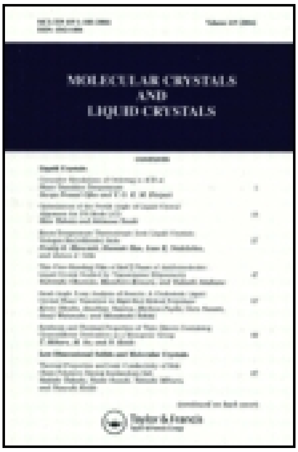

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Effect of Physical Structure of Matrix Copolyester on the Conductivity of Polypyrrole/Copolyester Composite Films

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Effect of Physical Structure of Matrix Copolyester on the Conductivity of Polypyrrole/Copolyester Composite Films

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The effect of physical structure of matrix copolyester 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 anion-containing copolyester films prepared from copolyester/phenol-TCE/$FeCl_3$ mixture. 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 interpreted according to the physical structure of the copolyester. From the observed and calculated T_g data, we found that after 10 mol% inhomogeneous distribution of DMS groups became serious, which suggested that many DMS groups gathered together. This micro-phase separation will lengthen the average distance between DMS units which can act as reaction sites for pyrrole polymerization and consequently reduce the electrical conductivity of the PPy composite film. These phenomenon may be one of the important reasons for the conductivity variation in this composite system.

Keywords: copolyester; polypyrrole; composite film; conductivity; physial structure; glass transition temperature

INTRODUCTION

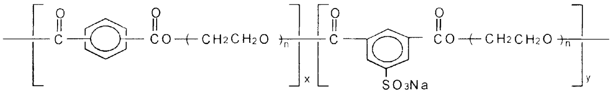
In the previous study[1] we synthesized the ionic group containing copolyesters and examined the effects of the ionic group content on the electrical conductivity of polypyrrole/copolyester composite films. We found that the conductivity of the composite films increased with the amount of 5-sodiosulfodimethyl isophthalate (DMS) in the copolyester up to 10 mol% and decreased with DMS content when DMS content was greater than 10 mol%. In the present study, we investigated the reason why the electrical conductivity was maximum when DMS content was around 10 mol% by correlating the physical structure of the matrix copolyester with its electrical conductivity.

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[2,3]. 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 polypyrrole/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 as descibed in the previous reports[2,3].

RESULTS AND DISCUSSION

The copolyesters used in this study have the following structure:



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

Table I shows the composition, intrinsic viscosity, glass transition temperature (T_g), and glass transition range of copolyester samples used. Figure 1 shows the variation of conductivity of polypyrrole/copolyester composite films with DMS content. The conductivity of the composite films increased with the DMS content up to 10 mol%. However, it decreases with DMS content when DMS content is greater than 10 mol%. In the composite film the anionic site will act as a polymerization site of pyrrole and therefore the conductivity may increase with anionic group content. However, Figure 1 shows maximum at 10 mol% of DMS.

In the previous reports[2,3] we found that the amount of ionic group governed the average distance between the polymerization centers and consequently the conductivity of the composite film increased with DMS

TABLE I. Properties of Anion-Containing Copolyesters

Sample	DMS (mol%)[a]	Diol composition(mole fration)[b]			$[\eta]$ (dl/g)[c]	T_g (°C)[d]	T_g range[d]
		EG	DEG	TEG			
1	0	0.961	0.039	-	0.771	62.8	8.6
2	1.9	0.893	0.107	-	0.512	58.9	12.9
3	4.5	0.874	0.126	-	0.409	58.6	12.7
4	6.5	0.822	0.178	-	0.379	56.2	13.0
5	8.0	0.618	0.303	0.079	0.350	45.4	13.0
6	10.3	0.648	0.283	0.069	0.310	44.6	14.0
7	12.2	0.617	0.305	0.078	0.309	48.1	17.9
8	14.5	0.646	0.283	0.071	0.270	49.6	23.0
9	16.8	0.632	0.273	0.095	0.224	49.5	28.6
10	19.0	0.570	0.314	0.116	0.217	53.4	32.9

[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(1:1 by vol.) at 30 °C
[d] Determined by TA Instruments DSC 2910 under nitrogen purging with a heating rate of 20 °C/min.

concentration in the conduction path. It means that a composite film having high DMS content may have low conductivity when DMS is distributed inhomogeneously. The data for glass transition range in Table I shows a sign of inhomogeneity. In order to draw out more information we calculated non-ionic matrix T_g and ionic matrix T_g according to the group contribution theory[4] and Fox equation[5]. We used 196 °C for T_g of the 100 mol% DMS polymer which was synthesized from DMS and ethylene glycol. Figure 2 shows variation of T_g's and T_g difference with DMS content, respectively. As can be seen in Figure 2 the observed T_g always shows the minimum value except sample 10. Generally ionic group stiffens the polymer chain and consequently increases T_g. However, the inclusion of DMS reduced the T_g in this copolyester system, which suggested the softening effect of DMS. As can be seen in Table I and Figure 2 non-ionic matrix T_g decreased with DMS content up to 10 mol% due to the increasing amount of the flexible ether groups in the copolyesters. The softening effect of DMS additionally lowered the T_g. As confirmed by the T_g range data in Table I, after 10 mol% inhomogeneous distribution of DMS groups became serious, which suggested that many DMS groups gathered together. This micro-phase separation will increase T_g. This will also lengthen the average distance between DMS units and consequently reduce the electrical conductivity of the composite film. This phenomenon may be one of the important reasons for the conductivity variation shown in Figure 1. Fugure 4 shows the relationship between conductivity and T_g.

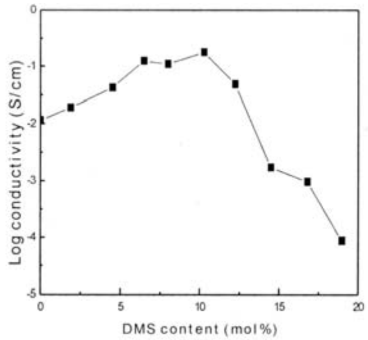


FIGURE 1. Variation of conductivity with DMS contents.

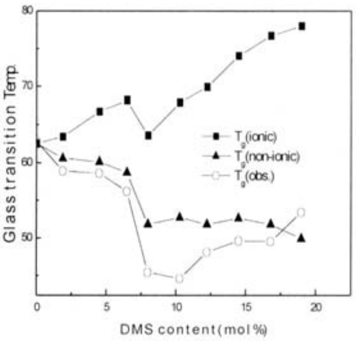


FIGURE 2. Variation of T_g with DMS contents.

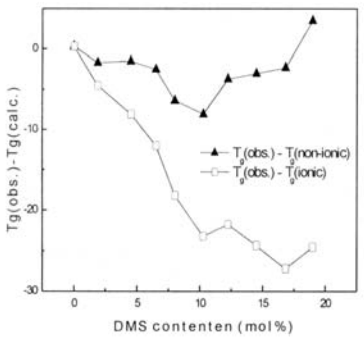


FIGURE 3. Variation of T_g difference with DMS contents.

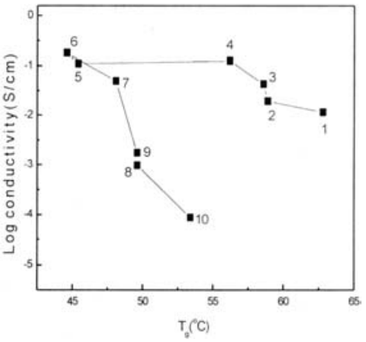


FIGURE 4. Relation between T_g and conductivity. Number denotes sample number.

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