

# Synthesis and Characterization of Cholesteric Thermotropic Liquid Crystalline Polyesters

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**ABSTRACT:** Cholesteric liquid crystalline polyesters were successfully synthesized from isosorbide, methyl hydroquinone, and isophthaloyl chloride. Homo/copolyesters were synthesized by the solution polycondensation method, for which a mild organic base such as pyridine was employed. Inherent viscosities of polyesters P-3–P-5 were in the range of 0.31–0.39 dL/g at 25°C in chloroform, and polyesters P-1 and P-2 were insoluble in chloroform. Homo/copolyesters based on isosorbide, methyl hydroquinone, and isophthalic acid had thermal stability at more than 300°C on the basis of 10% weight loss. The thermotropic liquid crystalline properties were examined by differential scanning calorimetry and polarizing optical microscopy. Wide-angle

X-ray diffraction study demonstrated that polyesters P-1, P-2, and P-3 were semicrystalline, whereas the degree of crystallinity of polyesters P-4 and P-5 was less than 5%. Copolyester P-4 showed formation of a yellow iridescent streak at 209°C on heating and development of a Grandjean texture at 270°C on heating. These are typical textures of the cholesteric liquid crystalline phase. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1232–1237, 2007

**Key words:** cholesteric liquid crystalline polymers (ChLCP); differential scanning calorimetry (DSC); optical microscopy; thermogravimetric analysis (TGA); viscosity; solution polycondensation

## INTRODUCTION

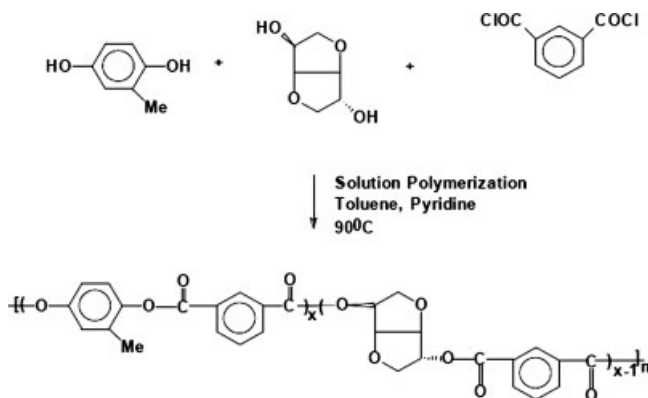
Cholesteric thermotropic liquid crystalline polymers (ChLCPs) are of special interest for several reasons.<sup>1–14</sup> They may form enantiotropic chiral melts, which show a selective transmission and reflection of circularly polarized light, if a macroscopic orientation of all domains (Grandjean texture) is feasible. Grandjean textures may be thermotropic, when the pitch of the helical order of the mesogen is sensitive to changes in temperature. ChLCPs have the ability to produce supermolecular structures characterized by a helical organization. This spatial organization is responsible for the unique optical properties of ChLCPs such as selective reflection of light at different wavelengths. Because of the high sensitivity of selective reflection of light, ChLCPs offer substantial advantages for practical applications in areas such as thermometers, thermoindicators, thermo-optics, photo-optics, and reversible holographic recording media. Main-chain ChLCPs that have mesogenic units in the backbone have been studied to a lesser extent than main-chain ChLCPs containing flexible spacer-based aliphatic diacids or diols. These types of aliphatic diacids or diols have lower thermal stability. The

synthesis of cholesteric polyesters based on a sugar diol such as isosorbide is an attractive chiral building block because it is easily accessible from renewable resources in the form of pure enantiomer. Isosorbide is known to possess a high twisting power but is more flexible and inexpensive.

Okada et al.<sup>15–16</sup> reported the development of biodegradable isotropic polyesters derived from isosorbide and aliphatic dicarboxylic acids. Kricheldorf et al.<sup>17</sup> reported the synthesis and characterization of cholesteric liquid crystalline polycarbonates derived from isosorbide, (*S*)-[(2-methyl butyl)-thio], and triphosgene by interfacial, solution, and melt polycondensation methods. Chatti et al.<sup>18</sup> synthesized and characterized polyethers derived from isosorbide and *n*-octyl-1,8-dibromide by the microwave-assisted polycondensation method.

The purpose of the present study was to synthesize high-performance ChLCPs soluble in chlorinated solvent based on methyl hydroquinone, isophthalic acid, and isosorbide. Copolyesters of methyl hydroquinone, isosorbide with isophthalic acid forms of ChLCPs possess low glass-transition temperatures and low crystallinity. We report here the synthesis and properties of a cholesteric (twisted nematic/chiral nematic) thermotropic polyester system with an asymmetric center based on methyl hydroquinone, isophthalic acid, and isosorbide. The cholesteric copolyesters had high thermal stability and a low transition temperature and were soluble in

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**Scheme 1** Synthesis of cholesteric liquid crystalline homo/copolyesters based on methyl hydroquinone, isosorbide, and isophthaloyl chloride.

chloroform as well in aprotic solvents like DMAC, NMP, DMSO, and DMF. Under polarizing microscopy the cholesteric copolyesters showed the formation of a yellow iridescent streak and also marble texture and had the characteristic texture of the cholesteric (twisted nematic) mesophase.

## EXPERIMENTAL

### Materials

Methyl hydroquinone (Aldrich) was recrystallized from acetone. Isophthalic acid (Sisco) was used as received. Thionyl chloride (Loba) was distilled prior to use. Isosorbide (Aldrich) was used as received. Dichloromethane (Merck) was distilled over calcium hydride. Toluene (Merck) was stored on calcium chloride, filtered, distilled, and stored on sodium wire. Pyridine (Merck) was refluxed and distilled on potassium hydroxide pellets.

### Polymerization (solution method)

Into a 100-mL two-necked round-bottom flask equipped with a nitrogen inlet, a magnetic stirrer, and an oil bath were added methyl hydroquinone (1.0 g,

8.2 mmol), isophthaloyl chloride (1.67 g, 8.2 mmol), and toluene (8.2 mL), and the reaction mixture was heated at 90°C for 30 min. To this solution pyridine (4.1 mL) was added dropwise over 30 min. The reaction mixture was stirred at 110°C for 48 h and was poured into methanol. The precipitated polymer was washed with methanol and dried under reduced pressure at 80°C for 8 h.

The inherent viscosity of the homo/copolyesters was measured at a concentration of 0.5 g/dL in chloroform using an Ubbelohde viscometer at 25°C. <sup>1</sup>H-NMR spectra were recorded on a Bruker AC300 spectrometer in deuterated chloroform (CDCl<sub>3</sub>) as the solvent. Tetramethylsilane was used as an internal standard. <sup>13</sup>C-NMR spectra were recorded on a Bruker AC300 spectrometer in deuterated chloroform (CDCl<sub>3</sub>) as the solvent. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer model TGA-7 under an N<sub>2</sub> atmosphere using a heating rate of 10°C/min. Thermal transition temperatures were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer model DSC-7 under an N<sub>2</sub> atmosphere using a heating rate of 10°C/min. Optical characterization was performed on a Mettler polarizing optical microscope equipped with an FP2 Mettler hot stage at a magnification of 50×. Wide-angle X-ray diffraction measurements were made by a Philips PW X-ray diffractometer equipped with an 1830 generator and 1710 adjustment with Cu Kα radiation of 1.54 Å. Optical rotations were measured with a JASCO-P-1020 polarimeter in a cuvette 100 mm in length at a concentration of 5 g/L in chloroform at 25°C.

## RESULTS AND DISCUSSION

### Polymer synthesis

The route of synthesis of the cholesteric thermotropic liquid crystalline homo/copolyesters based on methyl hydroquinone, isosorbide, and isophthaloyl chloride is depicted in Scheme 1. All homo/copolyesters were synthesized by the solution polycondensation method, in which a mild organic base pyridine was

**TABLE I**  
Compositions of Homo/Copolyesters of Methyl Hydroquinone, Isosorbide, and Isophthaloyl Chloride

Polymer code	me-Hq : Iso : IPCL (composition)	me-Hq (mmol)	Iso (mmol)	IPCL (mmol)	Pyridine (mL)
P-1	100 : 00 : 100	8.20	—	8.20	4.10
P-2	75 : 25 : 100	6.15	2.05	8.20	4.10
P-3	50 : 50 : 100	4.10	4.10	8.20	4.10
P-4	25 : 75 : 100	2.05	6.15	8.20	4.10
P-5	00 : 100 : 100	—	8.20	8.20	4.10

me-Hq, methyl hydroquinone; Iso, isosorbide; IPCL, isophthaloyl chloride.

**TABLE II**  
Solubility of Homo/Copolyesters of Methyl Hydroquinone,  
Isosorbide, and Isophthaloyl Chloride

Polymer code	Solvent					$\eta_{inh}^a$ (dL/g)
	CHCl <sub>3</sub>	DMAc	DMSO	DMF	NMP	
P-1	–	–	–	–	–	<sup>b</sup>
P-2	–	–	–	–	–	<sup>b</sup>
P-3	+	+	+	+	+	0.39
P-4	+	+	+	+	+	0.36
P-5	+	+	+	+	+	0.31

+ = Soluble at room temperature; – = insoluble.

<sup>a</sup> Inherent viscosity determined in chloroform at 25°C with  $c = 0.5$  g/dL using a Ubbelohde viscometer.

<sup>b</sup> Insoluble.

employed.<sup>19</sup> The interfacial polymerization method was not applicable to isosorbide-based system, in which a strong inorganic base such as sodium hydroxide is used. This would degrade isosorbide during polymerization and cause an imbalance in the stoichiometry results in polyesters with low inherent viscosity. The compositions used for the syntheses of high-performance cholesteric liquid crystalline homo/copolyesters based on methyl hydroquinone, isosorbide, and isophthaloyl chloride are presented in Table I.

Solubility data of the cholesteric liquid crystalline homo/copolyesters based on methyl hydroquinone, isosorbide, and isophthaloyl chloride are reported in Table II. The solubility of the homo/copolyesters was tested in solvents such as chloroform, *N,N*-dimethyl acetamide (DMAc), dimethyl sulfoxide (DMSO), *N,N*-dimethyl formamide (DMF), and 1-methyl-2-pyrrolidinone (NMP). Polyesters P-3, P-4, and P-5 were soluble in common organic solvents like chloroform because of the higher percentage of cycloaliphatic flexible isosorbide diol. Polyesters P-1 and P-2 were insoluble in chloroform and in aprotic solvents like DMSO, DMAc, NMP, and DMF. The solubility

of copolyesters increased with an increase in the percentage of isosorbide.

The inherent viscosity (Table II) of polyesters P-3–P-5 in chloroform was in the range of 0.31–0.39 dL/g, whereas the inherent viscosity of polyesters P-1 and P-2 was not determined because of their insolubility in both chloroform and aprotic solvents.

The properties of the cholesteric liquid crystalline homo/copolyesters based on methyl hydroquinone, isosorbide, and isophthaloyl chloride are presented in Table III.

### Infrared spectroscopy

The IR spectrum (neat) of copolyester P-3 is depicted in Figure 1, showing the characteristic peaks at 1760 cm<sup>-1</sup> (ester), 1470 cm<sup>-1</sup> (methylene), and 1118 cm<sup>-1</sup> (ether).

### <sup>1</sup>H- and <sup>13</sup>C-NMR

The <sup>1</sup>H-NMR spectrum of cholesteric liquid crystalline copolyester P-3 based on a 50 : 50 : 100 ratio of isosorbide/methyl hydroquinone/isophthaloyl chlo-

**TABLE III**  
Properties of Homo/Copolymers Based on Methyl Hydroquinone,  
Isosorbide, and Isophthaloyl Chloride

Polymer code	$T_{10}$ (°C)	$T_{max}$ (°C)	$T_g$ (°C)	$T_m$ (°C)	$T_i$ (°C)	$\Delta H$ (J/g)	Crystallinity (%)	$[\alpha]_D^b$
P-1	441	485	163	221	300	3.985	37.18	a
P-2	424	447	161	188	285	2.465	21.80	a
P-3	412	441	145	185	284	1.590	13.73	–05.32
P-4	404	436	122	183	280	1.687	2.10	–15.84
P-5	380	435	90	c	c	d	1.20	–20.61

<sup>a</sup> Insoluble.

<sup>b</sup> Optical rotation measured at 25°C with  $c = 5$  g/L in chloroform.

<sup>c</sup> Not observed.

<sup>d</sup> Very low crystallinity.

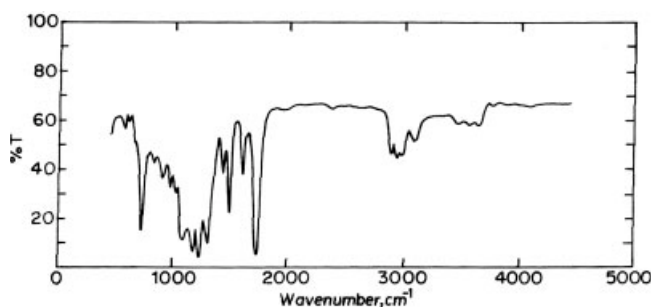


Figure 1 IR spectrum of copolyester of P-3.

ride is presented in Figure 2, showing the equimolar incorporation of isosorbide and methyl hydroquinone. The condensation of isosorbide and methyl hydroquinone with isophthaloyl chloride showed moderately high inherent viscosity, indicating the stoichiometric incorporation of both diols took place and that both monomers were equally reactive under the given reaction conditions.

The  $^{13}\text{C}$ -NMR spectrum shown in Figure 3 depicts the further investigation of the structure of copolyester P-3. Methyl  $^{13}\text{C}$  signals appeared at 16.47 ppm, and six  $^{13}\text{C}$  signals, corresponding to the isosorbide building block, appeared between 70.73 and 85.44 ppm. Ester carbonyl signals appeared at 164.63 ppm, and methyl hydroquinone carbon signals adjacent to the ester group appeared between 146.97 and 148.28 ppm. Isophthalic acid carbon signals adjacent to the ester group appeared between 130.02 and 134.68 ppm. Four carbon signals resulting from isophthalic units were found, in agreement with the polymer structure.

### Thermal analysis

TGA traces of the cholesteric liquid crystalline homo/copolyesters synthesized from methyl hydroquinone, isosorbide, and isophthaloyl chloride are depicted in Figure 4. Thermogravimetric analyses of the cholesteric liquid crystalline homo/copolyesters (Table III) showed single-stage degradation above 380°C. Homo-

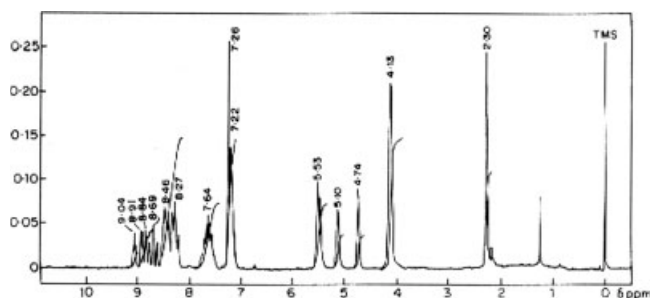


Figure 2  $^1\text{H}$ -NMR spectrum of copolyester of P-3 in  $\text{CDCl}_3$ .

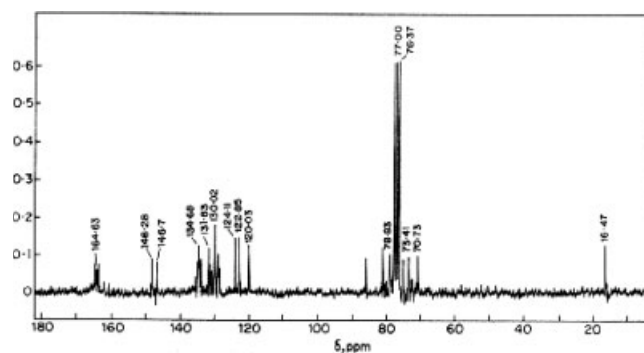


Figure 3  $^{13}\text{C}$ -NMR spectrum of copolyester of P-3 in  $\text{CDCl}_3$ .

polyester P-5 showed a degradation temperature ( $T_{10}$ ) of 380°C, whereas polyester P-1 showed a degradation temperature ( $T_{10}$ ) of 441°C. The maximum decomposition temperature ( $T_{\text{max}}$ ) of all homo/copolyesters was above 435°C. Homopolyester P-5 showed the lowest decomposition temperature, 435°C, whereas polyester P-1 showed the highest, 485°C, indicating that all the homo/copolymers were quite stable. Thermal stability decreased with an increased percentage of isosorbide.

The DSC thermogram of copolyester P-1 is presented in Figure 5, showing a mesomorphic range of 79°C. Copolyester P-2 showed that the glass-transition temperature and the mesomorphic range were both 97°C. The liquid crystalline transition temperatures of copolyesters P-3, P-4, and P-5 were determined by optical microscopy. The  $T_g$ ,  $T_m$ , and  $T_i$  transition temperatures (Table III) decreased with an increase in the percentage of isosorbide.

### Wide-angle X-ray diffraction

The wide-angle X-ray diffraction (WAXD) powder pattern of copolyester P-3, presented in Figure 6, shows P-1, P-2, and P-3 to be semicrystalline. The

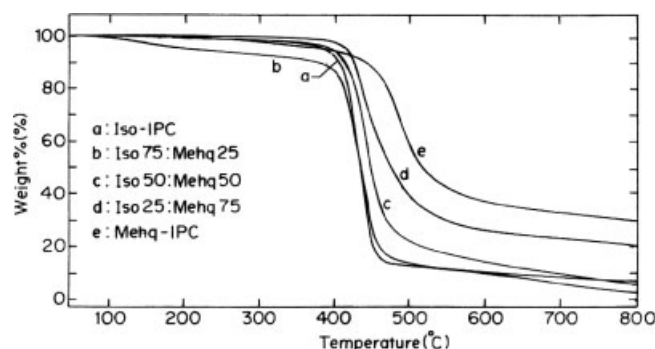


Figure 4 TGA curves of cholesteric liquid crystalline homo/copolyesters synthesized from methyl hydroquinone, isosorbide, and isophthaloyl chloride.



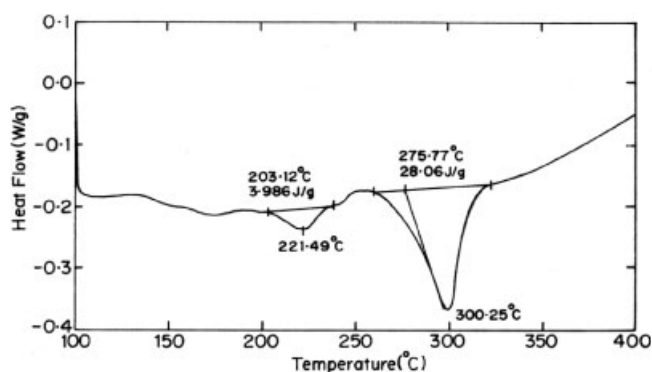


Figure 5 DSC trace of polymer P-1.

method to measure the percent crystallinity of a polymer was reported previously.<sup>20–24</sup> The WAXD pattern demonstrates that the incorporation of a higher molar fraction of isosorbide reduced crystallinity, so that in P-4 and P-5 the degree of crystallinity was below 5%. Methyl hydroquinone was used as a comonomer with isosorbide to improve solubility. The incorporation of isosorbide reduced the tendency to crystallize. Crystallinity decreased with an increase in the percentage of isosorbide.

### Optical rotation

Optical rotations of chloroform-soluble copolyesters were measured (Fig. 7). Optical rotation varied from  $-5.32$  to  $-20.61$ . The optical rotations of polyesters P-3, P-4 and P-5 were  $-5.32$ ,  $-15.84$ , and  $-20.61$ , respectively. Optical rotation increased with an increase in the percentage of isosorbide. Optical rotations of polyesters P-1 and P-2 were not determined because of their insolubility in chloroform.

### Optical microscopy

The optical microscopy textures of cholesteric liquid crystalline copolyester P-4 are presented in Figures 8 and 9. The most interesting optical microscopy texture (Fig. 8) was observed for copolyester P-4, which showed formation of a yellow iridescent streak

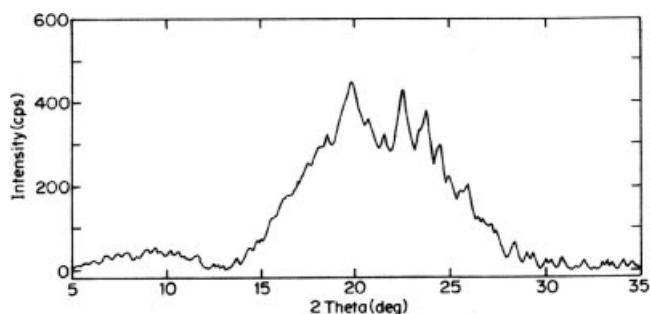


Figure 6 X-ray diffraction spectrum of P-3.

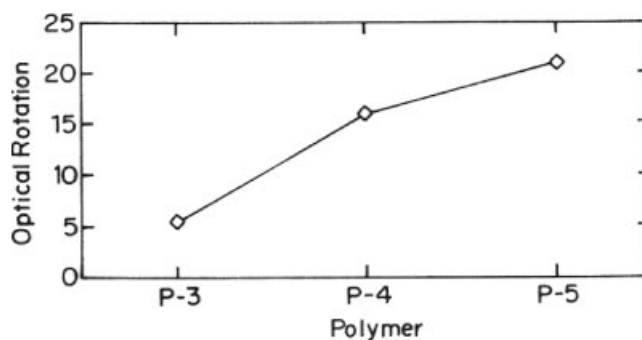


Figure 7  $[\alpha]_D$  plot of polyesters P-3, P-4, and P-5.

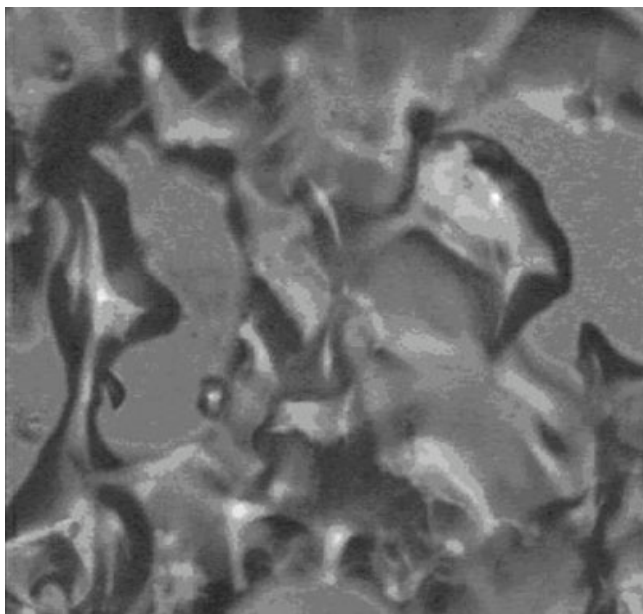
at  $209^\circ\text{C}$  on heating. The optical microscopy texture of P-4, depicted in Figure 9, showed the formation of a Grandjean texture at  $270^\circ\text{C}$  on heating. These are typical textures of the cholesteric liquid crystalline phase. Copolyester P-3 showed a marble texture at  $258^\circ\text{C}$  on heating. Copolyester P-5 showed a very weak LC texture at  $180^\circ\text{C}$  on heating.

### CONCLUSIONS

The results of the present study allowed the conclusion that cholesteric liquid crystalline polyesters can be synthesized from isosorbide, methyl hydroquinone, and isophthaloyl chloride. Isosorbide is an optically active and inexpensive cycloaliphatic diol used to synthesize high-performance cholesteric liquid crystalline polyesters. Homopolyester of isosorbide and isophthaloyl chloride are thermally



Figure 8 Optical texture of polymer P-4 at  $209^\circ\text{C}$  on heating.



**Figure 9** Optical texture of polymer P-4 at 270°C on heating.

stable up to 300°C. Homo/copolyesters based on isosorbide, methyl hydroquinone, and isophthalic acid have thermal stability to more than 300°C determined on the basis of 10% weight loss. Copolyesters based on isosorbide, methyl hydroquinone, and isophthalic acid are soluble in chloroform (when there is more than 50% isosorbide). The optical microscopy study revealed that at a 50 : 50 : 100 ratio of isosorbide/methyl hydroquinone/isophthalic acid ratio, a yellow iridescent strip appeared at 209°C on heating and a Grandjean texture formed at 270°C on heating. These

are typical textures of the cholesteric liquid crystalline phase.

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