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THERMOTROPIC POLYARYLATES DERIVED FROM SUBSTITUTED HYDROQUINONES AND 4,4'-DIPHENYLDICARBOXYLIC ACID

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Abstract As-spun fibers of poly(methylhydroquinone 4,4'-diphenyldicarboxylate) (Me-HQ/BB) exhibited a lower modulus than poly(phenylhydroquinone 4,4'-diphenyldicarboxylate) (Ph-HQ/BB) and poly(2-chlorophenylhydroquinone 4,4'-diphenyldicarboxylate) (CP-HQ/BB) due to the lower degree of elongational flow orientation and the lower value of orientation function of the nematic domains (F). However, injection molded specimens of Me-HQ/BB exhibited a higher flexural modulus than Ph-HQ/BB and CP-HQ/BB due to the higher packing density of the polymer chain. Thus, the packing density of polymer chain is a more influential factor than the F value to achieve a high modulus of injection molded specimens.

INTRODUCTION

Recently thermotropic polyarylates have been attracting much attention due to their high modulus, excellent processability, thermal resistance, dimensional stability, and so on.[1] In order to investigate the effects of chemical structures on the modulus of as-spun fibers, various polyether-polyesters from substituted hydroquinones (HQs) and substituted 1,2-bis(phenoxy)ethane-4,4'-dicarboxylic acid (PEC) were prepared, and it was concluded that both the stability of liquid crystallinity and the rigidity of polymer chain were important factors to achieve a high modulus of as-spun fibers.[2–4] Therefore, we expected that as-spun fibers and injection molded specimens of polyarylates derived from substituted-HQs and BB would exhibit higher moduli than polyarylates from substituted-HQs and substituted-PECs due to the higher stability of liquid crystallinity and the higher rigidity of the polymer chains.

The melting temperature (Tm) of polyethylene-4,4'-diphenyldicarboxylate is much higher than that of polyethylene terephthalate due to the higher rigidity of the polymer chain. Since poly(methylhydroquinone terephthalate) (Me-HQ/TA) did not exhibit the stir-opalescence due to its high Tm, it was assumed that more rigid Me-HQ/BB would not exhibit the stir-opalescence. However, Me-HQ/BB unexpectedly exhibited the stir-

opalescence at 324 °C (Tn). Therefore, we investigated the effects of the chemical structutres on the stability of liquid crystallinity and the moduli of as-spun fibers of polyarylates from substituted-HQs and BB, TA, and substituted-PECs. We also investigated the effects of the chemical structutres on the moduli of injection molded specimens of polyarylates from substituted-HQs and BB.

EXPERIMENTAL

Polymers

Me-HQ/BB was prepared from Me-HQ diacetate and BB by melt polymerization at 250-270 °C under a nitrogen atmosphere followed by solid-state polymerization at 340 °C under reduced pressure of 1 torr. [5]

Ph-HQ/BB and Ph-HQ/HQ/BB were prepared from Ph-HQ, HQ, acetic anhydride and BB by melt polymerization at 130-390 °C under a nitrogen atmosphere. After most of acetic acid was distilled off, the pressure was gradually reduced to reach 1 torr.

CP-HQ/BB was prepared from CP-HQ diacetate and BB by melt polymerization at 250-370 °C under a nitrogen atmosphere, and the pressure was gradually reduced to 1 torr.

It should be noted that when Me-HQ/BB was prepared only by melt polymerization, homogeneous polymers were not obtained and when Ph-HQ/BB and Ph-HQ/HQ/BB were prepared from Ph-HQ diacetate, HQ diacetate and BB, homogeneous polymers were not obtained, either.

Preparation of Fibers

Polyarylates were melt spun by using a flow tester having a capillary with a diameter of 0.3 or 0.5 mm. The measurements of modulus (dynamic storage modulus, M) of as-apun fibers were performed on a REO-VIBRON at a frequency of 110 Hz, a heating rate of 2 °C/min and with an interchuck distance of 40 mm.

Injection Molding

Test specimens of polyarylates were obtained by injection molding using a Sumitomo NESTAL injection molding machine (0.5 ounce). The measurements of flexural modulus were performed according to ASTM D790 using the injection molded specimens with thickness of 1/32 inch.

Anisotropic Melting Temperatures (Tn)

Anisotropic melting temperatures (Tn) were determined as onset temperatures of stir-opalescence observed on a hot stage equipped with a polarizing microscope.

Melting Temperatures (Tm) and Glass Transition Temperatures (Tg)

Tm's and Tg's were determined by differential scanning calorimetry (DSC). In the case of as-spun fibers, the maximum of dynamic loss modulus (E" max) measured on a REO-VIBRON was taken as Tg.

Inherent Viscosity (IV)

Inherent viscosities (IV) were measured on 0.1 g/dl solutions in pentafluorophenol at 60 °C.

Orientation Function of Nematic Domains (F)

F values of as-spun fibers and injection molded specimens along the flow direction were calculated according to the equation as follows;

$$F = (3\langle\cos^2\theta\rangle_{av} - 1) / 2$$

θ values were measured by wide-angle X-ray diffractometry. F = 1 means that the domains are perfectly aligned along the flow direction, and F = 0 means that the domains are randomly distributed.

Relative Degree of Crystallinity (I/Io)

In order to compare the crystallinity of polyarylates, X-ray diffraction patterns were observed in the temperature range of 25 - 250 °C, and I/Io was calculated according to the equation as follows;

I/Io = (peak intensity of polyarylates at $2\theta = 20$) / (peak intensity of Al_2O_3 as internal standard at $2\theta = 43.4$)

Morphology

Morphologies of the tensile fractured as-spun fibers and the flexural fractured injection molded specimens were studied by scanning electron microscopy (SEM).

Heat Distortion Temperatures (HDT)

HDT's of the injection molded specimens were determined under a load of 1.82 MPa according to ASTM D-648.

RESULTS AND DISCUSSION

Thermal Properties

Me-HQ/BB exhibited the stir-opalescence at 324 °C (Tn) and DSC thermograms of Me-HQ/BB exhibited two endotherm peaks (304-310 and 362-375 °C). The lower endotherm

peak was proven to be a crystal-crystal transition by the X-ray diffraction patterns and the higher endotherm peak was assigned to Tm.[5] Ph-HQ/BB and CP-HQ/BB also exhibited Tn's at 308 and 298 °C and Tm's at 364 and 317 °C, respectively. However, Ph-HQ/BB and CP-HQ/BB did not exhibited crystal-crystal transitions. In order to demonstrate the effects of the chemical structure of polymer chain on the stability of liquid crystallinity, polyarylates from substituted-HQs and BB, TA, PEC, and 1,2-bis(2-chlorophenoxy)ethane-4,4'-diphenyldicarboxylic acid (Cl-PEC) were prepared and their thermal properties were examined. As shown in Tables 1-4, Ph-HQ/BB and Ph-HQ/TA exhibited superior liquid crystallinity to Ph-HQ/PEC, and Ph-HQ/Cl-PEC did not exhibit liquid crystallinity. As for the polyarylates derived from CP-HQ, CP-HQ/BB exhibited liquid crystallinity, but CP-HQ/TA, CP-HQ/PEC and CP-HQ/Cl-PEC did not exhibit liquid crystallinity. Thus, it is concluded that among the dicarboxylic acids investigated, BB has the greastest effect on the stability of liquid crystallinity.

In order to compare the stability of liquid crystallinity of BB and TA based polyarylates, thermal properties of model compounds derived from BB and TA were investigated. As shown in Table 5, the model compound containing BB unit exhibited higher stability of liquid crystallinity.[2]

Polyarylates from substituted-HQs and BB exhibited high values of Tg and E''_{max}, and among them Ph-HQ/BB exhibited the highest E''_{max} of 205 °C.

TABLE 1. Thermal properties and modulus of polyarylates from Me-HQ.

Polymer	Thermal properties				Spinning temp.	Modulus of as-spun fibers		
	E"max (°C)	Tg (°C)	Tn (°C)	Tm (°C)	(°C)	d (mm)	M (GPa)	Fa)
Me-HQ/BB	175	-	324	304 362	370	0.46	5	0.62
Me-HQ/PEC	-	104	265	291	330	0.06	42	-
Me-HQ/Cl-PEC	138	129	303	310	355	0.11	72	0.90

a) $F=(3\langle\cos^2\theta\rangle_{av}-1)/2$

TABLE 2. Thermal properties and modulus of polyarylates from Ph-HQ.

Polymer	Thermal properties				Spinning temp.	Modulus of as-spun fibers		
	E"max (°C)	Tg (°C)	Tn (°C)	Tm (°C)	(°C)	d (mm)	M (GPa)	F
Ph-HQ/BB	205	-	308	364	385	0.07	40	0.95
Ph-HQ/TA	171	-	338	334	370	0.07	57	0.98
Ph-HQ/PEC	134	124	235	270a)	265	0.07	26	0.90
			265a)					
Ph-HQ/Cl-PEC	124	115	-	191a)	235	0.08	4	-

a) Isotropic melt temp.

TABLE 3. Thermal properties and modulus of polyarylates from CP-HQ.

Polymer	Thermal properties				Spinning temp.	Modulus of as-spun fibers		
	E"max (°C)	Tg (°C)	Tn (°C)	Tm (°C)	(°C)	d (mm)	M (GPa)	F
CP-HQ/BB	196	-	298	317	360	0.07	47	0.90
CP-HQ/TA	-	144	-	365a)	-	-	-	-
CP-HQ/PEC	-	121	-	212a)	-	-	-	-
CP-HQ/Cl-PEC	124	127	-	-	-	-	-	-

a) Isotropic melt temp.

TABLE 4. Thermal properties and modulus of substituted-HQs/BB.

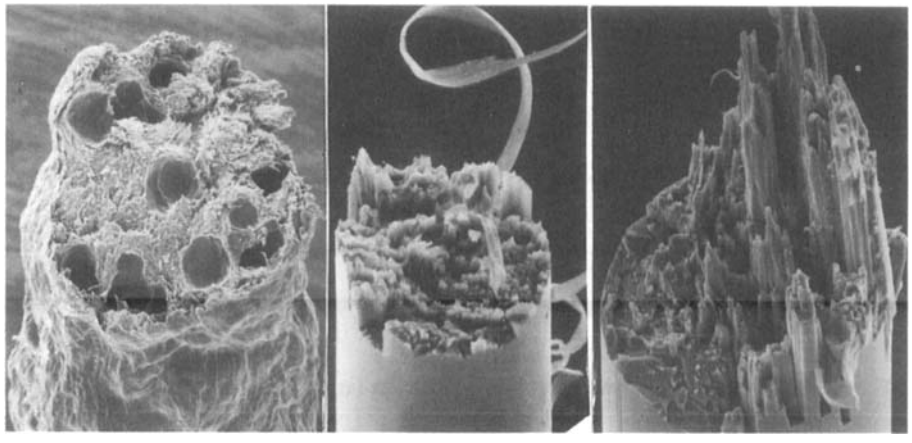
Polymer	IV (dl/g)	Thermal properties			Spinning temp.	Modulus of as-spun fibers		
		E"max (°C)	Tn (°C)	Tm (°C)	(°C)	d (mm)	M (GPa)	F
Me-HQ/BB	-	175	324	304	370	0.46	5	0.62
				362				
Ph-HQ/BB	1.22	205	308	364	385	0.07	40	0.95
CP-HQ/BB	1.24	196	298	317	360	0.07	47	0.90

TABLE 5 Stability of liquid crystalline model compounds derived from BB and TA.

Model compounds	Tn (°C)	H (cal/g)	Ti (°C)	H (cal/g)	Ti - Tn (°C)
HBA-BB-HBA	189	14.8	271	0.1	82
HBA-TA-HBA	207	22.1	241	0.2	34

HBA-BB-HBA ; EtOOC-⟨⟩-OCO-⟨⟩-⟨⟩-COO-⟨⟩-COOEt

HBA-TA-HBA ; EtOOC-⟨⟩-OCO-⟨⟩-COO-⟨⟩-COOEt



300μm 50μm 60μm

(I) (II) (III)

FIGURE 1. SEM of tensile fractured as-spun fibers of Me-HQ/BB(I), Ph-HQ/BB(II) and CP-HQ/BB(III).

As-spun fibers

As-spun fibers of Me-HQ/BB exhibited a modulus of 5 GPa which was lower than Me-HQ/PEC and Me-HQ/Cl-PEC in spite of the highly rigid chemical structure of Me-HQ/BB. The low modulus of Me-HQ/BB is referred to the low F value due to the low elongational flow orientation as shown in Table 1. The degree of elongational flow orientation was evaluated from the observed orientation of fibrils in the cross section of tensile fractured as-spun fibers.[2,6] As-spun fibers of Ph-HQ/BB and CP-HQ/BB exhibited higher moduli of 40 and 47 GPa compared to Me-HQ/BB, which was referred to the higher F value as shown in Fig. 2., and therefore, to the higher elongational flow orientation of Ph-HQ/BB and CP-HQ/BB as shown in Fig. 1. Thus, the elongational flow orientation (F value) seems to be a more influential factor than the rigidity of the polymer chain to achieve a high modulus of as-spun fibers.

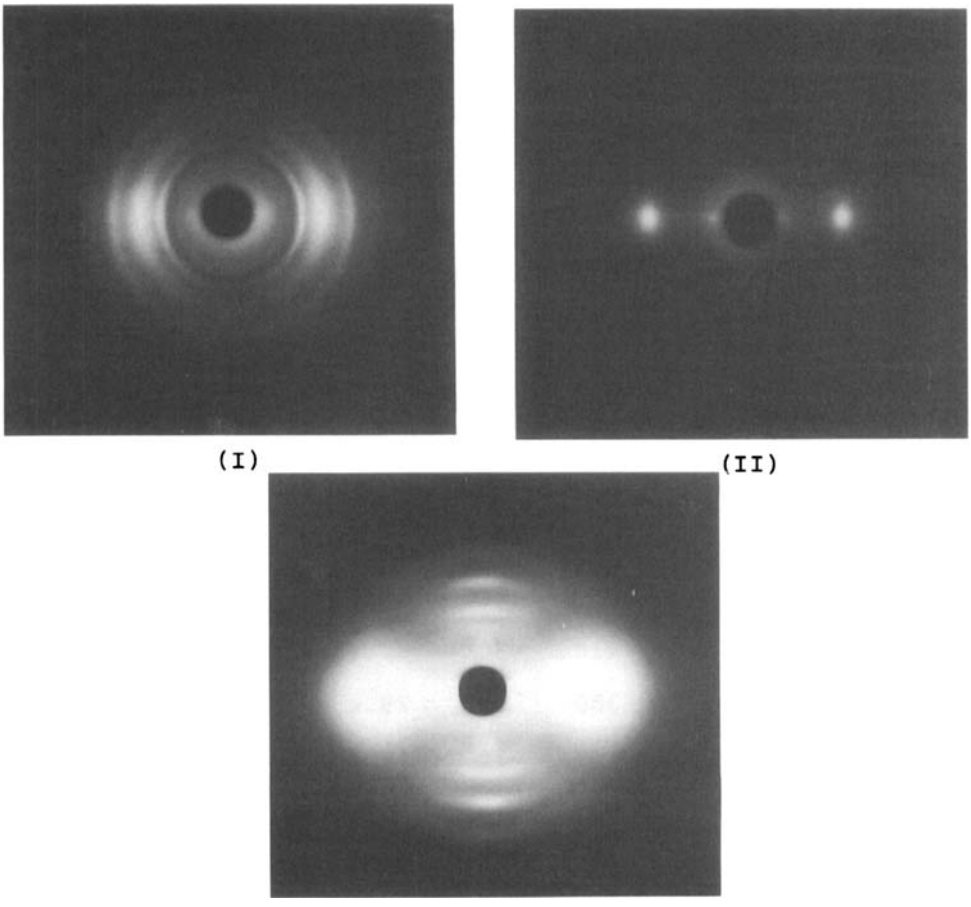


FIGURE 2. X-ray diffraction patterns of as-spun fibers of Me-HQ/BB(I), Ph-HQ/BB(II) and CP-HQ/BB(III).

Injection Molded Specimens of Substituted-HQ/BBs

Although as-spun fibers of Me-HQ/BB exhibited a lower modulus than Me-HQ/Cl-PEC due to the low elongational flow orientation, the flexural modulus of injection molded specimens of Me-HQ/BB exhibited a flexural modulus of 30.8 GPa which was higher than Me-HQ/Cl-PEC. Similarly, the flexural modulus of injection molded specimens of Me-HQ/BB was higher than Ph-HQ/BB (28.4 GPa) and CP-HQ/BB (19.9 GPa), although the modulus of as-spun fibers of Me-HQ/BB was lower than Ph-HQ/BB and CP-HQ/BB as shown in Table 6.

Fig. 3 shows SEM observations of the cross sections of flexural fractured injection molded specimens of Me-HQ/BB, Ph-HQ/BB In Fig. 3, fewer fibrils are observed in the case of Me-HQ/BB than Ph-HQ/BB and CP-HQ/BB, and the lower F value as shown in Fig.4.or the decreased elongational flow orientation of Me-HQ/BB is probably responsible for the fewer fibrils.

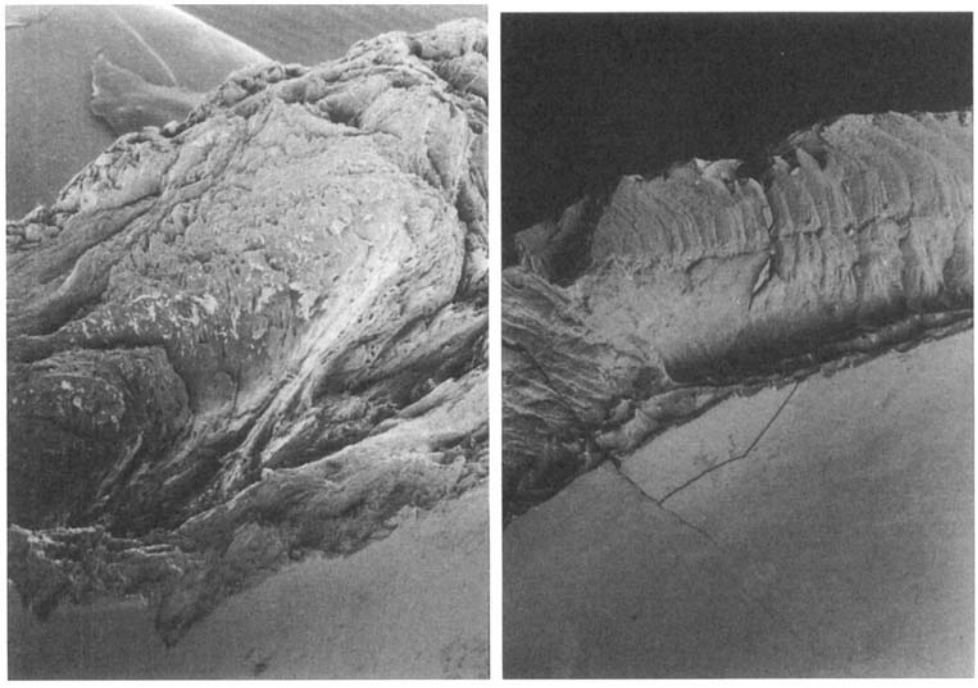
The flexural modulus of substituted-HQ/BBs seems to increase with the decrease of the size of substituents on HQ or with the increase of packing density of the polymer chain. Thus, both the rigidity and the packing density of polymer chain seem to be more influential factors than the F value to achive a high modulus of injection molded specimens.

While HDT's of Me-HQ/BB and Ph-HQ/BB exceeded 290 °C, the HDT of CP-HQ/BB was as low as 155 °C. The low HDT of CP-HQ/BB is probably referred to the low degree of crystallinity as shown in Fig. 5.

TABLE 6. Flexural modulus and HDT of substituted-HQs/BB.

Polymer	IV (dl/g)	Melt temp. (°C)	Mold temp. (°C)	Flexural modulus (GPa)	HDT (°C)	Fa)
Me-HQ/BB	4.09	410	30	30.8	>290	0.62
Ph-HQ/BB	1.22	380	30	29.4	>290	0.87
CP-HQ/BB	1.24	330	30	19.9	155	0.74

a) $F=(3\langle\cos^2\theta\rangle_{av}-1)/2$



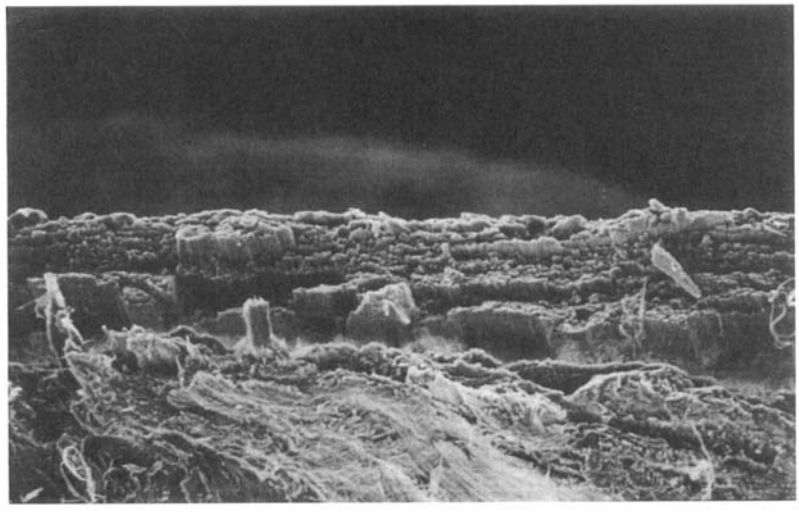


FIGURE 3. SEM of flexural fractured injection molded specimens of Me-HQ/BB(I),Ph-HQ/BB(II) and CP-HQ/BB(III).

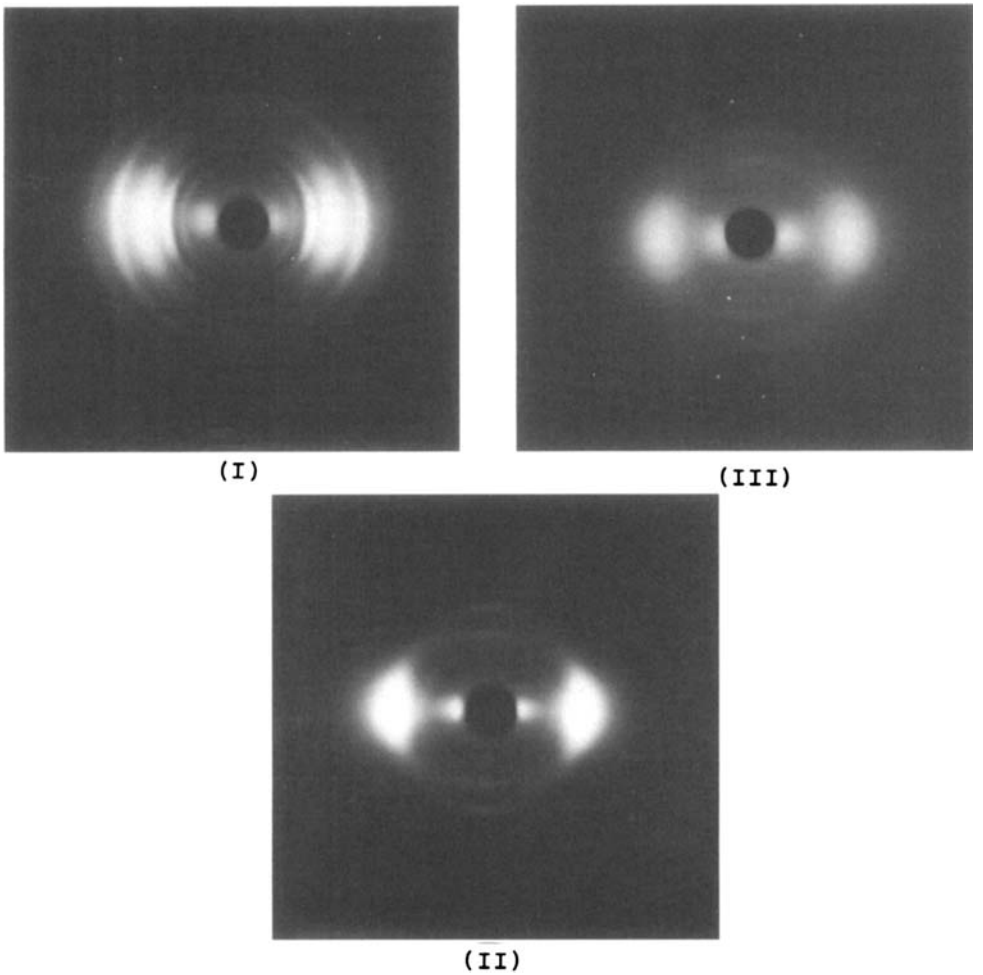


FIGURE 4. X-ray diffraction patterns of injection molded specimens of Me-HQ/BB(I), Ph-HQ/BB(II) and CP-HQ/BB(III).

Ph-HQ/HQ/BB Polyarylates

As an effort to increase the moduli of as-spun fibers and injection molded specimens of Me-HQ/BB at the same time, we studied copolymerization of Ph-HQ/HQ/BB. Thermal properties of Ph-HQ/HQ/BB with various compositions are summarized in Table 7. While the copolyarylates with the composition m/n = 0/10 - 3/7 did not exhibit the stir-opalescence, the copolyarylates with the composition m/n = 4/6 - 10/0 exhibited the stir-opalescence. Therefore, we prepared the copolyarylate with the critical composition m/n = 5/5 and measured the moduli of as-spun fibers and injection molded specimens. As-spun fibers of Ph-HQ/HQ/BB (m/n = 5/5) exhibited a much higher modulus than Ph-HQ/BB probably due to the increased F value, and E"max of Ph-HQ/HQ/BB (m/n = 5/5)

was observed at 217 °C which was higher than Ph-HQ/BB. Injection molded specimens of Ph-HQ/HQ/BB (m/n = 5/5) exhibited a much higher modulus of 35.7 GPa due to the increased packing density of the polymer chain by copolymerization of HQ as shown in Table 8. However, the F value of injection molded specimens of Ph-HQ/HQ/BB (m/n = 5/5) was not higher than Ph-HQ/BB. Thus, it is concluded that the packing density of polymer chain is a more influential factor than the F value in order to achieve a high modulus of injection molded specimens.

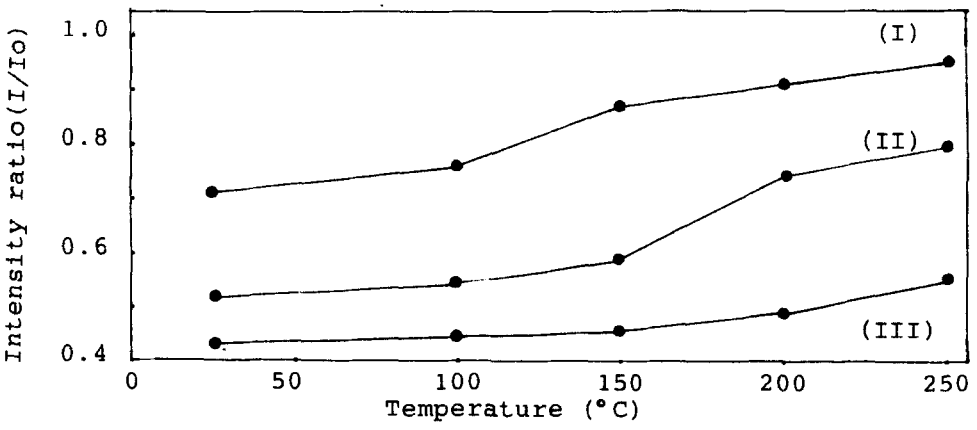


FIGURE 5. Temperature dependence of peak intensity(2θ = 20) (I/Io is non-dimentionallized intensity by α-Alumina as internal standard); (I),Me-HQ/BB ;(II),Ph-HQ/BB ; (III),CP-HQ/BB

TABLE 7. Thermal properties of Ph-HQ/HQ/BB polyarylates.

m/n	Tn (° C)	Tm (° C)	m/n	Tn (° C)	Tm (° C)
4/6	308	345	8/2	306	374
5/5	295	355	9/1	304	375
6/4	305	373	10/0	308	364
7/3	312	375			

TABLE 8 Modulus of as-spun fibers and injection molded specimens of Ph-HQ/BB and Ph-HQ/HQ/BB(m/n=5/5)

Polymer	IV	Thermal properties E''max (°C)	Tn (°C)	Tm (°C)	As-spun fibers d (mm)	modulus M (GPa)	F	Injection molded specimens t (mm)	Flexural modulus (GPa)	F
Ph-HQ/BB	1.22	205	308	364	0.07	40	0.95	0.8	29.4	0.87
Ph-HQ/HQ/BB (m/n=5/5)	2.75	217	295	355	0.07	100	0.97	0.8	35.7	0.82

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