

## Synthesis and Characterization of Copolyester Sizing Agents

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**Abstract:** The effect of main chain structure of anion-containing copolyesters on the properties of copolyester sizing agents was investigated. The copolyesters were prepared by conventional two step polymerization technique from DMT, DMI, DMS, EG, and DEG. The copolyesters synthesized were characterized by atomic absorption spectroscopy, <sup>1</sup>H-NMR Spectroscopy, GC, FTIR Spectroscopy, and DSC. The solubility decreased as the DMT content increased. The copolyesters having DMT:DMI = 1:1 showed the minimum viscosity. The effect of EG content on the solution stability was not clear and the samples having high DMI content showed better solution stability. The water resistance was best when only DMI and EG were used, while it was worst when DMT:DMI was 1.0.

**Keywords:** Anion-containing copolyester, Sizing agent, Solubility, Solution stability, Water resistance

### Introduction

Anion-containing copolyesters have been developed by many polyester manufacturing companies because they have unique properties. The anion-containing copolyesters are cation-dyeable. Copolyesters which have 5-sodiosulfodimethyl isophthalate (DMS) in the main chain can be dyed with cation dyes and consequently they can have a vivid color. Another important property of the anion-containing copolyesters is the water dispersibility. Since copolyesters having large amounts of DMS are soluble or dispersible in water, they can be used as sizing agents for weaving. These copolyester sizing agents usually have low viscosity and good adhesion power at the room temperature. Since many new synthetic fibers, e.g., Shin-Gosen, need low temperature sizing process, the applicability of these copolyester as low temperature sizing agents has drawn a considerable attention in the textile industries.

In the present study, the effect of molecular structure on the properties of anion-containing copolyester sizing agents was investigated. The DMS was used as an anion-containing group. We varied the DMT/DMI and EG/DEG ratios in order to obtain various main chain structures. The effects of molecular structure on the properties of copolyesters such as solubility, solution viscosity, solution stability, and water resistance were examined.

### Experimental

#### Synthesis of Copolyesters

Copolyesters were synthesized by conventional two-step polymerization technique in a lab-scale polymerization reactor. Dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), and 5-sodiosulfodimethyl isophthalate (DMS) were used as acid derivative parts and ethylene glycol (EG) and diethylene glycol (DEG) as diol parts[1,2]. Monomers were mixed with ester interchange catalysts, zinc acetate and *t*-butyl titanate,

and heated at 250°C for about 2 hours. After ester interchange reaction, polycondensation reaction was conducted under vacuum.

Nine samples of copolyesters having similar DMS contents, about 10 mol%, were synthesized with different DMT/DMI and EG/DEG ratios.

#### Intrinsic Viscosity Measurement

The intrinsic viscosities of the dilute polymer solutions were measured in a phenol/1,1,2,2-tetrachloroethane mixture (volume ratio 1:1) at 30°C using an Ubbelohde viscometer.

#### Copolyester Composition Determination

DMS contents were calculated from the sodium contents of copolyester samples[3]. The sodium contents of the samples degraded by H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and HClO<sub>4</sub> were measured by Perkin Elmer atomic absorption spectroscopy model-3300.

<sup>1</sup>H-NMR spectroscopy (BRUKER AVANCE DRX 300 FT-NMR) was used for determining DMT:DMI ratio in the copolyesters. CF<sub>3</sub>COOD was used for an NMR solvent.

GC (gas chromatography HP 5890 Series II) was used for determining diol ratios in the copolyesters. HP-20M (Carbowax 20 M) column and thermal conductivity detector (TCD) were used for GC analysis. The polymer samples were methanolized before GC analysis[4].

#### Thermal Analysis

The glass transition temperatures were determined by Perkin Elmer DSC-4 under nitrogen purging with a heating rate of 20°C/min. The second heating thermograms after quenching were used for T<sub>g</sub> measurement.

#### Solubility Measurement

Solubility of a copolyester in water was determined by measuring the critical concentration of a copolyester in water at 20°C, at which the solution lost its fluidity. About 40 wt% of a copolyester was completely dissolved in water at 80°C and then cooled to 20°C. If the solution still had a fluidity, a small amount of a copolyester was added. The process was

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repeated until the solution could not flow at 20°C.

### Solution Stability Determination

The stability of the copolyester aqueous solution was determined by measuring the concentration change of the solution. The 20 wt% aqueous solution of the copolyester in a long glass tube was maintained at 20°C in a temperature controlled water bath. After 24 hours, the solution at the top of the glass tube was sampled and dried. The concentration of the top solution was used to compare the solution stability.

### Water Resistance Evaluation

The 20 wt% aqueous solution of a copolyester was casted on the PET film and then dried at room temperature followed by subsequent vacuum drying at 80°C for 48 hours. The film of about 0.3 g was maintained in 20°C water for 2 hours and dried. The water resistance was calculated by the weight ratio of the film after and before treating in water.

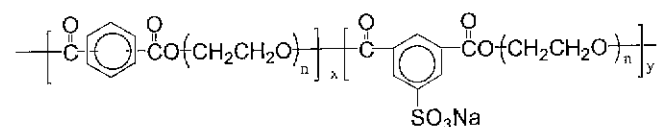
### Solution Viscosity Determination

The viscosity of 20 wt% aqueous solution of a copolyester was measured by Irvine-Park falling needle viscometer model FNV-200 at 60°C.

## Results and Discussion

### Compositions of the Copolyesters

In polymerization of a diol and a diacid, coupling between diols usually occurs[5]. Hence, even in a copolyester whose diol monomer is EG only, DEG or TEG (triethylene glycol) can be formed through coupling reaction. Hence, a copolyester synthesized in this study will have the following structure:



where  $n$  and  $x$  mean the average composition of diols and the DMS mole fraction in all the diacid derivatives present, respectively. The ring substitution in the first parenthesis can

vary depending on the DMT/DMI ratio.

Table 1 shows the monomer feed ratios and copolymer compositions, where DMT/DMI and EG/DEG/TEG ratios in copolymers were determined by  $^1\text{H-NMR}$  spectroscopy and GC, respectively. The DMS content was calculated from the sodium content in polymer, which was determined by atomic absorption spectroscopy, with the aid of DMT/DMI and EG/DEG/TEG ratios. It is generally known that DEG can be easily formed when zinc compound is used for an ester interchange catalyst and when DMS content is high[6]. The DMT/DMI ratio is found to be always the same as the feed ratio within reasonable error range.

### Thermal Properties of Copolyesters

Table 1 and Figure 1 show the glass transition temperatures of copolyester samples. The glass transition temperature ( $T_g$ ) increases with EG mole fraction at the same DMT/DMI ratio and shows higher value when DMT content is high. Since the glass transition temperature is dependent on the molecular flexibility, the ether linkage of DEG or TEG can make the chain more flexible and consequently  $T_g$  will decrease with

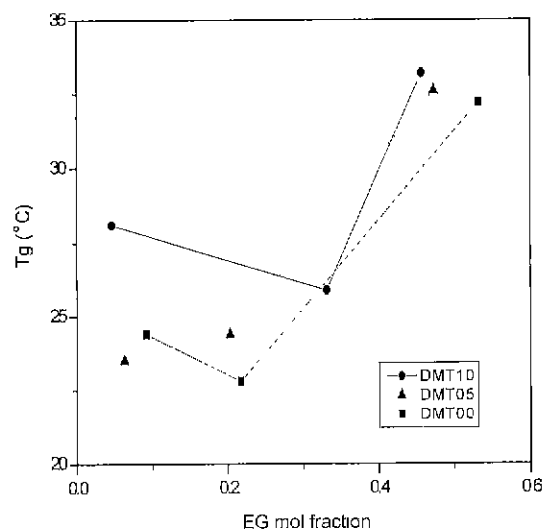


Figure 1. Variation of  $T_g$  with EG contents

Table 1. Properties of copolyesters

Sample	Feed ratio		Composition (mole ratio)		$x$	$n$	$[\eta]$ (dl/g)	$T_g$ (°C)
	DMT/DMI	EG/DEG	DMT/DMI	EG/EG/TEG				
1	1/0	1/0	1/0	0.457/0.285/0.258	0.103	1.801	0.313	32.2
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
3	0/1	1/0	0/1	0.532/0.331/0.135	0.108	1.599	0.317	32.2
4	1/0	0.5/0.5	1/0	0.331/0.460/0.209	0.116	1.878	0.397	25.9
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
6	0/1	0.5/0.5	0/1	0.217/0.532/0.251	0.104	2.034	0.450	22.8
7	1/0	0/1	1/0	0.046/0.914/0.039	0.095	2.034	0.462	28.1
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
9	0/1	0/1	0/1	0.092/0.762/0.146	0.105	2.053	0.476	24.4

increasing DEG or TEG content. The meta-link of DMI can prevent the close packing of the polymer chain and also reduce the  $T_g$  of the copolymer.

### Solution Properties of Copolyesters

Figure 2 shows the solubility of copolyesters. As shown in Figure 2, solubility decreases as increasing the DMT content. The sample 1, which has DMT:DMI = 1:0 and EG mole fraction is 0.457, shows the smallest solubility value. The effect of EG content is not serious except the sample 1. Figure 3 shows the variation of solution viscosity of a 20 wt% copolyester aqueous solution. It is difficult to draw any general rules from this figure. However, it is obvious that copolyesters having DMT:DMI = 1:1 show minimum viscosity. Figure 4 shows the solution stability of a copolyester aqueous solution. Solution stability is one of the key properties of a sizing agent. If a

sizing solution has an insufficient stability, in other words, the concentration varies with time due to coagulation or precipitation, one cannot get a uniform sizing effect. As shown in Figure 4, the effect of EG content is not clear and samples having high DMI content show better solution stability. Figure 5 shows the water resistance of copolyester films. The water resistance is very important when the sizing agent is applied to water jet loom. When the water resistance is insufficient, sizing agent can be eliminated by water jet. As shown in Figure 5, samples having DMT:DMI = 1:0 show the worst resistance, while sample 3 shows the best resistance. In general, high water solubility may result in poor water resistance. However, the samples having DMT:DMI = 1:0 showed poor solubility as well as poor water resistance as shown in Figures 2 and 5. It is thought to be due to the high  $T_g$  of the samples. High  $T_g$  could retard the wash out process

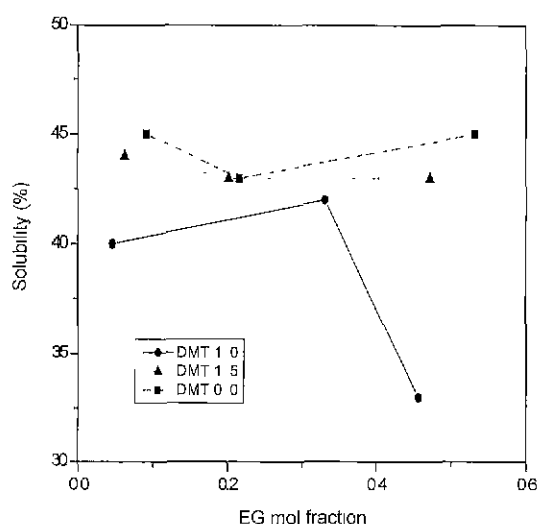


Figure 2. Variation of solubility with EG contents.

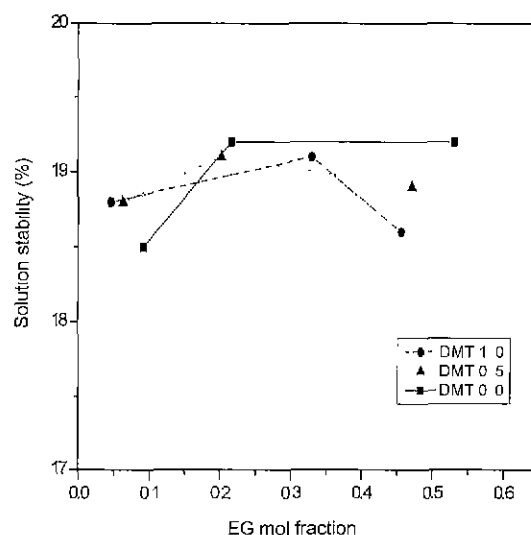


Figure 4. Variation of solution stability with EG contents.

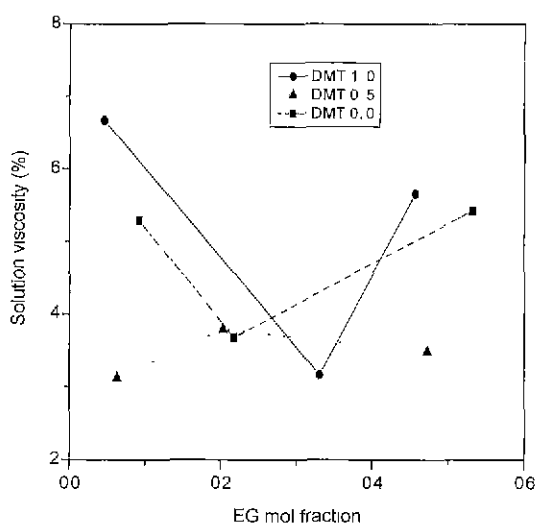


Figure 3. Variation of solution viscosity with EG contents.

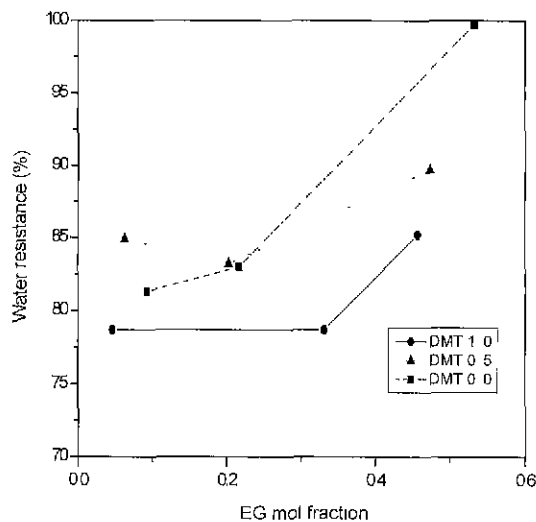


Figure 5. Variation of water resistance with EG contents.

during the water resistance evaluation experiments and also reduce the chain mobility in the concentrated aqueous solution.

### Conclusion

The effect of main chain structure of copolyesters on the properties of copolyester sizing agent was investigated. The glass transition temperature ( $T_g$ ) increased with EG mole fraction at the same DMT/DMI ratio and showed high value when DMT content was high, which was thought to be due to the ether linkage of DEG and TEG and non-linear structure of DMI. The solubility decreased as increasing the DMT content and the sample having DMT:DMI = 1:0 and EG mole fraction 0.457 showed the smallest solubility value. The copolyesters having DMT:DMI = 1:1 showed minimum viscosity. The effect of EG content on the solution stability

was not clear and samples having high DMI content showed better solution stability. The water resistance was best when only DMI and EG were used, while it was worst when DMT:DMI was 1:0.

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