A possible Effect of the Substituent Direction of Monosubstituted Hydroquinone upon the Transition Temperature of the Resulting Thermotropic Polyesters

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Abstract : Because of the difference in the relative reactivity between two hydroxyl groups of the hydroquinone due to the steric hindrance of the substituent, many combinations of the substituent direction in the polyesters derived from asymmetrical diphenol such as monosubstituted hydroquinone was expected. It was studied how the mode of the direction affected the properties of the resulting polyesters in terms of the transition temperatures of the thermotropic polyesters prepared from terephthalic acid, 2,4-dichloroterephthalic acid and phenylhydroquinone by the reaction using diphenyl chlorophosphate in pyridine. The direction was tried to control the relative reactivity by changing the reaction temperature and the addition time of hydroquinone, and by modifying it through an association of hydroquinone with LiCl.

Keywords : thermotropic Polyesters, hydroquinones, steric hindrance, terephthalic acid

1. Introduction

The sequence distribution of the dicarboxylic acid in the isophthalic acid(IPA) and terephthalic acid(TPA) and methylhydroquinone(MeHQ) affected to the transition temperatures of the resulting copolymer[1-2]. To control their distribution by differentiating the relative reactivity of the activated dicarboxylic acid, the reaction using diphenyl chlorophosphate was performed at lower temperature and by dropwise addition of MeHQ. Most of the results obtained could be explained by the sequence distribution, but

a few results could not be fully done, probably because the substituent direction of a methyl group in MeHQ might be involved.

Although the thermotropic polyesters of substituted hydroquinone such as methyl-and phenylhydroquinone, have been studied[3-5], the effect of the substituent direction in the polymers on their transition temperature has not been discussed, because they were usually prepared by an ester exchange reaction under severe conditions such as at higher temperatures so that the direction is difficult to control[6-8].

Generally, the polyesters derived from monosubstituted hydroquinone have three types of the substituent direction involved: one direction(A-type), the opppsite

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one(B-type), and the random one can be involved as shown below. The hydroxy group at the 1-position next to the substituent is less reactive than that at the 4-position owing to the steric hindrance so that B-type might be predominant in the polymer. When the hydroquinone was added dropwise to the solution of the activated dicarboxylic acids, the hydroxy group at the 4-position would become to react so easily that the participation of the random one together with A-type would be increased.

A-type

B-type
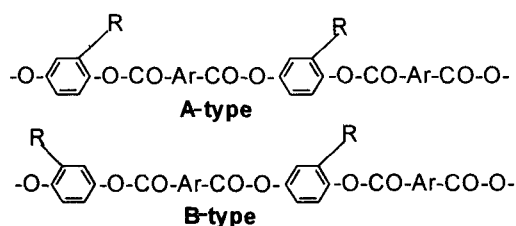
In the copolycondensation of two kinds of dicarboxylics acid and an asymmetric diphenol, both the acid sequence distribution and the substituent direction as mentioned above can affect in the transition temperature of the resulting polymer. To avoid the contribution of the sequence distribution and to clarify the effect of substituent direction alone, we here studied the polycondensation of TPA and dichloroterephthalic acid(DC-TPA) and phenylhydroquinone using diphenylchlorophosphate(DPCP) in pyridine in terms of the transition temperature of the resulting thermotropic polyesters[9-10].

2. Experimental

2.1. Materials

DC-TPA, MeHQ, and PhHQ were purchased from Tokyo Chemical Industry Co.(Japan) and DPCP and LiCl from Wako Pure Chemical Industry Co.(Japan), and used without further purification. Pyridine was distilled over solid KOH.

2.2. A Competitive Model Reaction of Benzoic Acid and Methylhydro-xyquinone

To a pyridine (10 mL) solution of DPCP (11 mmol) and LiCl (10 mmol) a pyridine (10 mL) solution of benzoic acid (10 mmol) was added, and the resulting mixture was kept at room temperature for 20 min and then heated at 120℃ for 10 min. To the mixture a pyridine(10 mL) solution of MeHQ(10 mmol) was added over a period of 0-30 min, and the whole solution was kept at 120℃ for 1 hour. After evaporation of pyridine under reduced pressure, the resulting residue was extracted with ethyl acetate, and the extract was washed successively in hydrochloric acid, sodium carbonate solution, and water, and then dried and evaporated. The residue was purified by recrystallization from methanol to give methylhydroquinone dibenzoate, in m.p.123℃, which showed good elementary analysis and the IR spectrum identical with that of authentic sample prepared by the conventional method using MeHQ and two equivalent moles of benzoyl chloride.

2.3. Polycondensation of IPA,TPA, and MeHQ, and of TPA and PhHQ

Similarly to the previously reported procedure, to the mixture of equal parts(2.5 mmol) of IPA and TPA, DPCP(12 mmol), and LiCl(10 mmol) in pyridine(20 mL) prepared at room temperature for 20 min and then at 60℃ for 10min, a pyridine(10mL) solution of MeHQ(5mmol) was added over a period of 0-20 min, and the whole mixture was maintained at 60℃ for 3 hour (see Table 1). Similarly, to the mixture of TPA(5 mmol), DPCP(12 mmol), and LiCl(10 mmol) in pyridine(20 mL) prepared as above at room temperature and then heated at 120℃ for 10 min, a pyridine(10mL) solution of PhHQ (5mmol) was added over a period of 0-30 min, and the whole solution was kept at 120℃ for 3 hour(see Table 3).

The resulting mixtures were diluted with N,N-dimethylformamide sufficiently enough to give and adequate size of particles when poured into methanol to precipitate the copolymer. The isolated copolymer was washed in boiling methanol for 1 hour and dried.

Table 1. Polycondensation of IPA,TPA and MeHQ[a]

Addition time of MeHQ(min)	ηinh[b] (dL/g)	Endotherms[c] (℃)
0	1.34	262. 283(w)
10	1.33	258. 280(w)
20	0.97	258. 283(s)

a) IPA=TPA=2.5mmol; MeHQ=5mmol ; DPCP=12mmo l; LiCl=10mmol ; Reaction temperature=60℃.

b) Measured in p-chlorophenol at 50℃.

c) Determined by DSC (first run at a heating rate of 20℃/min), and corresponding to the melting point(Tm, the transition Temperature to nematic mesophase) ; w=weak; s=strong.

Table 2. The Competitive Model Reaction of Benzoic Acid and MeHQ[a]

Addition time of MeHQ (min)	The yield of MeHQ dibenzoate[b] (%)
0	25
10	55
20	73

a) Benzoic acid=MeHQ=10mmol ; DPCP=11mmol ; LiCl=10mmol.

b) The yield calculated based on benzoic acid.

Table 3. Polycondensation of TPA and MeHQ[a]

Addition time of PhHQ (min)	ηinh[b] (dL/g)	Endotherms[c] Tm, Ti (℃)
0	2.68	341, 456
10	3.07	342, 464
30	2.79	341, 462

a) TPA= PhHQ = 5 mmol, DPCP=12mmol, LiCl=10mmol : Reaction temperature=120℃.

b) Measured in p-chlorophenol at 50℃

c) Determined by DSC (first run at a heating rate of 20℃/min).

2.4. Polycondensation of DC-TPA and PhHQ

To the reaction mixture of DC-TPA(5 mmol) and DPCP(12 mmol) in pyridine(20 mL) prepared as above at room temperature for 20 min and then at 80-120℃ for 10min, a pyridine(10 mL) solution of PhHQ(5 mmol) and LiCl(0-10 mmol) was added over a period of 0-30 min, and the resulting mixture was heated at 80-120℃ for 3 hour. The polymer was isolated by working up as above.

2.5. Characteristics of Polymers

Thermal properites were examined under a nitrogen atmosphere by Rigaku Thermoflex TG 8110, Japan, with thermal analyzer at heating rate of 20℃/min. The maximum of the endothermic peaks were equated with transition temperatures(Tm and Ti). The optical textures of the mesophases were observed by polarizing microscope (Nikkon POH-2) equipped with a hot-stage (Mettler FP-2). A mesophase texture of DC-TPA/PhHQ polyester was photographed from the quenched polymer.

The sample, placed between two thin microscope cover glasses on a modified melting point apparatus (Yazawa BY-2, Japan) equipped with two polarizing films, was rapidly heated at 320℃ where the polymer showed a complete anisotropic melt, removed from the apparatus, and rapidly quenched by cooled air.

3. Results and Discussion

As previously described in the copolycondensation of IPA, TPA, and MeHQ, the reaction at lower temperatures of 60 and 80℃ gave the copolymer exhibiting two melting points(Tm, the transition to a nematicmesophase) at 260℃ and 280℃ despite a single Tm at 275℃ for the copolymer obtained at 120℃. The reaction at lower temperatures favored the reaction of TPA more than IPA as shown in the competitive model reaction with p-cresol, resulting in the longer TPA-MeHQ segment[11].

Together with the results of the copolymers at higher TPA contents, the Tm at 260℃ was assumedly due to the segment. It was expected also the case for the copolymer prepared by varying the addition time of MeHQ, because longer addition time of the cresol in the model reaction was also favorable for TPA. However, The two Tms appeared at any addition time and even the Tm at 280℃ increased its intensity by longer time. These results could not be explained by the acid component distribution alone, and might be due to the substituent direction as mentioned above[12,13].

It seems to be difficult to quantitatively determine the substituent direction in the polyesters derived from monosubstituted hydroquinones, but can be qualitatively estimated from the relative reactivities of two hydroxy groups of the hydroquinones in the competitive acylation. Owing to the steric hindrance of a substituent, the hydroxy group

at the 2-position next to the substituent may be less reactive than that at the 4-position.
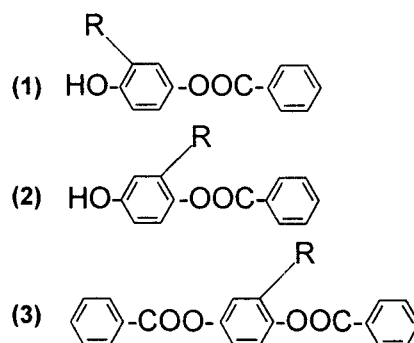


Scheme 1. Molecular structure of products.

The competitive model reaction of equimolar amounts of MeHQ and benzoic acid activated by the reaction using DPCP was preliminary studied. Generally, three types of the products, the monoesters [(1) and (2)], R=CH3 and the diester(3), R=CH3 were expected to be formed in the reaction, but monoester (2) might be minor one in this case because of the steric hindrance of a methyl substituent. When MeHQ was added in one portion, (1) may be more favorably formed than (3). On the other hand, its dropwise addition, which leads to the reaction of the activated benzoic acid with a smaller amount of MeHQ, may increase the formation of (3).

Indeed, the yield of (3) increased with the longer addition time(Table 2).

To discuss the effect of the substituent direction alone on the transition temperatures of the resulting polymers by avoiding the possible effect of the acid component distribution, the polyester of a single dicarboxylic acid and a monosubstituted hydroquinone should be studied[14,15].

To compare well with the results of the model reaction using MeHQ, the polycondensation of TPA and MeHQ was tried, but proceeded heterogeneously to give the polymer of only low inherent viscosity of

0.3. The polyester of TPA and phenyl hydroquinone(PhHQ) was initially examined. The thermotropic polyester of TPA and PhHQ has been already studied, but not in terms of phenyl substituent direction in the polymer.
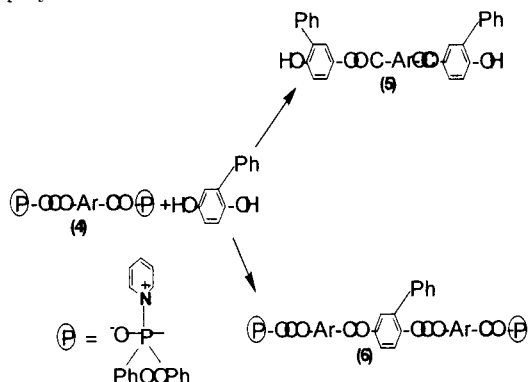
Sheme 2. Polycondensation process of products.

The polycondensation of TPA and PhHQ was carride out at 120℃ by dropwise addition of PhHQ in an attempt to control the phenyl substituent direction in the resulting polymer(Table 3). As suggested by the results of the competitive model reaction(see Table 2), when PhHQ was added in one portion, the monoacylated intermediate (5) might be initially formed preferably and then react with (4) to yield the polyester with a higher content of the segment having the B-type direction.

On the other hand, its dropwise addition increased the production of the diacyl intermediate (6), from which the segments of the random direction containing the A-type to some extent, would be formed, The polymer having the ordered B-type direction might shows higher transition temperature than that of random one. The polymer was obtained in nearly quantitative yield and its inherent viscosities of 3.0. obtained in this experiment were comparable to those reported in the literature. The resulting polymer exhibited a nematic melt in the range of 340 and 470℃ as shown in Fig.1. Along with microscopic observation, we assigned the peak at 340℃ to

the melting point(Tm, the transition to a nematic mesophase), and plural ones at 460℃ to the clearing temperatures(Ti, the transition from a nematic to an isotropic phase). In addition, an exothermic peak at 301℃ was observed. The Tm did not vary with the addition time, but the peak became broaden to the lower temperature with the time, indicating the involvement of some segments with the Tm lower than 340℃. The lowering of Tm was also observed microscopically. Although one of the Ti at 456℃ became higher to 463℃ together with the appearance of a new peak at 490℃ by the longer addition time, these were too complicated to discuss here in this study.
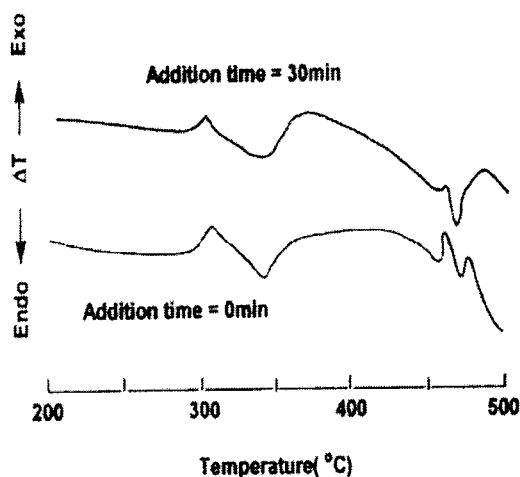

Fig. 1. DSC curves for TPA/PhHQ polyester prepared by dropwise addition of PhHQ.

These results suggested that the peak at 341℃ might be the Tm due to the segment of higher orderd B-type content, and the broad one at belows the temperature to the random direction of phenyl substituent in the polymer as assumed above.

Although the effect of the substituent direction upon the transition temperature of the resulting polymer was roughly estimated in TPA/PhHQ polyester, it was not enough to

discuss in more detail. In order to obtain more precise informations about the effect, we have examined several combinations of dicarboxylic acid and diphenol whose polymer's transition can be easily determined by DSC and the microscopic observation as well. we have found a new thermotropic polyester of dichloroterephthalic acid (DC-TPA) and PhHQ, which exhibited a nematic mesophase with the Tm at 270℃ and the Ti around 400℃(Fig. 2), which were also confirmed by the microscopic observation.
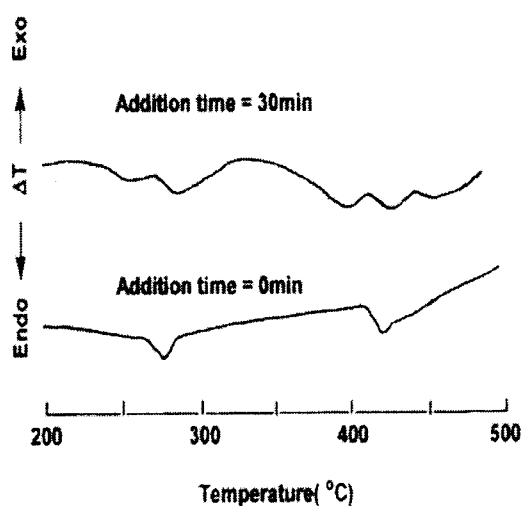

Fig. 2. DSC   curves   for   DC-TPA/PhHQ
        polyester   prepared   by   dropwise
        addition of PhHQ.

The polycondensation of DC-TPA and PhHQ was performed at several temperatures and changing the addition time of PhHQ, and carried out in the absence of LiCl(Table 4). The Tm of the resulting polymer was varied by the reaction temperatures(addition time=0), a little higher Tm and also higher Ti being obtained by the reaction at 100℃ than at 80 and 120℃. The addition time of PhHQ also affected the transition temperatures. As shown in Fig. 2, when PhHQ was added in one portion, the polymer showed the Tm at 277℃, which decreased to 274℃ by its dropwise addition.

Similarly to TPA/PhHQ polymer, small and broad peak at 250℃ probably due to another Tm was also observed, and its intensity appeared to increase with the addition time.

The polymer prepared at 100℃ by addition in one portion exhibited a single Ti at 412℃ whereas those obtained by dropwise addition showed complicated features of the Ti appearing at 380, 407, and 430℃. It was also the case for the polymer prepared at 80℃, showing the lowering of Tm and plural Ti by dropwise addition. The profiles of the Tm and Ti for DC-TPA/PhHQ were similar to those for TPA/PhHQ, and were assumed to be due to the segments involving several substituent directions in the polymer.

The polycondensation was conducted by adding a pyridine solution of PhHQ and two

Table 4. Polycondensation of DC-TPA and PhHQ in the Absence of LiCl[a]

Temperature (℃)	Addition time of MeHQ (min)	ηinh[b] (dL/g)	Endotherms[c] Tm, Ti (℃)
120	0	0.97	274, 393
100	0	1.89	277, 412
	20	0.76	277, 381,400
	30	0.88	275, 381,407
80	0	1.63	274, 406
	30	0.79	270, 381,407

a) DC-TPA=PhHQ=5mmol, DPCP=12mmol : Reaction temperature=60℃.
b) Measured in p-chlorophenol at 50℃.
c) Determined by DSC (first run at a heating rate of 20℃/min).

Table 5. Effect of Addition of PhHQ/LiCl upon the Polycondensation of DC-TPA and PhHQ[a]

Temperature (℃)	LiCl (mmol)	ηinh[b] (dL/g)	Endotherms[c] Tm, Ti (℃)
100	0	1.89	277, 412
	10	1.32	270, 400
80	0	1.63	274, 406
	10	1.04	268, 398

a) DC-TPA=PhHQ=5mmol, DPCP=12mmol, LiCl=10mmol : addition time of PhHQ/LiCl solution = 0min.

b) Measured in p-chlorophenol at 50℃.

c) Determined by DSC (first run at a heating rat e of 20℃/min).

equimolar amount of LiCl with respect to PhHQ was added in one portion to the reaction mixture of DPCP and DC-TPA in pyridine at 80 and 100℃(Table 5). As expected, more apparent decrease in Tm by 7℃ and Ti were observed at both reaction temperatures.

4. Conclusions

In alternative way to control the substituent direction, changing the relative reactivity of the hydroxy groups of hydroquinones by some interactions might be effective. As LiCl is expected to associate with PhHQ through a weak salt-like interaction to increase the reactivity of the two hydroxy groups, the difference between their reactivity due to steric hindrance might be decreased. In consequence, the randomness of phenyl substituent direction would be increased, resulting in more obvious changess in Tm and Ti of the resulting polymer.

The direction was tried to control the relative reactivity by changing the reaction temperature and addition time of the hydroquinone, and by modifying it through an association of the hydroquinones with LiCl.

References

1. F. Higashi, M. Watabiki, and K. Kimura, An Attempt to Control the Monomer Sequence Distribution in Copolymers of Isophthalic acid, Terephthalic acid, and Bisphenols Prepared by Use of Diphenyl Chlorophosphate in Pyridine, *J. of Polymer Sci. Part A*, **33**, 185 (1995).

2. A. F. Orifici, E. M. VallésRaúl, O. Garay, and R. W. Lenz, Preparation and Characterization of Thermotropic Liquid Crystal Copolyesters Containing m-Hydroxybenzoic Acid Units, *Polymer*, **37**, 4357 (1996).

3. F. Higashi and Y. Lee, Preparation of High Molecular Weight Polyhydrazides from Hydrazine Monohydrochloride Using Phenylphosphonic Dichloride and Phosphorus Compounds as Additives, *J. of Polymer Sci. Part A*, **31**, 1453 (1993).

4. F. Higashi, A. Kobayashi, and H. Shimazaki, Direct Polyesterification by Use of Phosphorus Oxychloride and LiCl in Pyridine, *J. of Polymer Sci. Part A*, **31**, 1301 (1993).

5. A. Saxena, V. L. Rao, and K. N. Ninan, Synthesis and Properties of Polyether

Nitrile Copolymers with Pendant Methyl Groups, *European Polymer J.*, **39**, 57 (2003).

6. F. Higashi, Y. Yoshida, and O. Matsuzaka, Propagation in the Two-step Solution Copolycondensation with p-Xyleneglycol and Bisphenols with the TsCl/DMF/Py Condensing Agent, *European Polymer J.*, **38**, 1137 (2002).

7. S. Vlad, S. Oprea, A. Stanciu, C. Ciobanu, and V. Bulacovschi, Polyesters Based on Unsaturated Diols, *European Polymer J.*, **36**, 1495 (2000).

8. W. Grasser, H.-W. Schmidt, and R. Giesa, Thermotropic Liquid Crystalline Copolyesters with Non-Coplanar Biphenylene Units Tailored for Blend Fiber Processing with PET, *Polymer,* **42**, 8529 (2001).

9. K. Miyata, K. Muraoka, T. Itaya, T. Tanigaki, and K. Inoue, Synthesis and Thermal Properties of Polyesters from Cyclotriphosphazene, *European Polymer J.,* **32**, 1257 (1996).

10. D. Acierno, R. Fresa, P. Iannelli, and P. Vacca, Segmented Liquid-Crystalline Polyesters with Allyl Groups as Lateral Substituents, *Polymer,* **41**, 4179 (2000).

11. N. S. Al-Muaikel, Synthesis and Characterization of New Unsaturated Polyesters and Copolyesters Containing Azo Groups in the Main Chain, *European Polymer J.,* **39**, 1025 (2003).

12. F. Higashi, W. Zhang, and K. Nakajima, Thermotropic Copolyamides from Triethyleneglycol Bis(4-carboxyphenyl) ether and Two Kinds of Aromatic Diamines, *J. of Polymer Sci. Part A,* **32**, 89 (1994).

13. F. Higashi, K. Nakajima, M. Watabiki, and W. Zhang, Thermotropic Liquid Crystalline Polyamides from Polyethyleneglycol Bis(4-carboxyphenyl) ethers, *J. of Polymer Sci. Part A,* **31**, 2929 (1993).

14. F. Higashi and E. Ikeda, Polycondensation of Aromatic Dicarboxylic Acids and Bisphenols with a New Tosyl Chloride/Triphenylphosphine Oxide/ Pyridine Condensing Agent, *Macromolecular Rapid Communications,* **21**, 1306 (2000).

15. F. Higashi and A. Kobayashi, Direct Polyamidation with Phosphorus Oxychloride in Pyridine, *J. of Polymer Sci. Part A,* **27**, 507 (1989).