate the water from the medium.

Weights and yields are upper to those gotten by electro-chemical oxidization of the monomer into a cation that act as initiator.

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