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Functional Metallomacrocycles and Their Polymers 36. Synthesis and Properties of Polyester Containing a Metallophthalocyanine Ring

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ABSTRACT: A novel class of copolyesters containing the metallophthalocyanine ring [M-Pc, M = Fe(III), Co(II)] in the chain was synthesized by polycondensation of (dicarboxyphthalocyaninato) metal [M-Dapc, M = Fe(III), Co(II)] diacid chloride, terephthalic acid chloride and aliphatic diols. The structures of the copolyesters were characterized by infrared, electronic as well as ESR spectra, and viscosity measurement. The thermal stabilities of the polymers were evaluated by dynamic thermogravimetric analyses. The polymers obtained thus were easily soluble in chloroform, dichloromethane, etc. The green or blue colored fiber was formed by melt spinning of the copolyesters containing below 1 mol % M-Pc component. The copolyester containing Co(II)-Pc in the chain obtained from 1,2-ethanediol as a diol component catalysed the autoxidation of 2-mercaptoethanol in the presence of oxygen. © 1998 John Wiley & Sons, Ltd.

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KEYWORDS: polyester; cobalt phthalocyanine; iron phthalocyanine; thermal stability; autoxidation; thiol; catalytic activity

INTRODUCTION

Phthalocyanine (Pc) polymers having various functions, for example, stacked polyphthalocyanines for electroconductors [1], copolymerized phthalocyanine polymers for organic photoconductors [2], thermally stable polymers containing metallophthalocyanines [3, 4] and so on, have already been prepared. Metallophthalocyanine (M-Pc) has also attracted considerable interest because of its structural similarity to the active centre of naturally occurring haemoenzymes. We studied a series of functional M-Pcs and their polymers as models for catalase, peroxidase, oxidase and oxygenase [5–8].

Foul odor is emitted from spoiled garbage and sewage. Such foul odor results from mercaptan, hydrogen sulfide and amines [9]. Recently, we found that mercaptan and hydrogen sulfide decomposes through the catalytic reaction of Fe(III)- and Co(II)-Pc supported on staple fiber [10]. Using this fact, we developed a new type of biomimetic odor-removing fiber [10]. For the purpose of the application to synthetic fiber with the odor-removing property, we recently synthesized thermoelastic polyurethane resins containing a Co(II)-Pc ring in the chain [11]. Polyester fibers are currently the most widely available synthetic fibers as textile goods. However, no evidence for the copolyester containing M-Pc in the main chain has been presented. The present paper concerns the synthesis and the catalytic property of polyesters containing M-Pc [M = Co(II),Fe(III)] in the main chain.

EXPERIMENTAL

Materials

(Dicarboxyphthalocyaninato)iron(III) as well as cobalt(II) (M-Dapc, M = Co(II) and Fe(III)) and the

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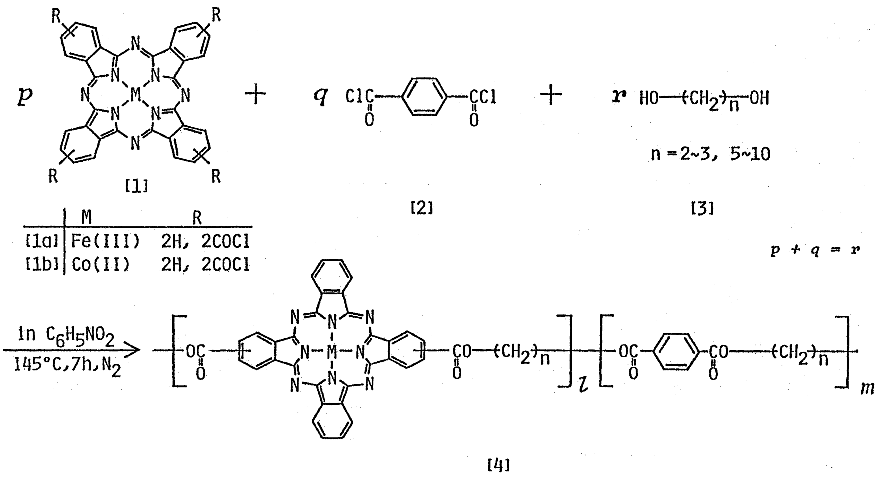

Scheme 1.

corresponding acid chlorides were prepared using the method reported earlier [12]. Aliphatic diols were of analytical grade from commercial origin and were purified by distillation under reduced pressure. Terephthalic acid chloride was prepared by the method of Shahoua and Eareckson [13]. Thionyl chloride and 1-decanol as well as the other solvents were reagent grade from commercial origin and used without further purification.

Preparation of Copolyesters Containing a M-Pc Ring in the Chain

A 100 ml three-necked flask fitted with stirrer, thermometer and reflux condenser was flushed with nitrogen with 7.2×10^{-5} mol of M-Dapc dichloride **1**, 7.2×10^{-5} mol of terephthalic acid chloride **2** and 20 ml of nitrobenzene. To the solution 14.4×10^{-4} mol of aliphatic diol **3** was added. The mixture was reacted with stirring at 175 °C for 7 h, and then the nitrobenzene was thoroughly distilled away. The resulting product was heated at 150 °C in vacuum for 2 h. A blue or green colored product was obtained. The crude polymer was purified by using chloroform–excess methanol as solvent–non-solvent combination, and dried at 60 °C in a vacuum oven for 40 h.

Measurement of Catalytic Activity

The reaction rates of autoxidation of thiol in the presence of the catalysts were measured based on the oxygen consumption in the reaction mixture with a micro-oxygen electrode. All experiments were conducted at 20–30 °C at a shaking speed of 150 rpm. Various pH solutions of 2-mercaptoethanol (RSH) were prepared by mixing 0.2 M Na_2CO_3 and 0.2 M $NaHCO_3$ aqueous solution. The exact concentration of the RSH stock solution was determined by reaction with an I_2 solution, followed by titrating the excess I_2 with a $Na_2S_2O_3$ solution. The initial reaction rate, ($V_0 = -d[O_2]/dt$ in mol^{-1} s^{-1}) was taken from the slope of the oxygen consumption. Actually, the amount of RSH oxidized by oxygen was calculated from the amount of oxygen consumed [14, 15].

General Procedure

The intrinsic viscosities were determined in 1,1,2,2-tetrachloroethane/phenol = 40/60 wt% mixed solution at 30 ± 0.1 °C in an Ubbelohde viscometer. The IR spectra were taken on KBr pellets with a JASCO-A-302 IR spectrophotometer and UV-vis spectra on a JASCO-UV DEC 525 apparatus. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were run on a RIGAKU- DENKI differential thermo-instrument of 8001 type at 10 K min^{-1} in air. Metal analyses were made with a Hitachi 170 - 70 Zeeman-effect atomic absorption spectrophotometer. ESR spectra were measured with a Varian E-line spectrophotometer that had 100 kHz field modulation. The operation was X-band (9.196 GHz for 77 K) and the microwave power was 100 MW. The samples in chloroform solutions were placed in quartz tubes of 4 mm i.d. for measurement at 77 K with liquid nitrogen. The g values were calculated by using solid 1,1-diphenyl-2-picrylhydrazyl (DPPH) as the g marker.

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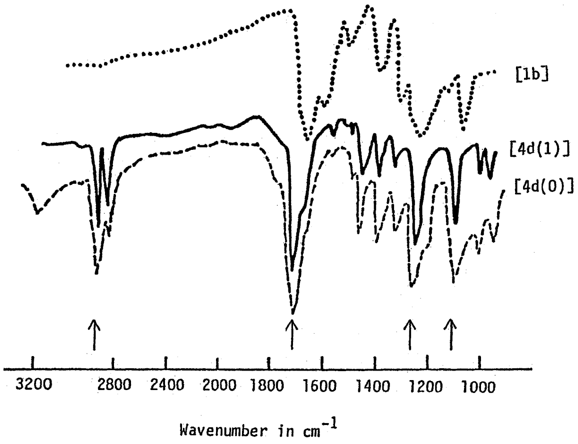

Fig. 1. Infrared spectra of **1b**, **4b(1)** and **4d(0)**

RESULTS AND DISCUSSION

Synthesis of Copolyesters Containing a M-Pc Ring in the Chain

As already described diacid chloride of M-Dapc **1** was synthesized from M-Dapc and thionylchloride [12]. **1** and terephthalic acid dichloride **2** were reacted with several aliphatic diols following Scheme 1.

The copolyesters containing a M-Pc ring in the chain were synthesized in two steps. The first-step reactions of **1** and **2** with several aliphatic diols were carried out at 175 °C for 7 h in nitrobenzene solution. The following compounds were used as the diol components: ethylene glycol, trimethylene glycol, 1,5-pentanediol, 1,6-hexanediol 1,7-heptanediol, 1,8-

Table 1. Preparation and properties of polyesters containing metallophthalocyanines

Compound			Mol.% of	Conc. of M-Pc	Yield	η_{inh}§	mp	Decomp. temp. (°C)	
	M	*n**	**1** in feed†	(mol%)‡	(%)	(dl/g)	(°C)	Initial	Main
4a	Co	2	1.0	8.47	4.4	0.020	204	260	368
4b	Co	3	1.0	4.89	10.5	0.039	124	258	351
4c	Co	5	1.0	5.28	19.3	0.152	128	318	374
4d(5)	Co	6	1.0	3.23	22.7	0.209	139	305	367
4e	Co	7	1.0	5.75	23.4	0.364	89	315	372
4f	Co	8	1.0	9.04	22.7	0.344	134	340	379
4g	Co	9	1.0	6.31	20.4	0.296	95	322	372
4h	Co	10	1.0	8.47	20.1	0.280	128	331	375
4i(1)	Fe	6	0.3	0.91	24.2	0.579	150	319	372
4i(2)	Fe	6	1.0	3.08	16.8	0.376	145	275	361
4d(0)¶	–	6	0.0	0.00	87.8	0.313	146	254	366
4d(1)	Co	6	0.1	0.25	22.9	0.680	149	310	379
4d(2)	Co	6	0.3	0.28	15.5	0.442	146	315	380
4d(3)	Co	6	0.5	1.15	19.5	0.173	138	312	367
4d(4)	Co	6	0.7	1.35	10.9	0.170	121	313	366
4d(5)	Co	6	1.0	3.23	22.7	0.209	139	305	367
4d(6)	Co	6	3.0	26.9	6.4	0.097	118	300	361

* Carbon number of diol.

† $100 \cdot p/(p+q+r)$ (see Scheme 1).

‡ Determined by metal analysis using an atomic absorption spectrometer $100 \cdot l/2\,(l+m)$ (see Scheme 1).

§ Measured in mixed solution 1,1,2,2-tetrachloroethane and phenol (40:60 wt %) at 30 °C.

¶ Poly(hexamethylene terephthalate).

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Table 2. Electronic spectra of copolyesters containing metallophthalocyanine in $CHCl_3$

Compound						
	M	*n*	λ_{max} in nm (log ε)			
4a	Co	2	372.6 (4.37)	616.2 (4.35)	320.1 (4.47)	288.5 (4.81)
4b	Co	3	669.3 (4.10)	619.6 (4.14)	318.5 (4.38)	286.3 (4.80)
4c	Co	5	668.4 (4.13)	617.7 (4.11)	321.7 (4.26)	286.1 (4.78)
4d(5)	Co	6	671.0 (4.42)	628.4 (4.49)	322.8 (4.63)	286.8 (4.48)
4e	Co	7	668.0 (4.21)	616.8 (4.18)	321.3 (4.34)	286.1 (4.76)
4f	Co	8	669.3 (4.15)	618.6 (4.08)	321.8 (4.25)	285.9 (4.65)
4g	Co	9	669.6 (4.32)	618.3 (4.23)	323.1 (4.39)	285.8 (4.82)
4h	Co	10	668.9 (4.23)	617.3 (4.14)	321.4 (4.35)	286.1 (4.70)
4i(1)	Fe	6	831.0 (4.05)	652.6 (4.63)	326.9 (4.73)	
4i(2)	Fe	6	832.8 (3.94)	651.3 (4.62)	331.5 (4.70)	
4d(1)	Co	6	673.0 (4.86)	622.5 (4.67)	325.1 (4.87)	
4d(2)	Co	6	669.7 (4.78)	622.6 (4.61)	323.4 (4.82)	
4d(3)	Co	6	670.9 (4.68)	614.5 (4.63)	325.8 (4.80)	
4d(4)	Co	6	669.6 (4.68)	616.0 (4.67)	324.0 (4.86)	
4d(5)	Co	6	670.2 (4.64)	630.5 (4.74)	323.8 (4.57)	
4d(6)	Co	6	669.7 (4.05)	616.3 (4.13)	323.4 (3.98)	

octanediol, 1,9-nonanediol and 1,10-decanediol. After the reaction, the nitrobenzene was distilled away. The resulting product was heated at 150 °C in vacuum for 2 h. The product was washed in alkaline water to remove the free M-Dapc in the product and was purified by dissolving it in chloroform and precipitating with excess methanol. By the purification, the polyester not containing M-Pc is removed from the reaction product. The intrinsic viscosities of the polymers **4a**–**4i** obtained from **1a**, **1b**, **2** and aliphatic diols ranged from 0.02–0.58 dl g^{-1}. The molecular weight of the copolyesters were *c*. 1.0–2.0 $\times$ 10^4 which were calculated by the Mark–Houwink–Sakurada equation using the literature data [16]. The infrared spectra of the film (a) obtained by the casting from chloroform solution of **4d(5)** and poly(hexamethyleneterephthalate) (b) are shown in Fig. 1. These spectra exhibited ester carbonyl bands at 1710, 1260 and 1095 cm^{-1}, and methylene bands at 2925 and 2850 cm^{-1}. All the copolyesters containing the M-Pc ring showed similar absorption bands.

From these results, it was confirmed that the copolyesters from **1**, **2** and 1,6-hexanediol were obtained. The similar reactions of the other diol components with **1** and **2** were also made. The yields and product characterizations of copolyesters containing the M-Pc ring are summarized in Table 1. Yields after purification were in the range of 4–88%. The loss of the polyester not containing the M-Pc component obtained from **2** and the diol component occurred during the purification of the products by a dissolution–precipitation process. The intrinsic viscosities of the copolyesters containing the Co(II)-Pc component decreased with increasing M-Pc components. The decreasing intrinsic viscosities of the copolyesters containing over 1.1 mol% M-Pc is due to the formation of the incompletely polymerized polymer by the large size of the Co(II)-phthalocyanine molecule. The green or blue fiber was formed by melt spinning of the copolyesters containing less than 1 mol% M-Pc component.

The electronic spectra for the copolyesters were measured in chloroform solution. The λ_{max} and log ε values of the polymers in the visible and ultraviolet region are listed in Table 2.

The absorption bands of the copolyesters containing

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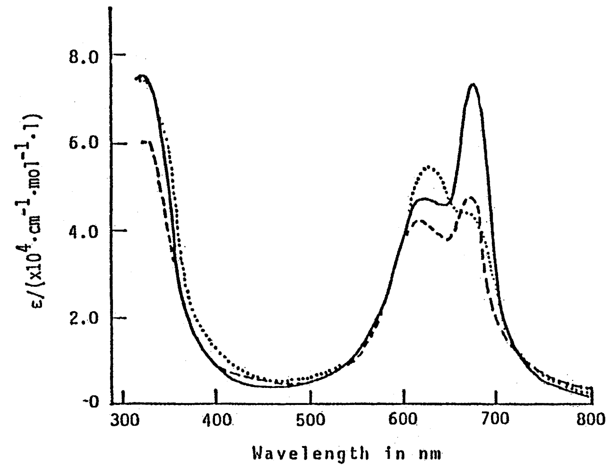

Fig. 2. Electronic spectra of polyesters containing Co(II)-Pc in $CHCl_3$ solution (—), **4d(1)**; (– – –), **4d(3)**; (....), **4d(5)**.

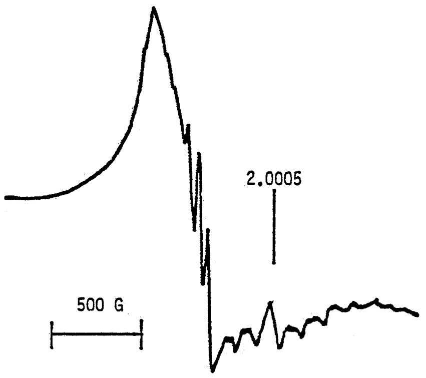

Fig. 3. ESR spectra of Co(II)-Pc in polyester **4d(5)** in $CHCl_3$ solution at 77K.

the Co(II)-Pc ring in the chain appear around 670 and 618 nm, which are attributable to a ligand-concentrated π–π^* transition (Q band) of cobalt phthalocyanine, similarly with an alkaline aqueous solution of Co(II)-Dapc.

The invisible region electronic spectra of the copolyesters containing 0.1 mol % **4d(1),** 0.5 mol % **4d(3)** and 1.0 mol % **4d(5)** of the Co(II)-Pc component in the main chain are shown in Fig. 2.

The absorption spectrum of **4d(1)** consisted of two absorption bands at 670 and 620 nm, which are assigned to the Q band of monomeric and aggregated cobalt phthalocyanine. On the other hand, **4d(3)** and **4d(5)** with the higher content of cobalt phthalocyanine exhibited a broad band around 620 nm, which is attributed to aggregation of cobalt phthalocyanine. The absorption coefficient at about 620 nm decreased with decreasing Co-Pc content in the polymer chain. This observation suggests that the dimerization of Co-Pc may be difficult by the steric hindrance of the polymer chain.

The ESR spectrum of copolyester **4d(5)** measured in chloroform solution at 77 K, is shown in Fig. 3. The value of $g_{\parallel} = 2.0005$ and $g_{\perp} = 2.269$ agree with the typical value of cobalt(II) $3d^7$ low-spin complexes, whereas eight lines h.f.s. in the higher magnetic field of the $g_{\perp}$ region are based on ^{59}Co ($I = 7/2$). The ESR spectrum agreed with that of Co(II)-Dapc. The results suggest that coordination of the oxygen atom on the hexamethylene chain to the central metal of the cobalt phthalocyanine ring does not occur.

The absorption bands of the copolymers containing the Fe(III)-Pc ring in the chain showed at 650 nm only. The absorption spectrum of monomer Fe(III)-Dapc exhibited absorption bands around 620 nm and a shoulder around 680 nm. The concentration of the Fe(III)-Pc monomer species may increase in the course of the polycondensation.

GENERAL PROPERTIES

Figure 4 shows TGA and DSC curves of three polymers **4d(0), 4d(1)** and **4d(5)**. The endothermic peaks at 139–149 °C can be attributed to the melting of these polymers. The T_m value of **4d(5)** was lower than those of **4d(0)** and **4d(1)**. These results show that the bulky Co-Pc component in the chain of the copolyesters distorts the orientation of the polymer chains. The T_m values of **4a** – **4h** showed zigzag irregularity for the number of methylene groups of the diol components, in analogy with many polycondensation

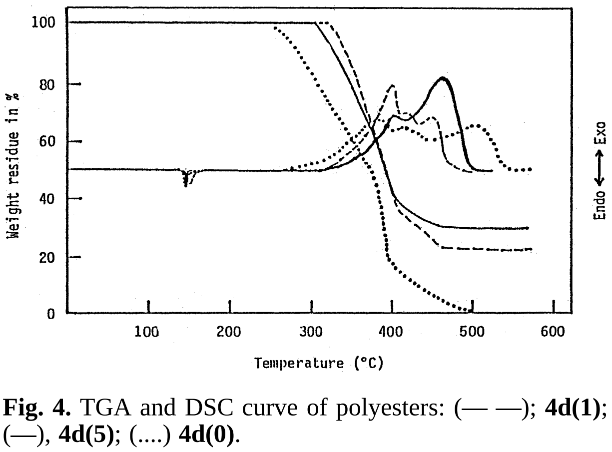

Fig. 4. TGA and DSC curve of polyesters: (— —); **4d(1)**; (—), **4d(5)**; (....) **4d(0)**.

Table 3. Solubility of polyesters containing metallophthalocyanines

Compound			Solvents										
	M	*n*	$CHCl_3$	CH_2Cl_2	p-Cre	NMP	DMAc	DMF	DMSO	Py	MeOH	Acetone	Ether
4a	Co	2	++	++	+	+	+	+	+	+	−	−	−
4b	Co	3	++	++	+	+	+	−	+	+	−	−	−
4c	Co	5	++	++	+	+	+	+	+	+	−	−	−
4d(5)	Co	6	++	++	++	+	+	+	+	+	−	−	−
4e	Co	7	++	++	+	+	+	−	−	+	−	−	−
4f	Co	8	++	++	++	−	+	+	−	+	−	−	−
4g	Co	9	++	++	++	+	+	+	−	+	−	−	−
4h	Co	10	++	++	++	+	+	−	−	+	−	−	−
4i(1)	Fe	6	++	++	+	+	+	+	−	+	−	−	−
4i(2)	Fe	6	++	++	+	+	+	+	−	+	−	−	−
4d(0)	–	6	++	++	+	+	+	+	+	+	−	−	−
4d(1)	Co	6	++	++	++	+	+	+	+	+	−	−	−
4d(2)	Co	6	++	++	++	+	+	+	+	+	−	−	−
4d(3)	Co	6	++	++	++	+	+	+	+	+	−	−	−
4d(4)	Co	6	++	++	+	++	+	+	+	+	−	−	−
4d(5)	Co	6	++	++	++	+	+	+	+	+	−	−	−
4d(6)	Co	6	++	++	+	++	+	+	+	++	−	−	−

++ : soluble at room temperature.
+ : soluble on heating.
− : insoluble.

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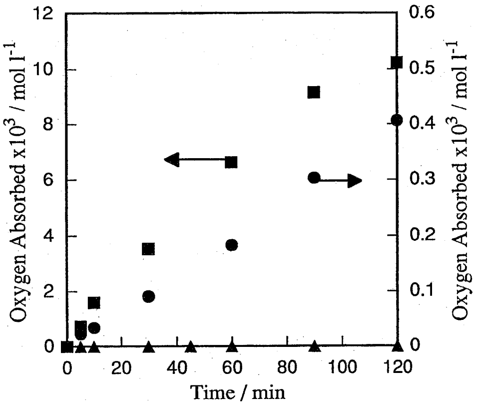

Fig. 5. Oxidation of 2-mercaptoethanol catalysed by Co(II)-Pc, [Co(II)-Pc] = 1.74×10^{-5} mol l^{-1}, [2-mercaptoethanol]$_0$ = 0.37 mol l^{-1}, [O_2]$_0$ = 2.38×10^{-4} mol l^{-1}, pH = 7.0, 25 °C. (■): **4a**, heterogeneous system; (●) Co(II)-Dapc, homogeneous system: ▲: **4d(0)**, **4b**, **4c**, **4d(5)**, **4e**, **4f**, **4g**, **4h**.

polymers containing aliphatic components [17]. TG curves of **4d(1)** and **4d(5)** containing 0.25 and 3.23 mol % Co-Pc, respectively, are shown in Fig. 4, compared with an original polyester **4d(0)**. **4d(0)** showed an initial weight loss at 245 °C, and extensive decomposition around 366 °C, and its DSC exhibited exothermic change in this region. On the contrary, the initial decomposition temperature of the Co(II)-Pc containing copolyester exhibited higher temperature above 90 °C. In this case, the rates of weight loss in the second-step region were very slow. The rates of weight loss in the second degradation step depend on the Co(II)-Pc content in the copolyesters. An increase in the content of Co(II)-Pc in the copolyesters increased the char yield. This indicates that the rigid molecular structure of phthalocyanine is resistant to thermal decomposition, and the Co(II)-Pc in the copolymer may act as a dehydration–carbonization catalyst, in analogy with metallophthalocyanine formaldehyde condensation resins [4] as reported by us previously.

The solubility of the copolyesters containing the M-Pc ring are summarized in Table 3. All the copolyesters are easily soluble in chloroform, dichloromethane etc and are soluble in aprotic solvents such as dimethylformamide (DMF) with heating.

Catalysis of Copolyesters Containing Co(II)-Pc for Autoxidation of Thiol

Figure 5 shows the amount of oxygen consumed in the autoxidation of 2-mercaptoethanol (RSH) catalysed by copolyesters containing 8.5 mol % Co(II)-Pc ring (**4a** – **4h**) in aqueous suspension at pH 7.0 and 25 °C, compared with Co(II)-Dapc in aqueous solution. Oxygen consumption was observed using only **4a** with 1,2-ethanediol as a diol component as a catalyst. It is well known that the autoxidation of thiols obeys equation 1, in which the consumption of four molecules of RSH is accompanied by that of 1 molecule of O_2 [18]. The consumption rate of 2-mercaptoethanol was determined by measuring the amount of O_2 consumed. The oxygen consumption was small using the copolyesters **4b** – **4h**, which contained diol components of long alkyl chains.

$$4\ \mathrm{RSH} + \mathrm{O_2} \xrightarrow{\mathrm{Cat}} 2\ \mathrm{RSSR} + 2\ \mathrm{H_2O} \qquad (1)$$

For this reason it is apparent that the hydrophobic groups in the copolyesters containing the long alkyl chains as diol components are hidden from hydrophilic RS$^-$. Therefore, RS$^-$ may not penetrate into the Co(II)-Pc active center. From Fig. 5, the copolyester obtained from 1,2-ethanediol as a diol component catalysed the autoxidation of RSH in the presence of oxygen. This polymer containing Co(II)-Pc can be molded into fibers, film, etc. Therefore, the polymers are useful as a new odor-removing fiber.

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