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POLYMER SOLVENTS FOR ELECTROCHEMICAL REACTIONS

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ABSTRACT

Solubility of inorganic salts and potential window of poly(ethylene oxide) (PEO) were analyzed. Sufficient potential window (−1.6 to +1.6 V vs Ag) was obtained for salt-containing PEOs when the ionic conductivity of the PEOs was higher than 3.0×10^{-4} S/cm. PEO was then used as a polymer solvent for electrochemical redox reactions of heme proteins. Myoglobin was solubilized in salt-containing PEO oligomers only after PEO modification, and their reversible redox reactions were confirmed. The electrochemical reduction was slow because of the very low diffusion coefficient of the proteins in PEO oligomers. PEO-modified myoglobin and hemoglobin showed reversible electron transfer reaction with ITO glass electrode at even 80 or 100°C in PEO oligomers.

INTRODUCTION

Electrochemical reactions are based on two requirements: 1) electron transfer from electrode to substrate, and 2) counterion migration to compensate for the charge change of the substrate through the electron transfer. When these two requirements are satisfied, electrochemical reactions should be carried out even in polymers. On the other hand, a group of synthetic polymers called "ion conductive polymers" has been attracting keen interest. Since one of the basic characteristics of these polymers is ion transport in the solid state, these polymers are being developed as solid electrolytes for film batteries. These polymers are therefore expected to

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change wet ionics devices into dry. We are applying these ion conductive polymers as solid solvents for electrochemistry.

Poly(ethylene oxide) (PEO) is one of the base polymers used to design ion conductive polymers. PEO can be regarded to be the polymerized water, and PEO dissolves a considerable amount of salts as expected from the structural similarity. It should be noted that the solubility of some inorganic salts is decreased in PEO oligomers by heating [1–3]. This was attributed to the thermal motion of PEO oligomers. That is, reduction of salt solubility was induced by reduction of cooperative coordination of the terminal hydroxyl groups of the polyether oligomers to the cation [3, 4]. Besides inorganic salts, there are some reports on the solubilization and/or electrochemical redox reactions of substrates in polymer solvents such as transition metal ions and lanthanide ions [5, 6], metal complexes [7], organic molecules and monomers (including electrooxidative polymerization) [8–10], alkyl viologens [11], polyviologen [12], poly(pyrrole) [13], poly(thiophene) [14], and even heme proteins [15–18]. Since PEO has a much wider applicable temperature range than water, the possibility of electrochemistry should spread even in the solid state.

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EXPERIMENTAL

Materials

ITO Glass Electrode. The ITO glass electrode was purchased from Oji Tobi Co. ITO layer thickness was 1500 Å and surface resistance was about 15 Ω/cm^2. The ITO glass electrode was washed with dehydrated chloroform and dried before use.

Poly(Ethylene Oxide) (PEO). PEOs with average molecular weights of 200, 400, and 600 were purchased from NOF Co. PEOs containing no additives such as anti-oxidants were dried in vacuo for a week before use.

Poly(Oligo(Oxyethylene) Methacrylate) (PMEO). MEO was also obtained from NOF Co. The monomer MEO was dissolved in a degassed isopropanol with azobisisobutyronitrile (AIBN) as a radical initiator. A polymerization of MEO was carried out at 60°C for 3 hours. PMEO was purified by the reprecipitation method. A supporting electrolyte was added to a chloroform solution of the purified PMEO, evaporated, and dried in vacuo for 2 days.

PEO-Modified Myoglobin (PEO-Mb). PEO-Mb was prepared in our laboratory. PEO succinimidyl succinate (activated PEO; average molecular weight of 2000) was reacted with myoglobin (horse skeletal muscle, Sigma) in an aqueous medium [16]. PEO-Mbs with 5–25 PEO chains were fractionated with HPLC and used for our experiments.

PEO-Modified Hemoglobin (PEO-Hb). PEO-Hb was a gift from Ajinomoto Co. The activated PEO (average molecular weight of 3500) was reacted with stroma-free human hemoglobin [19]. The average molecular weight of PEO-Hb containing 6 PEO chains was calculated to be 1.0×10^5 (including a small amount of crosslinked hemoglobin dimers) by laser light-scattering measurement [19].

Methods

Thin Layer Cell

In order to detect reactions on the working electrode, electrochemical studies were carried out with a thin layer cell composed of a glass plate and an ITO glass working electrode (0.9 × 0.1 × 3.5 cm). The light path length is 150 μm [13, 14].

Cyclic Voltammetry

Cyclic voltammetry (CV) was carried out using a potentiogalvanostat (Fuso, HECS-321B) under a nitrogen atmosphere. A carbon electrode (0.5 mm in diameter), Ag wire (0.5 mm in diameter), and Pt wire (0.5 mm in diameter) were used as a working, reference, and counterelectrode, respectively. The ITO electrode was also used as a working electrode.

Potentioabsorptometry

PEO-modified proteins were dissolved in PEO_{200} containing 0.50 M KCl bubbled with nitrogen gas preliminarily. A half milliliter of this solution was slowly introduced into the quartz cell. Then the thin layer cell was set in the quartz cell together with Pt and Ag electrodes, and the quartz cell was covered and sealed with parafilm. The PEO solution was raised in the thin layer cell by the capillary phenomenon, and the electrode reaction under potential was analyzed spectroscopically (Shimadzu, UV-2200). The reduction of PEO-Hb was carried out by applying a negative potential, -0.5 to -1.2 V (vs Ag). Potentiogalvanostat (Nikko Keisoku Co., NPGFZ-2501-A) was used for potentioabsorptometry. All experiments were carried out under a nitrogen gas atmosphere to avoid the formation of oxygen adducts with heme proteins under the reduced state.

For PEOs with an average molecular weight of more than 400, PEO-Hb was dissolved in distilled water and cast onto the ITO electrode with a micro syringe. The dried PEO-Hb cast ITO electrode was then faced with a glass plate at a 150 μm distance, and it was fixed with epoxy-type resins to prepare a thin layer cell. This was then soaked in the PEO oligomers containing KCl as supporting electrolyte.

PEO-Mb was also cast onto the ITO electrode. The dried PEO-Mb cast electrode was further covered with PMEO containing KCl. Then another ITO glass electrode (as counterelectrode) was attached instead of a glass plate. A polished silver wire (0.5 mm in diameter) was soaked in the PMEO layer as the reference electrode. This setup was used for potentioabsorptometry.

RESULTS AND DISCUSSION

Salt Solubility in PEOs

PEO is known to solubilize inorganic salts. This was comprehensible because of the structural similarity to water. However, the solubility of some inorganic salts showed an interesting temperature dependence [1–4]. The solubility of some salts in PEO oligomers decreased at higher temperature. It is interesting that a series of salts which show such a negative temperature dependence in solubility in PEO oligomers are known to be insoluble in PEOs of very high molecular weight. In other words,

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PEO oligomers can solubilize these salts in spite of their lack of solubility in high molecular weight PEOs. We have already reported that the inorganic salts were divided into two groups, one of which is salts showing negative temperature dependence in solubility in PEO oligomers. These were classified as "Type 1" salts. Other salts, i.e., no crystal was phase separated in the PEO oligomers by heating, were classified as "Type 2" salts. Typical examples of these salts are summarized in Table 1. The solubility of Type 1 salts decreases with increasing molecular weight of PEO oligomers, and the solubility becomes zero when the average molecular weight of PEO is more than 1000, whereas Type 2 salts are still soluble in a PEO with very large molecular weight. It should be noted that the terminal hydroxyl groups have a key role. Type 1 salts require terminal hydroxyl groups in order to be soluble; ether oxygens seem not to be important for solubilization. However, ether oxygens are effective for the solubilization of Type 2 salts [3].

The phase separation of salts in polyethers by heating was recently revealed to be affected by the following factors: 1) lattice energy of salt, 2) cation radius, 3) molecular weight of the polyether, 4) structure of the polyether, and 5) terminal hydroxyl group fraction. Since salts with a lower lattice energy provide more dissociated ions, these salts were preferred in the design of ion conductive polymers with higher ionic conductivity. One should be careful to choose suitable salts as supporting electrolytes in PEOs.

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Potential Window of Salt-Containing PEO

It is important to know the applied potential limits of polyethers when they are used as solvents for electrochemical measurements. The so-called potential window of the PEOs were analyzed [13]. A series of PEOs with different molecular weights was mixed with a known amount of lithium perchlorate. These were checked by cyclic voltammetry, and the given potential range was gradually spread

TABLE 1. List of Alkali Metal Salts Which Were Crystallized by Heating in PEO Oligomers (molecular weight 200)[a]

	Cation[b]			
Anion	Na^+	K^+	Rb^+	Cs^+
Cl^-	NaCl	KCl	RbCl	CsCl
NO_3^-	×	KNO_3	[c]	[c]
Br^-	NaBr	KBr	RbBr	CsBr
I^-	×	×	[c]	[c]
SCN^-	×	×	×	×

[a] × = no salt was phase separated by heating to 180°C.

[b] No lithium salt was crystallized in PEO_{200} by heating.

[c] Not examined.

during potential cycling. The potential, which gave a Faraday current of more than 2 μA, was recorded as the limit of the given potential. Figure 1 showed the cathodic and anodic potential limits of the salt-containing PEOs. It is clear that the potential window reached a constant range (between -1.6 V and $+1.6$ V vs Ag) by increasing the ionic conductivity ($>3.0 \times 10^{-4}$ S/cm) of the corresponding PEOs [13]. This means that the most effective factor on the potential window of PEOs is the bulk ionic conductivity. However, PEOs having less than 3.0×10^{-4} S/cm are applicable for electrochemical experiments, and the potential obtained is not as accurate because of potential depression at the interface between the electrode and the bulk PEO with its relatively high ohmic resistance.

Since PEO has a very low glass transition temperature (around -80°C) and a high boiling (decomposition) point (>180°C), PEOs are expected to be excellent solvents with a much wider applicable temperature range than water or other organic solvents.

Reduction of PEO-Hb in PEO Oligomers

Cyclic voltammetry revealed that PEO-modified hemoglobin (PEO-Hb) received electrons directly from the electrode in PEO oligomers containing 0.5 mol/L KCl. As shown in Fig. 2, the reduction and oxidation peak potentials of PEO-Hb in PEO_{200} were -0.120 and -0.050 V vs Ag, respectively. The redox potential was

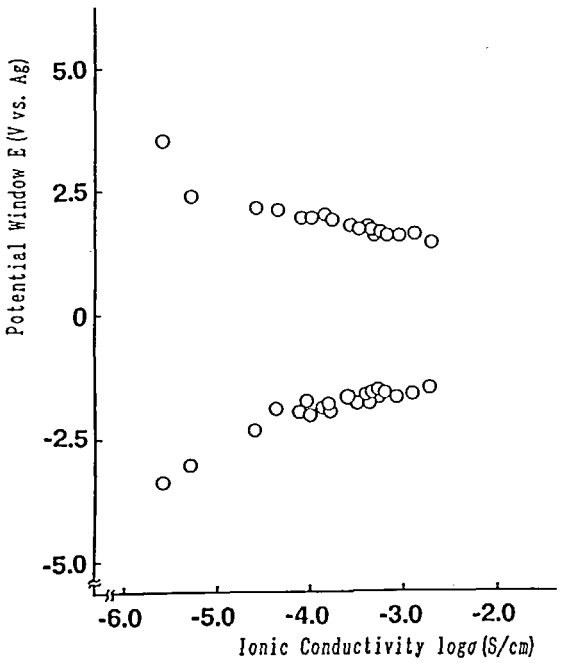

FIG. 1. Effect of ionic conductivity of salt-containing PEO on the potential window of the PEO. Carbon electrode, platinum wire, and silver wire were used as the working, counter, and reference electrodes, respectively.

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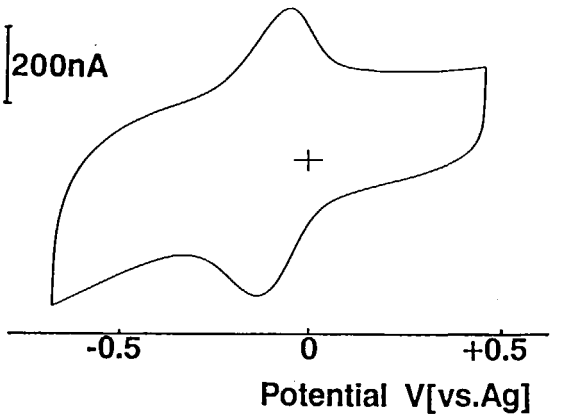

FIG. 2. Cyclic voltammogram for PEO-Hb in PEO_{200} containing 0.5 mol/L KCl at 25°C. The same electrode set was used as mentioned in Fig. 1. Scan rate = 30 mV/s. [PEO-Hb] = 4.0×10^{-4} mol/L.

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calculated to be −0.085 V vs Ag. Since the potential difference between the two peak potentials was 70 mV, the redox reaction of PEO-Hb in PEO was suggested to be semireversible. It should be noted here that there is a serious supporting electrolyte dependence of the redox response of PEO-Hb in PEO oligomers [20]. As far as we know, potassium chloride is the best supporting electrolyte for the reversible redox reactions of PEO-Hb in PEO oligomers.

The redox reaction of PEO-Hb is also confirmed by visible spectrometry [17]. A thin layer cell was used to detect electrochemical reduction at the working ITO electrode. It took about an hour to reduce PEO-Hb in the cell by applying a negative potential of about −1.0 V vs Ag. This slow reduction was improved at higher temperature. It was surprising that the reversible redox reaction of PEO-Hb was repeatedly carried out in PEO_{200} containing 0.5 mol/L KCl at 80°C. Figure 3 shows the visible spectra for reduced and oxidized PEO-Hb in PEO_{200} at 80°C. The absorption maximum of oxidized and reduced PEO-Hb was 409.2 and 420.6 nm, respectively. The reduction and reoxidation was fast (<5 minutes), and exactly the same spectrum was obtained during repeated potential cycling (between +1.20 V and −1.20 V vs Ag) at 80°C. It should be noted that hemoglobin was electrochemically active in PEO even at 80°C. There was a possibility that the "heme," the active center of hemoglobin (so-called iron protoporphyrin IX), came out and showed a reversible redox reaction in PEO. We previously reported that the heme itself was soluble in PEO oligomers and showed a reversible redox reaction [7]. To clarify the presence of the came-out heme in PEO, the spectral change of heme in PEO at 80°C was analyzed similarly [21]. Heme (oxidized) showed an absorption maximum at 384.5 nm in PEO_{200}. Against this, PEO-Hb (oxidative) showed it at 409.2 nm in PEO_{200}. Because of this great difference, heme is strongly suggested to remain in the heme pocket of hemoglobin even at 80°C. However, a conformational change of PEO-Hb from its compact form with a high alpha-helix content to a more random conformation was suggested in PEO at higher temperature [21]. A detailed discussion on this thermal stability of proteins, especially on their conformation in PEO, will be reported elsewhere.

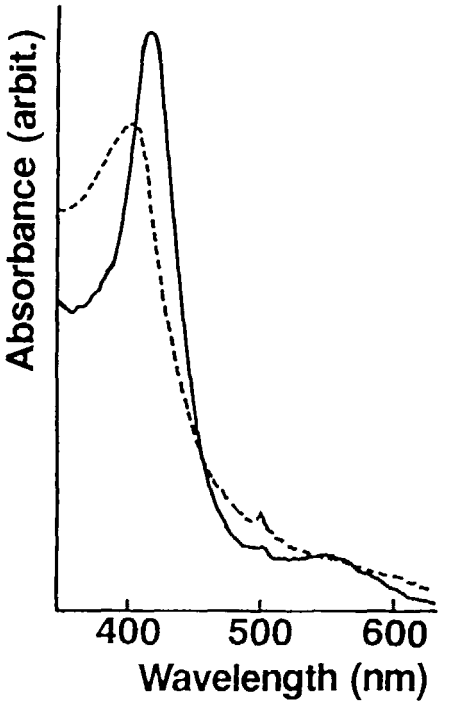

FIG. 3. Spectral changes for PEO-Mb in PEO_{200} reflecting the reduction and oxidation by applying −1.2 V and +1.2 V vs Ag alternately to the ITO electrode at 80°C. (- -) Oxidized, (—) reduced, [PEO-Hb] = 1.0×10^{-4} mol/L.

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Reduction of PEO-Hb and PEO-Mb on the ITO Electrode in PEO Oligomers

Since PEO solution is a viscous medium and the electrochemical redox reaction of PEO-Hb is strongly suggested to be diffusion controlled, PEO-Hb was cast on the electrode and their redox reactions were analyzed in PEO oligomers. PEO-Hb was cast on the carbon electrode and was further soaked in the salt-containing PEO. Figure 4 shows the reversible cyclic voltammogram for PEO-Hb in PEO_{400}. Reductive and oxidative peak potentials were found at −0.135 V and −0.040 V vs Ag, respectively. The redox potential was calculated to be −0.88 V vs Ag. The redox potential of PEO-Hb was almost the same as that of PEO-Hb homogeneously solubilized in PEO_{200}, as seen in Fig. 2. However, the difference between the reduced and oxidized peak potentials was larger (95 mV) than that for a homogeneous solution (70 mV). This means that electron transfer between the electrode and PEO-Hb cast on the electrode was less reversible than the homogeneous solution system (Fig. 2).

Since no diffusion of PEO-modified heme proteins was required for electrochemical reaction when they were cast on the electrode, a faster redox reaction was expected. The reduction rate was, however, not accelerated [18]. Since Hb and Mb were not electron transport proteins, no rapid electron transfer between adjacent PEO-Hbs in the cast layer was expected. The electron transfer between the ITO

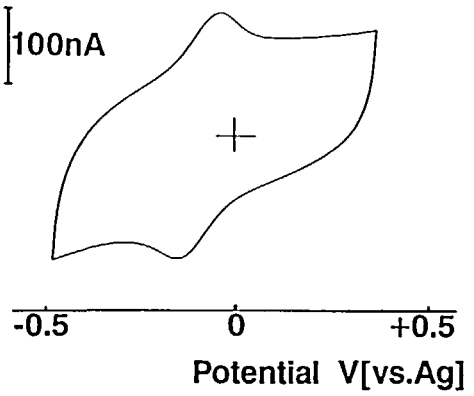

FIG. 4. Cyclic voltammogram for PEO-Hb cast on the carbon electrode in PEO_{400} containing 0.5 mol/L KCl at 25°C. The same electrode set was used as mentioned in Fig. 1. Scan rate = 30 mV/s.

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electrode and the directly contacted PEO-Mb on the electrode was revealed to be much faster than that between two neighboring PEO-Mbs in the cast layer [18]. The rate-determining step might therefore be the electron transfer between PEO-modified heme-proteins in the cast layer. In order to accelerate the electron transfer, wiring of the electrode and proteins with electroconductive polymers is now in progress.

The redox reaction of PEO-Hb cast on the ITO electrode was analyzed in PEO_{400} because PEO-Hb is insoluble in PEO_{400}. Reversible redox reactions of PEO-Hb were confirmed in a wide temperature range (5 to 130°C) as seen in Fig. 5. Surprisingly, PEO-Hb is still active for reversible redox reaction in this temperature range. As mentioned above, the electrochemical reduction of PEO-Hb cast on the ITO electrode became faster with increasing temperature. Up to 100°C, the oxidized form of PEO-Hb gave the same spectrum with the absorption maximum at 405 nm. The absorption maximum shifted to 412 nm after heating at above 100°C in spite of there being no potential. This might be due to a shift of the redox potential of PEO-Hb at higher temperature. Some part of PEO-Hb is considered to be reduced automatically at higher temperature in PEO_{400}; however, no supporting data for this has been obtained. Since the redox potential of cytochrome c has been reported to be affected by heating [22], CV measurement of this system at higher temperatures is essential. The reversible redox reaction of cast PEO-Hb in PEO_{400} was also carried out [21]. It is concluded that biological materials such as proteins are still effective at temperatures higher than 100°C when they are PEO-modified and soaked in PEO oligomers.

PEO-Mb was cast on the ITO electrode, and this was further covered with poly(oligo(oxyethylene) methacrylate) (PMEO) containing 0.2 mol/L KCl. Salt-containing PMEO has been frequently used as a typical ion conductive solid polymer [23]. Another ITO electrode was contacted with this as a counterelectrode. Then a silver wire was inserted in the PMEO as the reference electrode. Reduction of PEO-Hb gave −0.7 V vs Ag to the ITO working electrode; however, no isosbestic point was observed, as seen in Fig. 6. This might be due to the gradual spectral

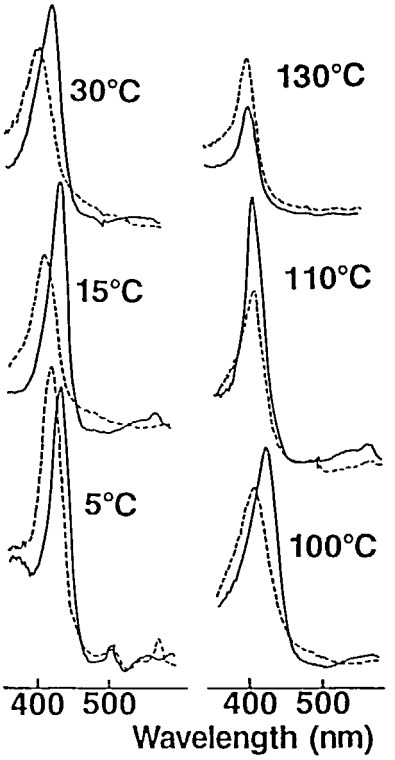

FIG. 5. Effect of temperature on the visible spectra of PEO-Hb cast on the ITO electrode in PEO_{400}. (- -) Oxidized, (—) reduced.

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change that occurs after the PEO-Mb layer is contacted with PMEO [24]. This step prevents us from analyzing the reversible spectral change of PEO-Hb in PMEO. In this solid state cell, PEO-Mb was reduced and oxidized reversibly to give −0.7 V and +0.7 V vs Ag alternately. Since the thermal motion of the PEO side chains of PMEO might be less than that of linear PEO oligomers, the reversible redox reaction of PEO-Mb and PEO-Hb should be detected over a wide temperature range. The extremely wide temperature range of the electron transfer reaction of PEO-modified heme proteins in PMEO will be carefully analyzed soon.

Future Trend

In principle, electrochemical redox reactions should be similar in PEO oligomers. PEOs are expected to be used as polymer solvents for a variety of substrates including biological materials such as proteins. PEO-Mb is stable, and it is redox active from 5 to above 100°C in PEO oligomers. A slight conformational change of Mb is observed after PEO modification, but no further conformational change was seen in PEO. It is interesting that biological materials play similar higher performance roles in polymer solvents. Since polymer solvents have some better characteristics than ordinary solvents, including water, they are expected to be applied in a variety of research fields.

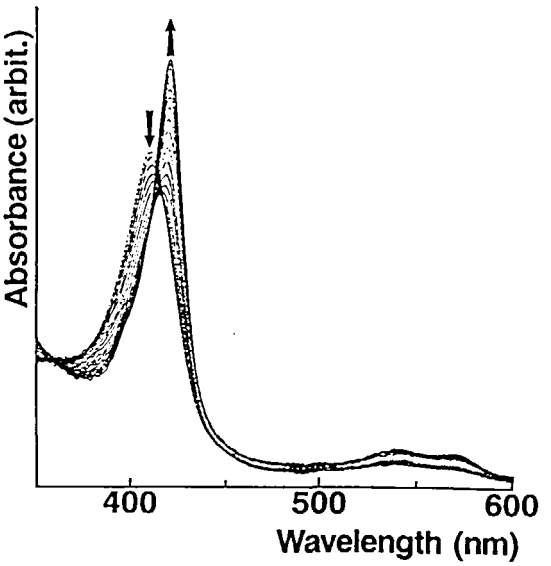

FIG. 6. Spectral changes for PEO-Mb cast on the ITO electrode further covered with PMEO by applying −0.7 V vs Ag.

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CONCLUSION

The advantages of polymer solvents include wide potential window, excellent salt solubility, wide temperature range, light weight, easy to handle, cheap, stable. Some heme-proteins (such as myoglobin and hemoglobin) are soluble in PEO after PEO modification. The reversible redox reaction of these heme-proteins in PEO was carried out in a wide temperature range up to 100°C. The relatively high resistance of salt-containing PEO is a serious disadvantage for polymer solvents. The electrochemical redox reactions of some substrates should be successful when polymer solvents of higher performance are available.

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