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Synthesis of disulfide polymer by electrochemical polymerization of α,ω-alkanedithiols

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Abstract

Electrochemical polymerization of 1,3-propanedithiol (PRDT), 1,4-butanedithiol (BUDT), 1,5-pentanedithiol (PEDT), and 1,10-decanedithiol (DEDT) for synthesizing polymers containing disulfide bonds was investigated. PRDT, BUDT, PEDT and DEDT gave polymers by electrochemical polymerization under high diluted α,ω-alkanedithiols. The polymerization activity was found to depend on the alkyl chain of the α,ω-alkanedithiols. In the electrochemical polymerization of PRDT, the molecular weight of polymer gave a maximum at a supplied current quantum of 1 F/mol. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: α,ω-Alkanedithiol; Electrochemical polymerization; Polymer containing disulfide bond

1. Introduction

The chemistry of thiol–disulfide interchange reaction is very interesting and useful, e.g. thiol and disulfides are very useful cross-linking reagents in rubber chemistry, and the ease with which the disulfide bond can be converted to thiols makes it possible to form reversible polymer systems. Polymers containing disulfide bonds have been synthesized by oxidation of α,ω-dithiols in the presence of oxidation reagents such as iodine and hydrogen peroxides [1] and by ring-opening polymerization of cyclic disulfides [2].

In the ring-opening polymerization of cyclic 1,2-disulfides for synthesizing polymers containing disulfide bonds, α,ω-alkanedithiols were used as a starting material to make cyclic 1,2-disulfides [3,4]. If α,ω-alkanedithiols remain as an impurity in cyclic 1,2-disulfide, they act as a strong chain transfer reagent to suppress drastically the polymerization [5,6]. Moreover, it was pointed out that the cyclic 1,2-disulfides hardly polymerize thermally under a dilute monomer concentration.

Redox polymerization of lithium dithiolate salts as monomers has been reported [7,8]. Aqueous solution of the lithium dithiolate salts was converted to the corresponding disulfide polymers upon oxidation by iodine or tri-iodine species as shown in Scheme 1. Many dithiolate salts were also investigated by this method, but α,ω-alkanedithiols except for ethandithiol were not examined [1].

$$n(\mathrm{Li{-}SRS{-}Li}) + n(\mathrm{LiI_3}) \longrightarrow \left(\mathrm{SRS}\right)_n + 3n(\mathrm{LiI})$$

Scheme 1. Synthesis of polymer containing disulfide bond by redox polymerization (R: alkyl, aromatic, thiazole).

Electrochemical polymerization is likely to be an attractive method to synthesize polymers containing disulfide bonds from direct polymerization of α,ω-dithiols under a highly diluted monomer concentration, and polymerization may provide a reversible polymer system. However, electrochemical polymerization of α,ω-alkanedithiols has not been systematically studied. This paper describes the preliminary results of preparation of polymer containing disulfide bonds from various α,ω-alkanedithiols by electrochemical polymerization.

2. Experimental

2.1. Materials

1,3-propanedithiol (PRDT), 1,4-butanedithiol (BUDT), 1,5-pentanedithiol (PEDT) and 1,10-decanedithiol (DEDT) (Aldrich Chem.) were used after distillation before use. Other reagents and solvents were used after purification by conventional methods.

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2.2. Polymerization procedure

Polymerization was carried out in a single compartment cell in CH_3CN under nitrogen atmosphere at a constant voltage of below 7.0 V at 0°C. The required amount of reagents was charged in the cell by syringes through a rubber septum under nitrogen atmosphere. A Pt-plate was used as an electrode, and tetrabutylammonium perchlorate (Bu_4NClO_4) was used as a supporting electrolyte. After the polymerization, the contents of the cell were poured into a large amount of methanol to isolate the polymer formed. Conversion was estimated from the consumed monomer determined by ^1H NMR spectroscopy. Polymer yields were determined by gravimetry as a methanol insoluble part.

2.3. Electrochemical measurement

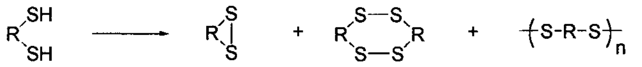
The cyclic voltammogram of PRDT was obtained using a potentiostat combined with a function generator (Type HAB-151, Hokuto Denko Ltd., Japan) and an X–Y recorder (WX-1000, Graphtec Co., Ltd., Japan). The measurement was carried out using a three-electrode cell at 0°C. A two compartment cell divided with a glass filter was used. The electrolyte solution was CH_3CN solution containing 0.15 M Bu_4NClO_4. The electrode assembly consisted of a platinum wires (diameter 0.5 mm, length 5 mm) as the working electrode and the counter electrode, and an $Ag|AgCl|NaCl_{(sat)}$ electrode as the reference electrode.

2.4. Characterization of the polymers

The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the polymer were determined by GPC using THF as an eluent at 38°C calibrated as standard polystyrenes. The structure of polymers was determined from ^1H NMR spectra taken in $CDCl_3$ at 25°C with TMS as an internal standard on a JEOL α-400 NMR spectrometer.

3. Results and discussion

Electrochemical polymerization of α,ω-alkanedithiols was carried out under a high diluted monomer concentration (3.2×10^{-2} mol/l) at 0°C, and the results are summarized in Table 1. The electrochemical polymerization of α,ω-alkanedithiols was found to proceed giving methanol insoluble polymers. Although the conversion of α,ω-alkanedithiols was very high regardless of the monomers examined, the polymer yields depended on the α,ω-alkanedithiols, and PRDT gave high molecular weight polymers. In the electrochemical polymerization of the α,ω-alkanedithiols, it is possible to yield in undesirable low molecular weight products such as cyclic compounds, dimers as shown in Scheme 2 [1]. To clarify this point, GPC measurements of the polymers were performed.



Scheme 2. The products from polymerization of α,ω-alkanedithiols (R: alkyl group).

The GPC elution curves of poly(PRDT) and poly(BUDT) obtained from electrochemical polymerization are shown in Fig. 1. The low molecular weight fraction was not observed for the polymer obtained from PRDT. On the other hand, considerable amounts of low molecular weight products were observed for the polymers obtained from BUDT. A stable 1,2-dithiane as compared with others [9,10] was also observed in the reaction mixture after the electrochemical polymerization of BUDT. Thus, we suppose that the polymer yield may be related to the formation of methanol soluble products. The reason why the electrochemical polymerization of PRDT gave highest M_n is not clear now, but it may be explained by the formation of oligomers. Because PRDT is not easy to form of cyclic 1,2-disulfide and the dimer [9].

The structure of the polymer was analyzed by ^1H NMR spectroscopy. The ^1H NMR spectrum of poly(PRDT) is shown in Fig. 2 as an example, in which the spectrum of PRDT is also indicated to comparison. From the spectrum of poly(PRDT), the peaks based on the methylene proton adjacent disulfide bonds introduced in the main chains by polymerization appeared at 2.12 and 2.81 ppm, respectively, and shifted toward lower field as compared with the corresponding methylene proton of PRDT. Moreover, very small peak

Table 1
The electrolytic polymerization of α,ω-alkanedithiols with the Pt electrode at 0°C (α,ω-alkanedithiol = 3.2×10^{-2} mol/l, [Bu_4NClO_4] = 0.15 mol/l, constant potential = 7 CV, current quantum = 2 F/mol)

Run	Number of carbon chain	Conversion (%)[a]	Polymer yield (%)[b]	$M_n \times 10^{-3}$	M_w/M_n
1	C_3	93	8.5	13.0	2.22
2	C_4	90	0.0	0.2	1.01
3	C_5	89	16.0	7.8	1.86
4	C_{10}	87	30.5	3.5	2.10

[a] Determined by ^1H NMR spectroscopy.

[b] MeOH insoluble part.

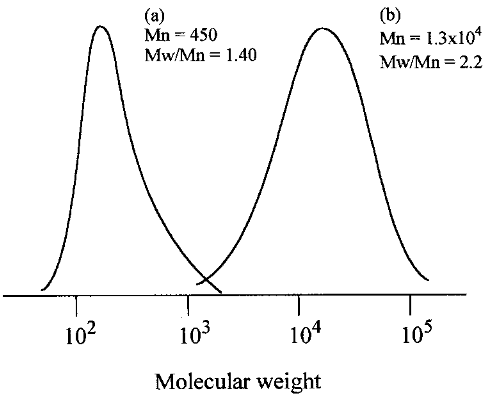
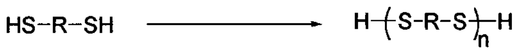


Fig. 1. GPC elution curves for the polymer obtained from electrochemical polymerization of: (a) BUDT; and (b) PRDT.

at 1.38 ppm based on the thiol group still remained in the polymer, suggesting that the resulting polymer has the thiol group at the chain end. The M_n estimated from peak area ratios of proton peaks between the main methylene and thiol group at the chain end nearly coincided with M_n determined from GPC measurement. Similar of other α,ω-alkanedithiols results were obtained in the polymerization. Thus, the electrochemical polymerization of α,ω-alkanedithiols seems to proceed as shown in Scheme 3.



$$\text{HS–R–SH} \longrightarrow \text{H}\!\left(\text{S–R–S}\right)_n\!\text{H}$$

Scheme 3. The electrochemical polymerization of *α,ω*-alkanedithiol (R: *n*-propyl, *n*-pentyl, *n*-dodecyl).

In the electrochemical polymerization of α,ω-alkanedithiols, the thiol groups must make disulfide bonds for producing polymeric materials. This was clarified by the electrochemical reaction of *n*-butanethiol as a model reaction, i.e. the model reaction of *n*-butanethiol gave di(*n*-butane)disulfide in high yield (Scheme 4). Thus, the electrochemical polymerization conditions for α,ω-alkanedithiols were clarified to be suitable for synthesizing disulfide polymers.

Scheme 4. The electrochemical reaction of *n*-butanedithiol as a model reaction.

Since PRDT gave a high molecular weight polymer in electrochemical polymerization, we further carried out the polymerization of PRDT at different current quantum. The results are shown in Fig. 3. The polymer yields increased with an increase of the current quantum. On the other hand, the molecular weight of the poly(PRDT) gave a maximum at current quantum of 1 F/mol, although the M_w/M_n decreased as a function of the current quantum. To elucidate this point, the electrochemical reaction of the poly(PRDT) was conducted under the polymerization conditions. The M_n of the polymer decreased from 9400 to 5000 with electrolytic reaction of the poly(PRDT).

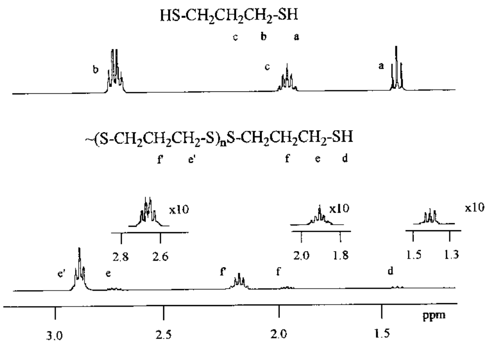


Fig. 2. ^{1}H NMR spectrum of PRDT as a monomer and polymer obtained from electrochemical polymerization of PRDT.

To examine the formation and cleavage reactions of disulfide bonds, oxidation and reduction potentials of PRDT was determined by cyclic voltammetry. The voltammogram is illustrated in Fig. 4. In the single-sweep voltammogram of PRDT in CH_3CN solution, an oxidation peak appeared at +1.08 V, suggesting that the oxidation peak potential is attributed to the oxidation of thiol groups to form disulfide bond. The electrochemical reaction of poly(PRDT) was performed using a two compartment cell to clarify the cleavage of disulfide bond. When the polymer was supplied oxidative current of 1 F/mol, which based on a monomer unit, the methanol insoluble polymer was recovered in 18.3% yield. The methanol soluble parts were found to be oligomers by GPC measurements. On the contrary, the degradation of the polymer was not observed in the electrochemical reaction of poly(PRDT) with reductive current.

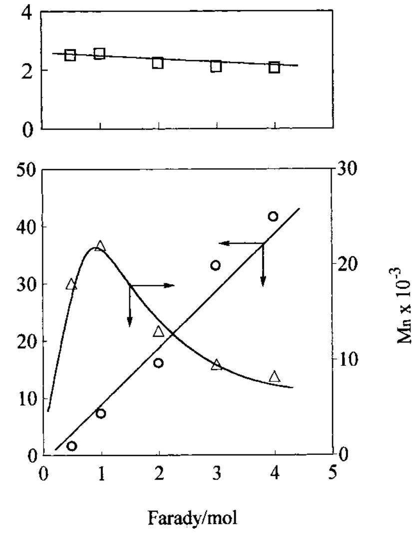


Fig. 3. The electrochemical polymerization of PRDT at different current quantum with the Pt electrode in CH_3CN at 0°C; [PRDT] = 0.12 mol/l.

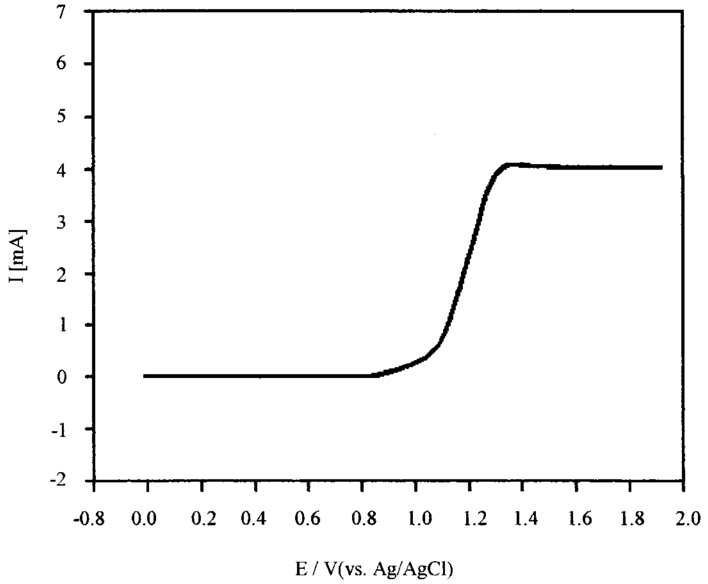


Fig. 4. Single-sweep voltammogram of PRDT (0.12 M) containing in CH_3CN solution. Electrolyte was 0.15 M Bu_4NClO_4, and scan rate was 10 mV s^{-1}.

These results indicate that the disulfide bond of poly(PRDT) is cleaved by the reduction process. Although we examined the reduction potentials of poly(PRDT) by cyclic voltammetry, the reduction peak owing to the cleavage of the disulfide bond was not obtained. This seemed to be due to that poly(PRDT) is insoluble in CH_3CN. Thus, we presumed that the polymerization of α,ω-alkanedithiols may accompany the cleavage of forming disulfide bond of the polymer.

Based on these findings, the reason why M_n gave a maximum current quantum may be explained as follows. The concentration of thiol groups of the polymerization system is very high at the initial stage of the polymerization. Under such conditions, the reaction from thiol to disulfide proceeded preferentially, and the cleavage of forming the disulfide bond may be almost neglected. On the other hand, the concentration of thiol group decreases as the polymerization proceeded, so that, the cleavage of the disulfide bond may occur with comparable rate at the final stage of polymerization, whereby the decrease in the molecular weight of the polymer ceases. Similar polymerization behavior was also observed in the polymerization of other α,ω-alkanedithiols. A detailed study is now underway, and will be reported in a forthcoming paper.

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