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Effect of copolyester structure on the conductivity of polypyrrole/copolyester composite films

Doo Hyun Baik[1,*], **Gil Lae Kim**[1], **Yun Heum Park**[2], **Youngkwan Lee**[3], **Yongkeun Son**[4]

[1] Department of Textile Engineering, Chungnam National University, Daejon 305-764, Korea
[2] Department of Textile Engineering, Sung Kyun Kwan University, Suwon 440-746, Korea
[3] Department of Chemical Engineering, Sung Kyun Kwan University, Suwon 440-746, Korea
[4] Department of Chemistry, Sung Kyun Kwan University, Suwon 440-746, Korea

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Summary

The effect of ionic group content and main chain structure of 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 and reached its maximum when the DMS content reached about 10 mol%. The conductivity increased dramatically when DMS content was more than 5 mol% that was considered as the critical composition for polypyrrole continuity. The conductivity increased with the EG content at the same DMT/DMI ratio and showed maximum when DMT:DMI ratio was 1:1.

Introduction

Since their discovery[1,2], electrically conducting polymers have drawn considerable attention as possible substitutes for metallic conductors or semiconductors in a wide variety of electrical devices[3,4]. However, most conducting polymers are environmentally unstable and have poor processability and physical properties[4]. Many investigations have been carried out in order to overcome these difficulties. Preparation of conducting polymer composites by polymerizing conductive polymers in thermoplastic polymer matrices is one of those investigations. These conductive polymer composites are strong and environmentally stable, while maintaining good electrical conductivity.

Polypyrrole has attracted great interest for these conductive polymer composites applications because it can be easily prepared by electro-chemical or chemical polymerization. Morita et. al.[5] prepared polypyrrole/PMMA composite film with the chemical oxidative polymerization by spreading the water-insoluble solvent solution of pyrrole and PMMA mixture on the surface of the aqueous solution containing oxidizing agent. Ruckenstein and Park[6] made a polypyrrole/(porous crosslinked polystyrene) composite whose conductivity can be as high as 0.80 S/cm. Polypyrrole/PVA[7], polypyrrole/PVC[8], polypyrrole/polyimide[9], and polypyrrole/polyurethane composites[10] were also investigated. All these studies revealed that the polypyrrole composites have good mechanical properties and environmental stability retaining their high electrical conductivity.

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[*] Corresponding author

In the present study, copolyesters containing ionic groups were synthesized with various main chain structures and then polypyrrole/copolyester composites were prepared by polymerizing pyrrole through vapour phase absorption onto the copolyester films. The effects of the ionic group contents and the copolyester molecular structures on their electrical conductivity were investigated.

Experimental

Synthesis and characterization of copolyesters

Copolyesters were synthesized by conventional two-step polymerization in a lab scale polymerization reactor from dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), and 5-sodiosulfodimethyl isophthalate (DMS) as acid derivative parts and ethylene glycol (EG) and diethylene glycol (DEG) as diol parts[11,12]. Monomers were mixed with ester-interchange catalysts, zinc acetate and tetrabutyl titanate, and heated at 250°C for about 2 hours. Polycondensation reaction was conducted under vacuum just after ester-interchange reaction. All the polymerization reactions were performed under the same reaction conditions.

Two series of copolyesters were synthesized. The "A-series" copolyesters were copolyesters synthesized from DMT, EG, and DMS with different DMS contents, which resulted in total eight copolymers based on poly(ethylene terephthalate) having various DMS contents upto about 10 mol%. The "B-series" copolyesters were synthesized from different DMT/DMI and EG/DEG ratios although they all had similar DMS contents, about 10 mol%. A-series and B-series copolyesters were designed for investigating the effects of DMS contents and copolyester main chain structures on the electrical conductivity, respectively.

DMS contents were calculated from the sodium contents of copolyester samples. Samples degraded by H_2SO_4, HNO_3, and $HClO_4$ were analyzed by Perkin Elmer Atomic Absorption Spectrometer Model-3300 for the determination of sodium contents. ^{1}H-NMR spectroscopy(BRUKER AVANCE DRX 300 FT-NMR) was used for determining DMT:DMI ratio in the copolyesters. CF_3COOD was used for an NMR solvent. GC (Gas Chromatography HP 5890 Series II) were used for determining diol ratios in the copolyesters. HP-20M (Carbowax 20M) column and thermal conductivity detector (TCD) were used for GC analysis.

The intrinsic viscosities of the dilute solutions in a phenol/1,1,2,2-tetrachloroethane mixture (volume ratio 1:1) at 30 °C was measured using an Ubbelohde viscometer. The melting temperatures and the glass transition temperatures were determined by Perkin Elmer DSC-4 under nitrogen purging with a heating rate of 20 °C/min.

Preparation of polypyrrole/copolyester composite films

Copolyesters were solvated with 30 wt% of oxidizing agent ($FeCl_3$) by phenol/1,1,2,2-tetrachloroethane. The solution was cast onto glass plate and dried in vacuum at room temperature for 72 hours. The final films were of 50-70 μm thickness.

The prepared films were exposed to pyrrole vapor in a glass reactor controlled in a static vacuum of 60 torr. Under reduced pressure liquid pyrrole molecules vaporized and were absorbed in the film. The absorbed pyrrole was polymerized on the anionic sites of copolyesters with the aid of $FeCl_3$. The exposure time was selected as 15, 30, and 60 minutes because there showed no significant changes in electrical conductivity after 60 minutes from a preliminary experiment.

Measurement of electrical conductivity

The electrical conductivity of polypyrrole/copolyester composite films was measured at room temperature by van der Pauw method[13]. The voltage changes (V) when the films were under constant electrical current (I) were measured. The electrical conductivity was calculated from the equation, $\sigma = V^{-1}I\ (\ln 2/\pi d)$, where d is the thickness of film.

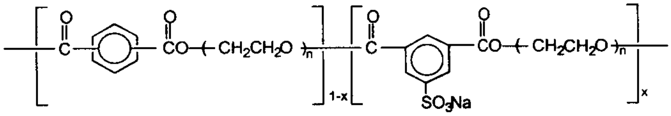
Results and discussion

Compositions of the copolyesters

In polymerization of polyesters, coupling between diols always occurs[14]. Hence, even in A-series copolyesters whose diol monomer is EG only, DEG or TEG (triethylene glycol) can be formed through coupling reaction. It means that the copolyesters synthesized in this study should be considered as random copolymers synthesized from DMT(T), DMI(I), DMS(S), EG(E), DEG(D), and TEG(Tr), which have the following general structure:

$$\text{-(-T-E-)}_a\text{-(-T-D-)}_b\text{-(-T-Tr-)}_c\text{-(-I-E-)}_d\text{-(-I-D-)}_e\text{-(-I-Tr-)}_f\text{-(-S-E-)}_g\text{-(-S-D-)}_h\text{-(-S-Tr-)}_i\text{-}$$

where subscripts denote mole fractions of structural units. Since the sulfonate anion will play an important role in conductive polymer formation, we have simplified the above structure as follows:



where n means the average composition of diols and x is the DMS mole fraction in all the diacid derivatives present. Obviously, n and x are equal to (a+d+g)+2(b+e+h)+3(c+f+i) and (g+h+i), respectively. The ring substitution in the first parenthesis is para and meta.

Table 1 and Table 2 show the copolymer compositions, where DMT/DMI and EG/DEG/TEG ratios in copolymers were determined by ^{1}H-NMR spectroscopy and GC, respectively. The A-8 and B-1 are the same samples. The DMS content can be calculated from the sodium content in polymer, which was determined by atomic absorption spectrometry, with the aid of DMT/DMI and EG/DEG/TEG ratios.

Table 1. Properties of A-series copolyesters

sample	x	n	diol composition(mole fraction)			[η] (dl/g)	T_g (°C)	T_m (°C)
			EG	DEG	TEG			
A-1	0.013	1.07	0.930	0.070	-	0.724	75.9	239.7
A-2	0.025	1.05	0.952	0.048	-	0.571	76.3	237.6
A-3	0.035	1.08	0.922	0.078	-	0.448	75.1	228.7
A-4	0.047	1.07	0.933	0.067	-	0.506	70.9	224.8
A-5	0.061	1.04	0.963	0.037	-	0.360	74.7	220.0
A-6	0.073	1.10	0.903	0.097	-	0.311	78.4	-
A-7	0.087	1.20	0.818	0.168	0.014	0.310	70.7	-
A-8	0.103	1.80	0.457	0.285	0.258	0.313	32.2	-

Table 2. Properties of B-series copolyesters

sample	feed ratio		composition (mole ratio)		x	n	[η] (dl/g)	T_g (°C)
	DMT/DMI	EG/DEG	DMT/DMI	EG/DEG/TEG				
B-1	1/0	1/0	1/0	0.457/0.285/0.258	0.103	1.801	0.313	32.2
B-2	0.5/0.5	1/0	0.505/0.495	0.473/0.372/0.155	0.103	1.682	0.434	32.6
B-3	0/1	1/0	0/1	0.532/0.331/0.135	0.108	1.599	0.317	32.2
B-4	1/0	0.5/0.5	1/0	0.331/0.460/0.209	0.116	1.878	0.397	25.9
B-5	0.5/0.5	0.5/0.5	0.505/0.495	0.203/0.569/0.228	0.100	2.025	0.414	24.4
B-6	0/1	0.5/0.5	0/1	0.217/0.532/0.251	0.104	2.034	0.450	22.8
B-7	1/0	0/1	1/0	0.046/0.914/0.039	0.095	2.034	0.462	28.1
B-8	0.5/0.5	0/1	0.504/0.496	0.063/0.856/0.080	0.106	2.015	0.470	23.5
B-9	0/1	0/1	0/1	0.092/0.762/0.146	0.105	2.053	0.476	24.4

Exact copolymer compositions or compositional parameters from a to i can be easily calculated with these data. For example, in sample B-2, since DMT:DMI:DMS=(1-0.103)×0.505:(1-0.103)×0.495:0.103= 0.453:0.444:0.103, a, d, and g will be (EG mole fraction)×(0.453), (EG mole fraction)×(0.444), and (EG mole fraction)×(0.103), respectively. Other compositional parameters can be calculated with similar method.

As can be seen in Table 1, DEG or TEG content increases with DMS content and there is a dramatic increase near 10 mol% of DMS. It is generally known that DEG can be easily formed when zinc compound is used for ester-interchange catalyst and DMS content is high[15]. The DMT/DMI ratio in B-series copolyesters is found to be always the same as the feed ratio within reasonable error range.

Table 1 shows the intrinsic viscosities decrease with increasing DMS content for the A-series samples. In case of B-series copolyesters, high EG contents samples have low intrinsic viscosity except sample B-2 as shown in Fig. 1.

Thermal properties of copolyesters

The glass transition temperatures (T_g) and the melting temperatures (T_m) of copolyester samples are shown in Tables 1 and 2. The glass transition temperatures were measured at the second heating thermogram after quenching. In A-series copolyesters melting temperature decreases with increasing DMS content. Samples A-6 to A-8 do not show any traces of melting as confirmed by Fig. 2. Since the melting temperature is a transition temperature of crystalline solid to liquid or melt, a copolymer which has high DMS content or high molecular irregularity will have low chance of crystallization and consequently have low melting temperature and low crystallinity.

The glass transition temperature of A-series samples, which does not vary significantly when DMS content is less than 7.3 mol%, decreases dramatically when DMS content is greater than 8.7 mol%. Fig. 3 shows the variation of T_g with EG mole fraction for A-series copolyesters, which implies that EG mole fraction is very important for T_g. Since the glass transition temperature is highly dependent of the molecular flexibility, the ether linkage of DEG or TEG can make the chain more flexible and consequently T_g will decrease with increasing DEG or TEG content. Since the samples A-1 through A-6 have similar amounts of DEG, they have similar T_g. In Fig.4, T_g of B-series samples is thought to increase with EG mole fraction, though this trend is not obvious in low EG content samples.

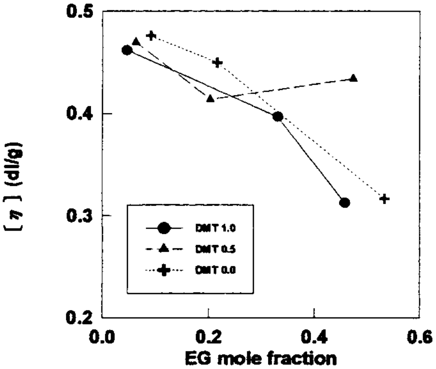


Fig. 1. Variation of intrinsic viscosity, [η], with EG mole fraction for B-series copolyesters.

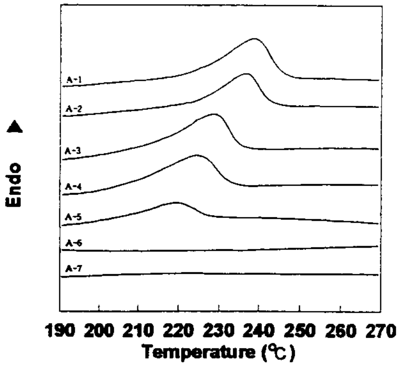


Fig. 2. Melting behavior of A-series copolyesters.

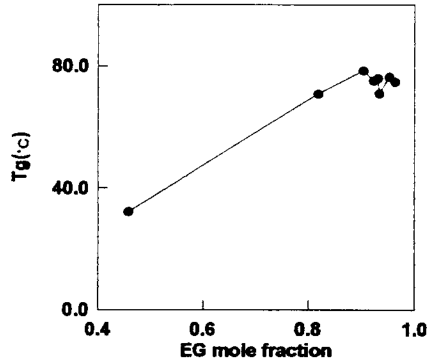


Fig. 3. Relation between T_g and EG mole fraction for A-series copolyesters.

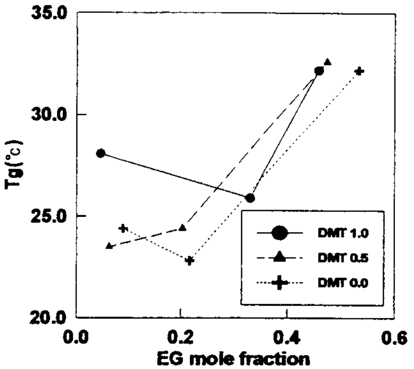


Fig. 4. Relation between T_g and EG mole fraction for B-series copolyesters.

Electrical conductivity of polypyrrole/copolyester composites

Fig. 5 shows how the amount of DMS affects the electrical conductivity of pyrrole/copolyester composite films obtained from A-series samples. The conductivity increases with exposure time and DMS content. When the DMS content is greater than 5 mol%, we can find considerable increase of the conductivity. Since the sulfonate anion is the initiation site of pyrrole polymerization, the increase of DMS content can make the neighboring polypyrrole more close. Finally, just above a certain critical DMS content, they can form a continuous conduction path. The DMS content of 5 mol% is considered as the critical composition for polypyrrole continuity. The conductivity converges to a maximum value when DMS content reaches 10 mol%.

The effect of molecular structure on the conductivity is investigated for B-series copolyesters. Fig. 6 through Fig. 8 show the variation of conductivity with copolymer composition at the exposure time of 15, 30, and 60 minutes, respectively. As can be seen in Figures 6 through 8 the conductivity shows high value when DMT:DMI is 1:1. In the case of DMT:DMI=1:1, the amorphous matrix may have less dense structure than those of pure DMT or DMI and help the diffusion of pyrrole molecules, which may result in conductivity increase.

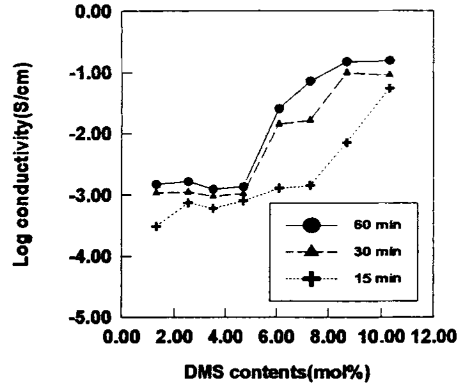


Fig. 5. Variation of conductivity with DMS contents for A-series copolyesters.

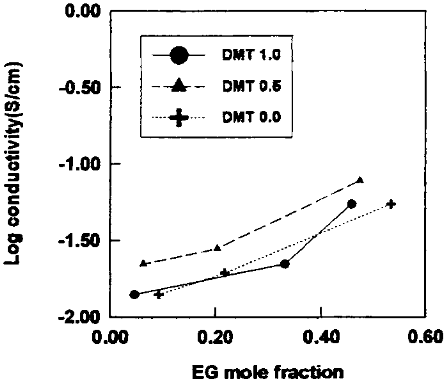


Fig. 6. Plots of Log(conductivity) vs. EG mole fraction for B-series samples at the exposure time of 15 min.

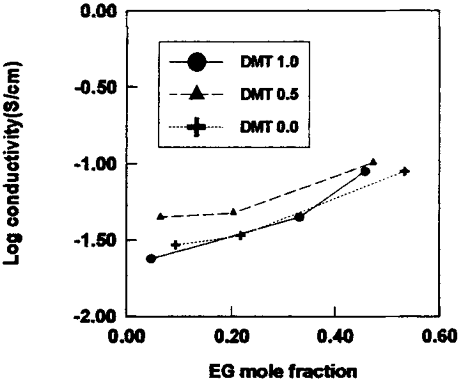


Fig. 7. Plots of Log(conductivity) vs. EG mole fraction for B-series samples at the exposure time of 30 min.

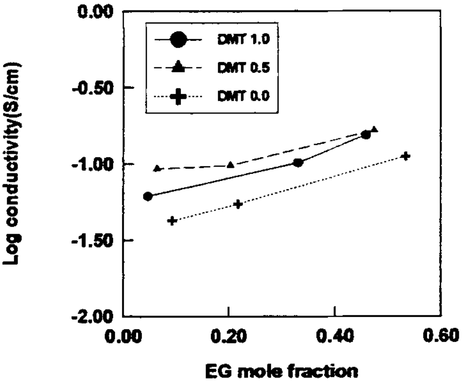


Fig. 8. Plots of Log(conductivity) vs. EG mole fraction for B-series samples at the exposure time of 60 min.

Figures 6 to 8 also show that the conductivity increases with EG content. However, the reason why EG helps electrical conduction is not clear. As can be seen in Figures 1 and 4, the EG content in B-series copolyesters is closely related to the intrinsic viscosity and T_g. As the EG content increases, from the general trends shown in Figures 1 and 4, the intrinsic viscosity decreases, while T_g increases. It means that the increasing conductivity with EG content may be due to the increased T_g or the decreased intrinsic viscosity. The high T_g means low flexibility of molecular chain. It is not reasonable to say that less flexible amorphous chain can help the electrical conduction, because flexible or loose amorphous chain may help the pyrrole vapor diffusion into the film. We have checked the effects of EG content and intrinsic viscosity, separately. Fortunately, we had three copolyester samples that have nearly 10 mol% of DMS with the same DMT/DMI ratio and various diol fractions, where the intrinsic viscosity increases with EG content. The electrical conductivity measurement of the pyrrole composite film from these three samples showed that electrical conductivity increased with decreasing intrinsic viscosity or with increasing EG content[16]. These results imply that the conductivity increase is not because of the decreased copolyester molecular weight but because of the increased EG content. Though the effect of EG content on conductivity cannot be explained successfully at the present time, the effect seems to be obvious. Further investigation will be pursued on this subject.

Conclusions

The effect of ionic group content and main chain structure of copolyesters on the electrical conductivity of polypyrrole/copolyester composite film was investigated. The conductivity of polypyrrole/copolyester composite film increased with the DMS content of the matrix copolyester and converged to a maximum value when the DMS content reached 10 mol%. The conductivity increased dramatically when DMS content was greater than 5 mol% that was thought to be the critical composition for polypyrrole continuity. Examinations concerning the effect of copolyester molecular structure on the conductivity revealed that the conductivity increased with the EG content at the same DMT/DMI ratio and reached its maximum when DMT:DMI ratio was 1:1.

Acknowledgement

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