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The effect of ionic groups in copolyesters on the electrical conductivity of polypyrrole/copolyester composite films was investigated. The composite films were prepared by polymerizing pyrrole through vapor phase absorption onto the copolyester films that contained $FeCl_3$. The conductivity of polypyrrole/copolyester composite films increased with the DMS content up to 10 mol%. However, it decreased with DMS content when DMS content was greater than 10 mol%. This phenomenon was thought to be due to the inhomogeous distribution of DMS in the copolyesters. The ionic group was found to enhance the stability of composite films.

Keywords: anionic-group; copolyester; polypyrrole; composite; conductivity

INTRODUCTION

Preparation of conducting polymer composites by polymerizing polypyrrole in thermoplastic polymer matrices has been studied by many researchers in order to enhance the stability and the physical properties of polypyrrole[1-3].

In the previous study[4] we examined the effects of the ionic group content and the copolyester molecular structures on the electrical conductivity of polypyrrole(PPy)/copolyester composite films. We found that the conductivity of the composite films increased with the amount of 5-sodiosulfodimethyl isophthalate (DMS) in the copolyester up to 10 mol% and that the copolyesters having equal amounts of dimethyl terephthalate (DMT) and dimethyl isophthalate (DMI) with ethylene glycol (EG) showed the best electrical conductivity at the same DMS content. In the present study, we synthesized the copolyesters of the most promising structure with various DMS group content

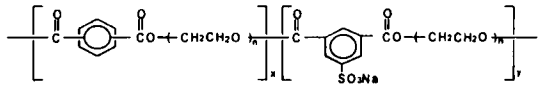
(from 0 to 19 mol%) and examined the electrical conductivity of the PPy/copolyester composite films.

EXPERIMENTAL

Copolyesters having DMT:DMI=1:1 and EG:DEG=1:0 were synthesized by conventional two-step polymerization as described in the previous study[4]. The DMS content was controlled to be from 0 to 19 mol%. Copolyester films were prepared by solution cast method from phenol/1,1,2,2-tatrachloroethane with 30 wt% of $FeCl_3$. The PPy/copolyester composites were prepared by vapor phase polymerization with the exposure time of 1 hr. The electrical conductivity was measured at room temperature by van der Pauw method[5].

RESULTS AND DISCUSSION

Table I shows the composition, intrinsic viscosity, and glass transition temperature of copolyester samples. DEG (diethylene glycol) and TEG (triethylene glycol) were formed by coupling reaction between diols[6]. Since the sulfonate anion will play an important role in conductive polymer composites, we have simplified the copolyester structure as follows:



where n means the average composition of diols and x is the DMS mole fraction in all the diacid derivatives present.

TABLE I. Properties of Anion-Containing Copolyesters

Sample	DMS (mol%)[a]	Diol composition(mole fration)[b]			[η] (dl/g)[c]	T_g(°C)[d]
		EG	DEG	TEG		
1	0	0.961	0.039	-	0.771	62.8
2	1.9	0.893	0.107	-	0.512	58.9
3	4.5	0.874	0.126	-	0.409	58.6
4	6.5	0.822	0.178	-	0.379	56.2
5	8.0	0.618	0.303	0.079	0.350	45.4
6	10.3	0.648	0.283	0.069	0.310	44.6
7	12.2	0.617	0.305	0.078	0.309	48.1
8	14.5	0.646	0.283	0.071	0.270	49.6
9	16.8	0.632	0.273	0.095	0.224	49.5
10	19.0	0.570	0.314	0.116	0.217	53.4

[a] Determined by Perkin Elmer Atomic Absorption Spectroscopy Model-3300
[b] Determined by Gas Chromatography HP 5890 Series II
[c] Measured from the dilute solutions in a phenol/1,1,2,2-tetrachloroethane mixture (volume ratio 1:1) at 30°C
[d] Determined by TA Instruments DSC 2910 under nitrogen purging with a heating rate of 20°C/min.

Figure 1 shows the variation of conductivity of PPy/copolyester composite films with DMS content. The conductivity increases with the DMS content up to 10 mol%. However, it decreases with DMS content when DMS content is greater than 10 mol%. In the previous study we have tested the effect of anionic group on the conductivity of the polypyrrole composite of PET based copolyesters containing DMS from 0 to 10 mol%. We found that conductivity increased with DMS content and converged to some saturated value when the DMS content reached 10 mol%. However, we did not expect that conductivity decreased after passing 10 mol%. Figure 2 shows the PPy content in composite films, which was determined by elemental analysis. PPy increased with DMS content and reached maximum value when DMS content was 14.5 mol% and decreased after then. However, the behavior does not coincide with the conductivity results. The samples having DMS over 6.5 mol% still show high PPy content, which means that conductivity decrease after 10 mol% is not due to the decrease in PPy content. Figure 3 shows the DSC heating thermograms in the glass transition temperature region. As can be seen in Figure 3 and Table I, T_g decreases with DMS content till 10 mol% and increases after that composition. The temperature range of glass transition is narrow when DMS content is up to 10 mol%. However, when DMS content is greater than 10 mol%, the temperature range is broaden and Tg increases. This means that the ionic groups in copolyesters are uniform throughout the samples when DMS content is less than 10 mol%, while they are not when DMS is greater than 10 mol%. If the DMS groups are not uniformly distributed, the attached PPy could not form an effective conduction path, which results in the decrease in conductivity. This may be an explanation for the conductivity decrease when the DMS content is greater than 10 mol%.

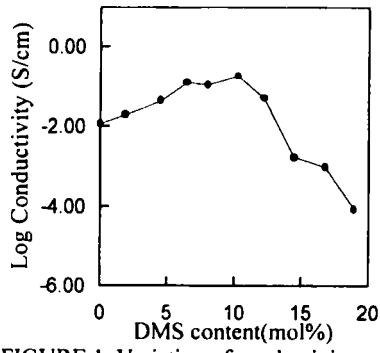


FIGURE 1. Variation of conductivity with DMS contents.

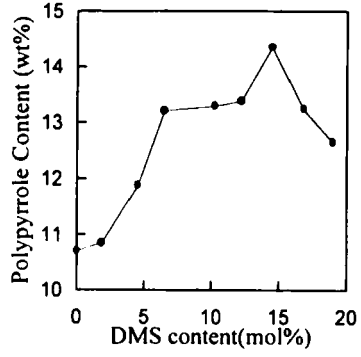


FIGURE 2. Plot of PPy content vs. DMS content in copolyesters.

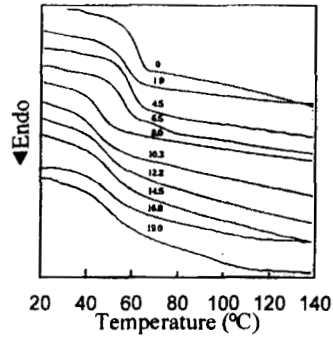


FIGURE 3. DSC thermograms of copolyesters.

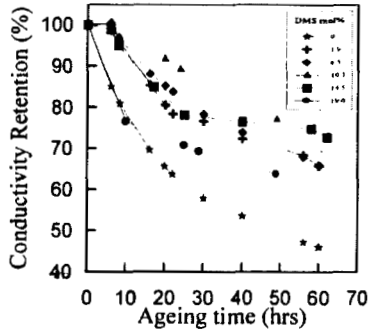


FIGURE 4. Variation of conductivity retention with ageing time.

Figure 4 shows the effect of ionic group on the stability of the composite films. The conductivity of samples which were aged at 100°C was plotted with ageing time. The DMS containing samples show enhanced thermal stability of conductivity.

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