Metallization of Crosslinked Epoxy Resins Derived from Diglycidyl Ethers of Poly(ethylene glycol) and Bisphenol A by Reduction of Polymer-Incorporated Cobalt Ion

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ABSTRACT: The surface of the blend films of poly(ethylene glycol) diglycidyl ether (PEG-E) and bisphenol A diglycidyl ether (BPA-E) cured with 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride at 200°C for 5 h was metallized by the reduction of polymer-incorporated cobalt acetate with aqueous sodium borohydride at 20–50°C. Although the cured films of PEG-E/BPA-E, weight ratio 100/0–80/20, were successfully metallized, the blend ratio 60/40 did not afford a metallized film by this reduction method. The glass transition temperature (T_g) of the cured resin measured by dynamic viscoelastic analysis rose with an increase of BPA-E content. The difficulty of surface metallization in the case of blend ratio 60/40 is related to the hindrance of migration of cobalt ion due to the restriction of molecular chain motion. Electron probe microanalysis and X-ray photoelectron spectroscopy measurement revealed that the cobalt ion that was homogeneously distributed in the inner part of the film before reduction migrated to both sides of the film and then was reduced to pure metal by the reduction treatment. The X-ray diffraction analysis of the reduced films revealed that the generated cobalt was almost amorphous. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2164–2169, 2004

Key words: metal–polymer complexes; ESCA/XPS; FT-IR; surfaces; resins

INTRODUCTION

Metallization of a polymer surface has received considerable industrial and academic attention because metallized plastics combine the properties of metal, such as high conductivity and metallic luster, with the processability, electric insulation, and light weight of the polymer.[1] The wet plating method known as electroless plating, the dry plating method known as vacuum deposition or metal spraying, and the coating method such as using a metallic paint are well known as techniques for metallization of a polymer surface.[2] These techniques sometimes require preliminary surface treatment, such as mechanical roughing, chemical modification, etching, sensitizing, or activation. As a more convenient metallization technique, a novel method by reduction of polymer-incorporated metal ions[3–12] or polymer–metal chelates[13,14] with an aqueous solution of sodium tetrahydroborate was developed by a few groups. This method was known to be applicable to the surface metallization of highly polar linear polymers such as polyacrylonitrile, poly(vinylidene fluoride), poly(vinyl alcohol), polyamide, poly-amide-imide, and polyurethane. The surface metallization of crosslinked thermosetting resins such as epoxy resin and phenol resin is an important technology in the field of electronic materials such as printed wiring board. Recently, we found that the crosslinked films of poly(ethylene glycol) diglycidyl ether (PEG-E) cured with 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride (DMCDA) can be metallized by reduction of polymer-incorporated cobalt chloride or nickel chloride.[15] Diglycidyl ether of bisphenol A (BPA-E), which is used in a wide range of applications, is expected to afford the polymer network with a higher heat resistance and mechanical strength than PEG-E. The present study describes the metallization of the blend of PEG-E and BPA-E cured with DMCDA by reduction of polymer-incorporated cobalt acetate with aqueous sodium tetrahydroborate. Our attention focuses on the elucidation of the relationship between the metallization behavior and the structure of the network polymer.

EXPERIMENTAL

Materials

PEG-E (Epiol E-400, NOF Corp., Tokyo, Japan) (epoxy equivalent 283 g/eq, degree of polymerization for ethyleneoxy unit *ca.* 10) and BPA-E (Epikote 828, Japan

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Epoxy Resins Co. Ltd., Tokyo, Japan) (epoxy equivalent: 186 g/eq) were used as epoxy resins. As a curing reagent DMCDA (Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan) was used without further purification. Reagent-grade cobalt (II) acetate, *N,N*-dimethylformamide (DMF), 2-ethyl-4-methylimidazole (EMI), and sodium tetrahydroborate were used without further purification.

Preparation of samples

A typical procedure in the case of PEG-E/BPA-E, weight ratio 80/20, is as follows: DMF (16 mL) solution of PEG-E (4.00 g, 14.1 mmol), BPA-E (1.00 g, 5.38 mmol), DMCDA (2.58 g, 9.76 mmol), cobalt acetate (0.442 g, 2.50 mmol), and EMI (0.25 mL) were poured on a polypropylene plate at room temperature and dried at 100°C for 15 h. The stripped film was put on a poly(tetrafluoroethylene-*co*-perfluoroalkyl vinyl ether) (PFA)-coated stainless-steel plate and cured at 140°C for 5 h and further at 200°C for 5 h. The cured samples in the case of PEG-E/BPA-E 100/0, 95/5, 90/10, and 60/40 were prepared by the same procedure.

Metallization by reduction treatment was performed by dipping the cured films containing cobalt acetate in a 0.05 wt % sodium tetrahydroborate aqueous solution at 20–50°C for 8–30 min, followed by washing with ethanol and subsequently with toluene and drying.

Measurements

Surface resistance of the metallized films was determined by the conventional four-probe method using a digital multimeter (Model R6871E, Advantest Co., Ltd., Tokyo, Japan). Infrared (IR) spectra of the films with and without cobalt acetate were measured on a Shimadzu 8100 FT-IR spectrometer (Kyoto, Japan) using the ATR method. Dynamic viscoelastic measurements of the films were performed on a Rheolograph Solid (Toyo Seiki Co., Ltd, Tokyo, Japan) with a chuck distance of 20 mm, a frequency of 10 Hz, and a heating rate of 2°C/min. The elemental distribution of metal in the film was observed by use of an electron probe microanalyzer (EPMA, Jeol Ltd., Tokyo, Japan, JXA-8800) with an accelerating voltage of 15.0 kV and probe current of 0.05 μA. X-ray diffraction analysis of the deposited metal was carried out with a X-ray diffractometer (Rigaku Denki Co. Ltd., Tokyo, Japan, RINT-2100), using CuKα radiation at 40 kV and 20 mA. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a photoelectron spectrometer (Jeol Ltd., JPS-90SX) using MgKα radiation at 12 kV and 5 mA, after argon ion beam etching for 5 s (depth *ca.* 5 nm) at the condition of accelerating voltage of 500 V and ion beam current of 50 mA to avoid
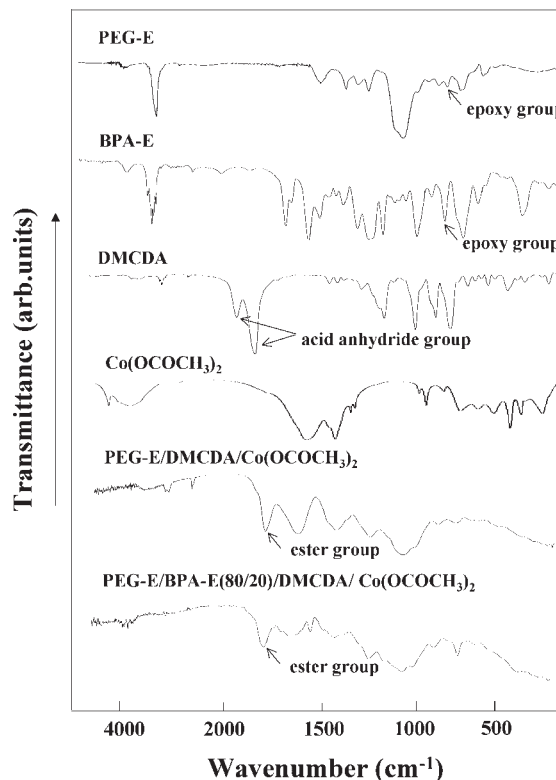

Figure 1 IR spectra of starting materials and the cured films of PEG-E/DMCDA/Co(OCOCH$_3$)$_2$ and PEG-E/BPA-E(80/20)/DMCDA/Co(OCOCH$_3$)$_2$.

contamination of uppermost surface of the metallized film.

RESULTS AND DISCUSSION

Various properties of the crosslinked epoxy resins containing cobalt acetate

In the previous paper, we used cobalt chloride for the surface metallization of PEG-E cured with DMCDA.[15] In that case, the carboxylic acid group, probably generated by the reaction of DMCDA with water at the air side, chelated with cobalt ion in the polymer during the curing stage. As a result, the film surface at the air side had a higher cobalt ion concentration than that at the side of the polypropylene (PP) plate used for casting. When cobalt acetate was used instead of cobalt chloride in this study, cobalt ion homogeneously distributed in the depth direction of the cured film. The curing reaction by use of cobalt acetate was characterized by means of FT-IR spectroscopy (Fig. 1). The absorption peaks at 1870 and 1800 cm^{-1} characteristic of an acid anhydride group in the IR spectrum of DMCDA disappeared, and a new absorption peak at 1750 cm^{-1} characteristic of an ester group was observed in the IR spectra of the cured epoxy resins containing cobalt acetate. In addition, the absorp-
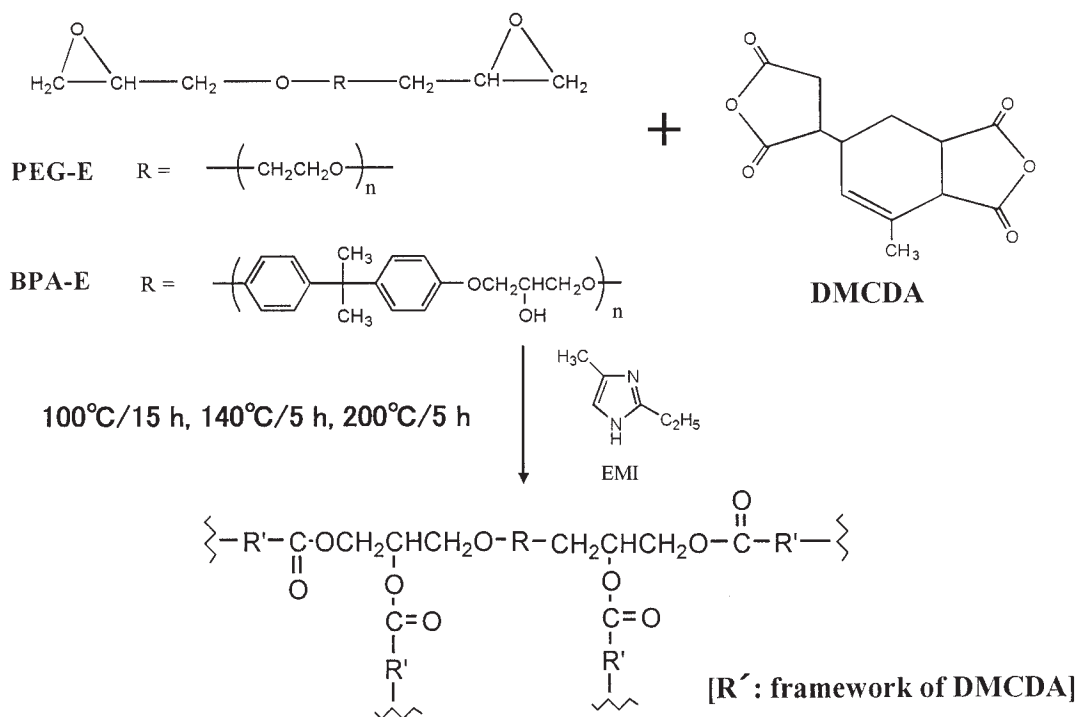
Figure 2 Formation of crosslinked structure by the reaction of PEG-E/BPA-E and DMCDA.

tion peak at 910 cm^{-1} characteristic of epoxy group observed for PEG-E and BPA-E disappeared. These results indicate that the curing reaction of PEG-E/BPA-E with DMCDA smoothly proceeds to give the crosslinked product with an ester group (Fig. 2). The air side of the film showed the same ATR-IR spec-
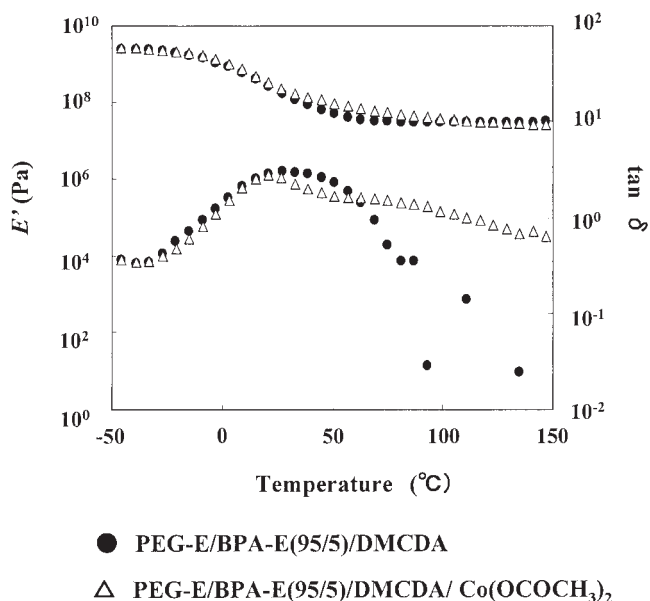
trum as that of the PP side, indicating that special chelation of carboxyl group generated by the hydrolysis of DMCDA with cobalt ion does not occur at the air side.

Figure 3 shows the influence of cobalt acetate on the curing reaction by means of dynamic viscoelastic measurement. The cured film of PEG-E/BPA-E(95/5)/DMCDA/Co(OCOCH$_3$)$_2$ showed almost the same storage modulus (E') curve as that of
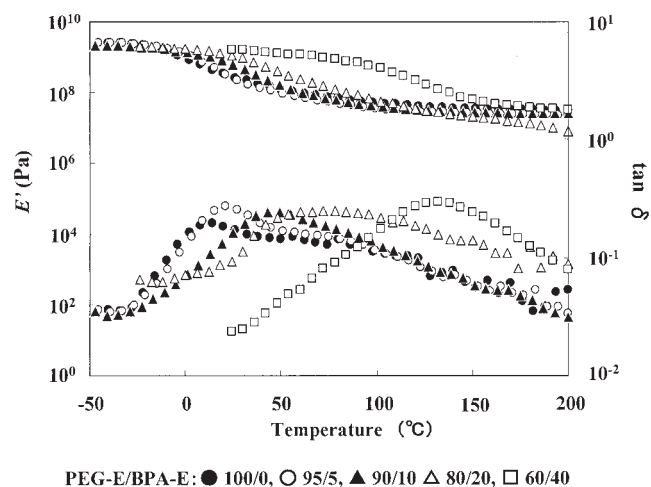

● PEG-E/BPA-E(95/5)/DMCDA

△ PEG-E/BPA-E(95/5)/DMCDA/ Co(OCOCH$_3$)$_2$

Figure 3 Dynamic viscoelastic curves of the cured films of PEG-E/BPA-E(95/5)/DMCDA and PEG-E/BPA-E(95/5)/DMCDA/Co(OCOCH$_3$)$_2$.

PEG-E/BPA-E: ● 100/0, ○ 95/5, ▲ 90/10 △ 80/20, □ 60/40

Figure 4 Influence of PEG-E/BPA-E ratio on dynamic viscoelastic curves of the cured PEG-E/BPA-E/DMCDA/Co(OCOCH$_3$)$_2$ films.
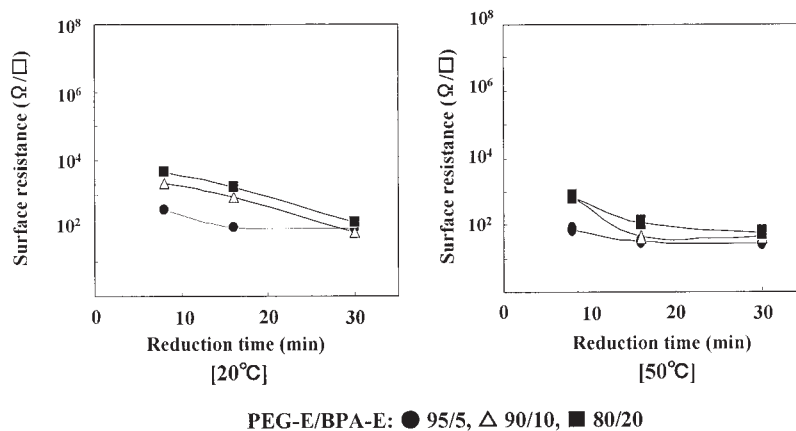
PEG-E/BPA-E: ● 95/5, △ 90/10, ■ 80/20

Figure 5 Relation between surface resistance and reduction time at 20 and 50°C of the cured PEG-E/BPA-E/DMCDA/Co(OCOCH$_3$)$_2$ films.

PEG-E/BPA-E(95/5)/DMCDA, indicating that cobalt acetate does not disturb the curing reaction of epoxy resins and DMCDA. Their tan δ curves showed somewhat different patterns. The cured film containing cobalt acetate showed a new broad tan δ peak at a higher temperature region (*ca.* 70°C). The peak may be attributed to some interaction of cobalt acetate and epoxy resin network. Figure 4 shows the influence of the PEG-E/BPA-E ratio on the dynamic viscoelastic behavior. The tan δ peak temperature related to T_g (13, 21, 45, 72, 131°C) increased with decreasing PEG-E/BPA-E ratio (100/0, 95/5, 90/10, 80/20, 60/40, respectively). The cured PEG-E/BPA-E (60/40) film is in a glassy state at the reduction temperature (20–50°C), suggesting that the motion of molecular chain is highly restricted.

Surface metallization of the crosslinked epoxy resins containing cobalt acetate

The reduction of the crosslinked PEG-E/BPE-E (100/0–80/20) film containing cobalt acetate with aqueous

sodium tetrahydroborate at 20 or 50°C successfully afforded a film with metallic luster. The PEG-E/BPE-E 60/40 film did not afford a surface-metallized film. The change of surface resistance of the metallized film is shown in Figure 5. The insulated film before reduction became a surface conductive film after reduction. The surface resistance at the air side was almost the same as the PP side in all cases. Surface resistance of the metallized PEG-E/BPA-E/DMCDA reached to the order of 10^2 Ω/□ at both reduction temperatures (20, 50°C). The surface resistance during the reduction at 50°C dropped at a shorter reduction time than that at 20°C. Although the finally attained surface resistance is not so different, the film with a higher PEG-E/BPA-E ratio showed a lower surface resistance at the reduction time of 8–16 min.

Figure 6 shows the XPS spectra of the metallized PEG-E/BPA-E(95/5) film on the PP side. The air side of the film showed almost the same spectra as the PP side. The intense peak related to pure Co metal was observed at 778.5 eV (Co 2p), and the peak around
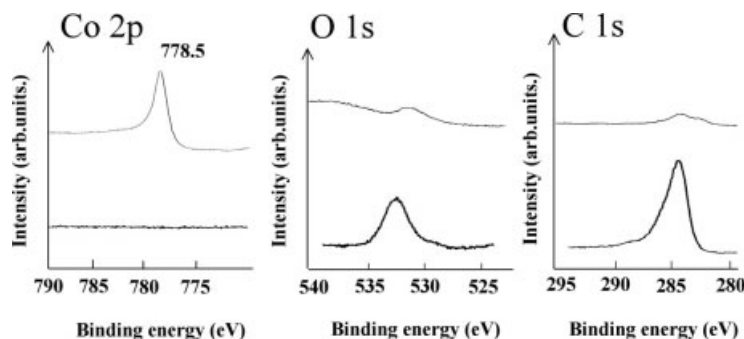

Figure 6 XPS spectra of the Co 2p, O 1s, and C 1s regions of the metallized PEG-E/BPA-E (95/5) film (top) and the corresponding film without cobalt acetate (bottom) on the PP side.
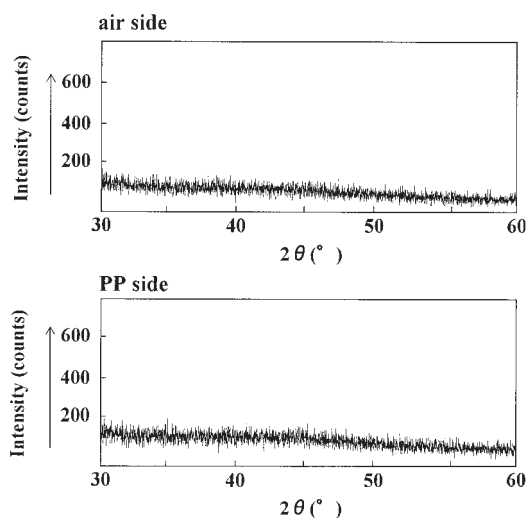
Figure 7 X-ray diffraction patterns of the metallized PEG-E/BPA-E (95/5) film.

780–781 eV related to cobalt (II) ionic compounds did not appeared for the metallized film after the reduction. The C 1s and O 1s peaks related to the cured epoxy resin on the surface of the metallized film were much weaker than those of the film without cobalt acetate. These results indicate that the metal ion migrates to the surface and is reduced to pure metal. Figure 7 shows the X-ray diffraction pattern of the metallized film. No peak related to a crystalline cobalt was observed on either side, indicating that the formed metal is not crystalline. The generated metal may have defects in the lattice or contain some impurities. Figure 8 shows the change of the elemental distribution of cobalt in the depth direction of the film

(thickness *ca.* 0.4 mm) during the reduction obtained by EPMA line analysis. Before reduction, the metal ion was homogeneously distributed in the inner part of the film. The cobalt ion migrated to the polymer surface by the reduction treatment, becoming more densely distributed on the polymer surface except in the case of PEG-E/BPA-E 60/40. The remaining cobalt ion at the inner part of the film increased with decreasing PEG-E/BPA-E ratio. In the case of 60/40, migration of cobalt to the film surface did not occur.

CONCLUSION

The influence of the PEG-E/BPA-E ratio on the surface metallization behavior of the $Co(OCOCH_3)_2$-containing epoxy resins cured with DMCDA was investigated. The cobalt ion incorporated in the cured films of PEG-E/BPA-E (100/0–80/20) smoothly migrated to the film surface and then reduced to pure metal when the film was dipped in aqueous $NaBH_4$ solution at 20–50°C for 8–30 min. The remaining cobalt ion at the inner part of the film increased with decreasing PEG/BPA-E ratio for the metallized films. The cured epoxy resin (100/0–80/20) networks are in a rubbery state or their molecular motion starts at the reduction temperature, judging from the dynamic viscoelastic curves of the cured films (100/0–80/20). The PEG-E/BPA-E 60/40 film, which is in a completely glassy state at the reduction temperature (20–50°C), did not afford a surface metallized film. This novel metallization method of epoxy resins may be applicable to some field of electronic materials.
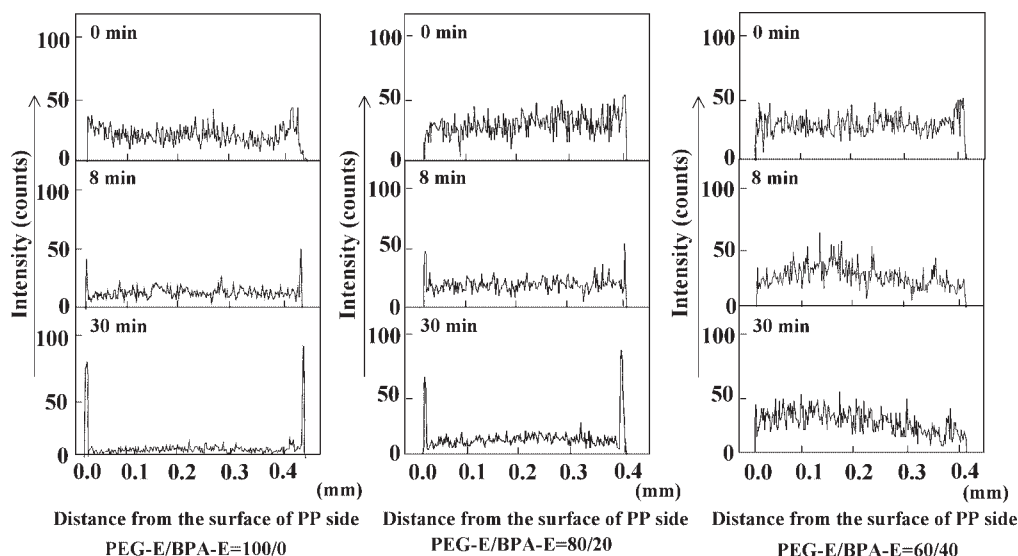

Figure 8 EPMA line analysis in the depth direction of the cured PEG-E/BPA-E/DMCDA/$Co(OCOCH_3)_2$ films at reduction temperature 50°C.

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