

Residual Birefringence of Amorphous Polymers for Optical-Disk Substrates

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SYNOPSIS

Based on the Mueller matrix approach, we have successfully designed and constructed a highly sensitive instrument for measuring optical birefringence (LB) by using a polarization modulation method and phase-sensitive technique. Our instrument can measure the retardation of a sample up to 10^{-2} radian. Using this instrument, we have measured the residual birefringence of thermosetting resins, CR-39 resin and epoxy resin, for optical-disk substrates. CR-39 resin results are summarized as follows: (1) Annealing is very effective in reducing LB of samples; (2) samples prepared from raw material 2 (monomer purity, 96%, oligomer, 4%) have smaller LB than those from raw material 1 (monomer purity, 99.9%); and (3) annealed samples prepared from 2 satisfy the requirement on LB to be used as optical-disk substrates. For epoxy resin: (1) "Second curing" largely reduces LB of samples; (2) "slow cooling" is more effective in reducing LB of samples than "fast cooling;" (3) after the second curing, cutting does not induce any residual stress birefringence in samples; and (4) slow-cooled samples have good optical properties to be used as optical-disk substrates.

INTRODUCTION

Plastics are the most promising materials to be used as optical-disk substrates for computer memory units because of their light weight, processability, and cost performance in mass production.¹ However, such materials that satisfy quality requirements are not yet available because plastics for computer use must be more reliable than polymethyl methacrylate (PMMA) used for videodisks and the polycarbonate (PC) for compact disks. The affinity for water and residual birefringence are two of the decisive factors in the properties being required as optical-disk substrates. This is because the large affinity for water induces warps in disks, and the residual birefringence is directly related to the carrier-to-noise ratio and bit error rate.² In particular, a magneto-optical disk using a delicate Kerr rotation angle as a signal requires birefringence less than 5 nm (double pass),

and nearly zero must be targeted. PMMA is not suitable because of its large affinity for water, while the weak point of PC is its rather large residual birefringence.

We have tried to make thermosetting resins that satisfy the above two requirements for optical-disk substrates. Thermosetting resins have a fixed network structure that does not readily melt even if heated. This not only indicates that such a structure is unaffected by heat but also that the physical and optical properties remain unchanged as long as the structure is not destroyed. One drawback of thermosetting resins is their mouldability, particularly a long curing time required by the cast molding method using a liquid resin.

Checking *Chemical Abstracts* for the past 10 years, we found only one paper reporting the residual static birefringence of epoxy resins developed for computer memory units,² but no article on the residual static birefringence of CR-39. In this article, we focus on the residual birefringence of CR-39 and an epoxy resin that were specially developed for utilizing as optical-disk substrates.

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EXPERIMENTAL

Outline of Our Instrument

Since intensive discussions on the principle, design, and analysis of our highly sensitive instrument for measuring optical birefringence (LB) are presented in our previous paper,³ we briefly explain the outline of our apparatus. Figure 1 shows the block diagram of our LB instrument and the optical arrangement and axis orientation of optical components. We can express monochromatic incident beam, I_{in} , by the Stokes vector. We can formulate a polarizer, P , a photoelastic modulator (PEM), M , a sample, S , and an analyzer, A , in the Mueller matrices.³ With a simple matrix computation of $A S M P I_{in}$, we can get the light intensity, I_d , at the detector as

$$I_d = 1/4 I_0 [1 - \sin \delta \cdot 2J_1(\delta_0) \sin \omega t]. \quad (1)$$

Here, all notations and conventions are given in our previous paper.³ We can detect the DC (V_{dc}) and ω component (V_{ac}) of the photocurrent by a DC voltmeter and a lock-in amplifier tuned to $\omega/2\pi$. By taking the ratio of V_{ac} to V_{dc} , we can get the retardation of the sample, δ , as

$$\delta = -GV_{ac}/V_{dc} = 2\pi\Delta n d/\lambda = 2\pi\Gamma/\lambda. \quad (2)$$

Here, δ is in radian, G an apparatus constant, Δn the sample birefringence, d the sample thickness in cm, λ the wavelength of the monochromatic light in cm, and Γ the retardation in cm.

Components

The light source used is a He-Ne laser (Nihon Kagaku Engineering Co. Ltd., Model NEO-FP). A neutral filter (Osaka Megane Glass Co. Ltd., OMG, B-480) is used to cut the intensity of laser light. The polarizer is a Glan-Taylor calcite prism (Karl Lambrecht, MGTYE 8). The analyzer is a Glan-Thompson calcite prism (Karl Lambrecht MGTA 12). The polarizer and analyzer are mounted on specially designed prism holders, which are based on rotatory stages with mechanism for precise adjustment (Shiguma Koki Co., Model Σ -401 S-(2)). The PEM used is a fused quartz photoelastic modulator (Morvue Electronic System, Model PEM-3, PEM Head FS-3, and Control Unit C-3). A photo diode is used as the detector (Scientific Instrument Inc.). The lock-in amplifier is a tuned type lock-in amplifier (NF Circuit Block, LI-573). The digital multimeter is a Takeda Riken TR 6840.

Calibration and Performance

We carried out the calibration of our LB instrument following the same procedure described in our previous article.³ Our instrument can measure LB up to 10^{-2} degree. The total performance of our instrument depends upon the following factors⁴: (1) the residual static birefringence of PEM; (2) the residual static birefringence of the Glan-Thompson calcite prism used as the analyzer; (3) the position of the analyzer's optical axis; and (4) the second harmonic response of lock-in amplifier.

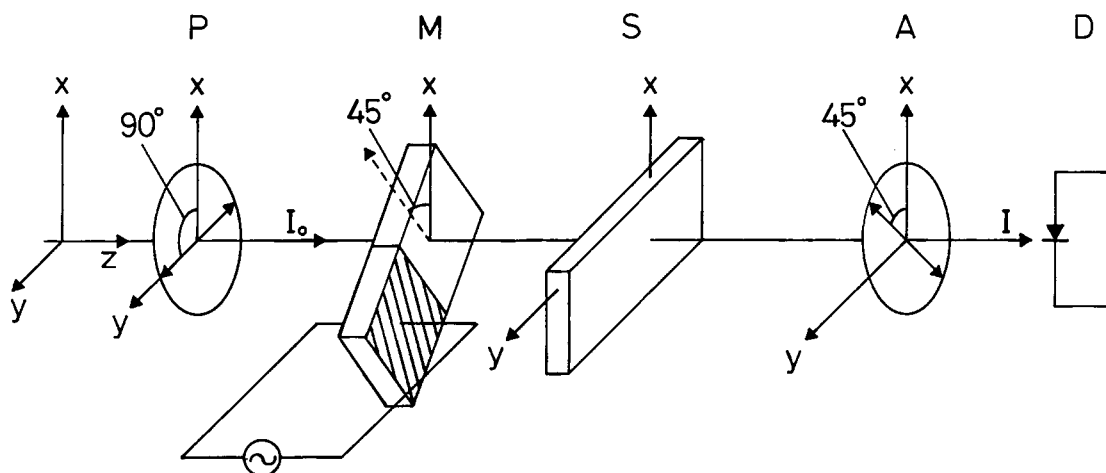


Figure 1 Block diagram and optical arrangement of our LB instrument. P , polarizer; M , photoelastic modulator; S , sample; A , analyzer; D , photodetector

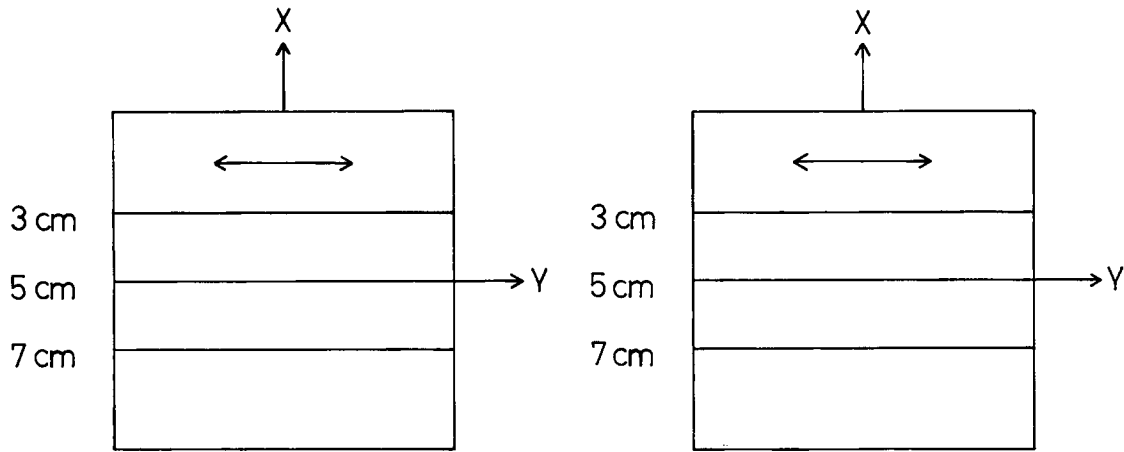


Figure 2 Locations of LB measurements in CR-39.

Sample Preparation

Sample preparations were carried out in a clean room and cast molds were washed by an automatic washing machine.

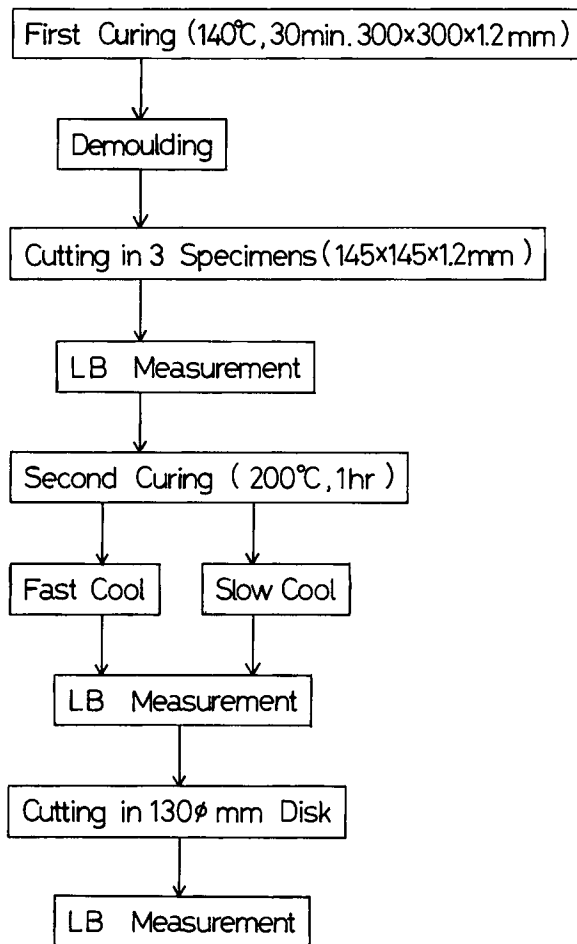


Figure 3 Flowchart of procedures for sample preparation and LB measurements.

CR-39

Monomer used was diethyleneglycol bisarylcarbonate, and di-isopropylperoxydicarbonate was used as a polymerization initiator. Sample specimens were prepared from two raw materials: 1 (monomer pu-

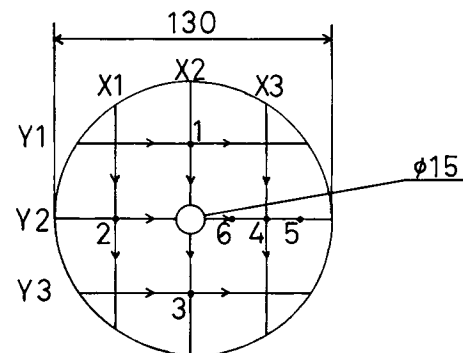
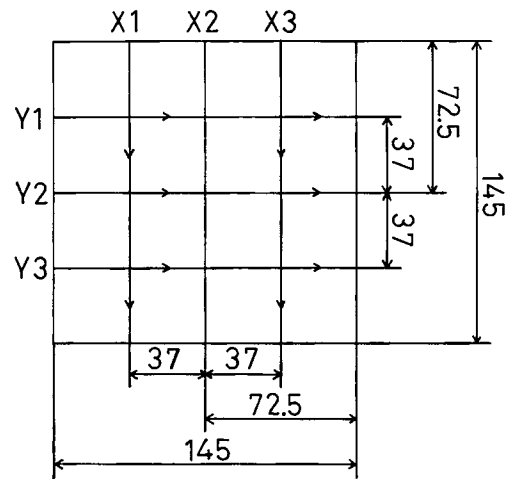


Figure 4 Locations of LB measurements in epoxy resin.

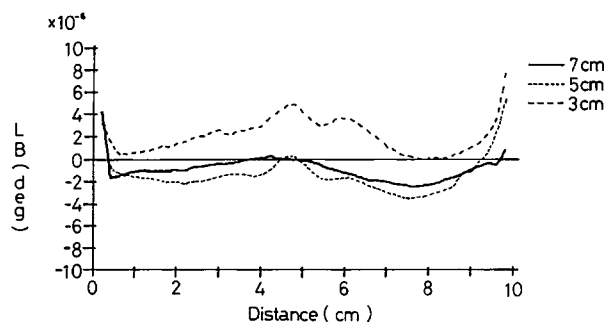


Figure 5 LB of CR-39 specimen 1 prepared from raw material 1 without annealing.

rity, 99.9%) and 2 (monomer purity, 96%, dimer and trimer, 4%). Monomer was filtered through a 1- μ m membrane filter before polymerization. One hundred parts of the monomer were mixed with 3 parts of the polymerization initiator.

Polymerization and curing conditions are as follows:

- 40–50°C: 8 h
- 50–65°C: 4 h
- 65–85°C: 3 h
- 85°C: 1 h

After curing, polymer sheets (300 \times 300 \times 2 mm) were allowed to cool freely to room temperature, and were cut in nine specimens for LB measurements (100 \times 100 \times 2 mm) with a diamond cutter. Annealing was carried out in an air oven at 120°C for 1 h, and specimens were allowed to cool freely inside the air oven to room temperature. The following four different kinds of specimens were prepared:

- Specimen 1: raw material 1, without annealing
- Specimen 2: raw material 1, with annealing

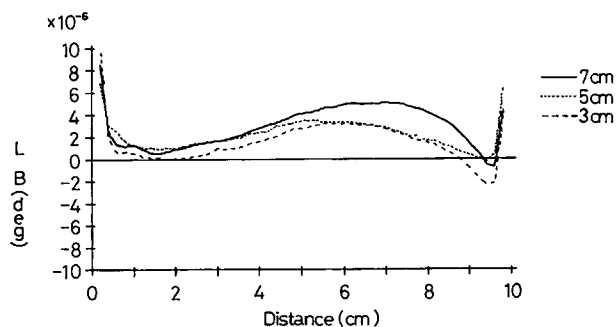


Figure 6 LB of CR-39 specimen 4 prepared from raw material 2 with annealing.

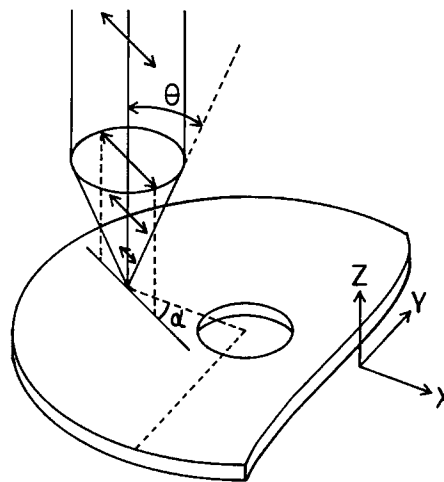


Figure 7 Coordinates of disk substrate.

- Specimen 3: raw material 2, without annealing
- Specimen 4: raw material 2, with annealing.

Experimental conditions of LB measurements are as follows: Temperature, 12 \pm 2°C; wave length, 632.8 nm. LB measurements of specimens were carried out along the lines shown in Figure 2.

Epoxy Resin

The epoxy monomer employed was EHPE-3150 (Daisel Chemical Co.) cured with 4-methylhexahydrofutaric anhydride and triphenylphosphine. The compositions of raw materials are 100 parts EHPE-3150, 69 parts 4-methylhexahydrofutaric anhydride, and 0.5 parts triphenylphosphine in weight ratio. Both the epoxy monomer and the curing agent were filtered through a 1- μ m membrane filter before reaction.

“First isothermal curing” was carried out at 140°C for 30 min, and specimens were allowed to cool freely to room temperature. “Second curing” took place at 200°C for 1 h. For “slow cool,” specimens were allowed to cool freely inside the air oven

Table I Apparent Optical Axis in x - y Plane for CR-39 Specimens 1, 2, 3, and 4 at Their Centers

Specimen	Apparent Optical Axis in x - y Plane
1	20° right from x axis
2	38° left from x axis
3	18° left from x axis
4	On the x axis

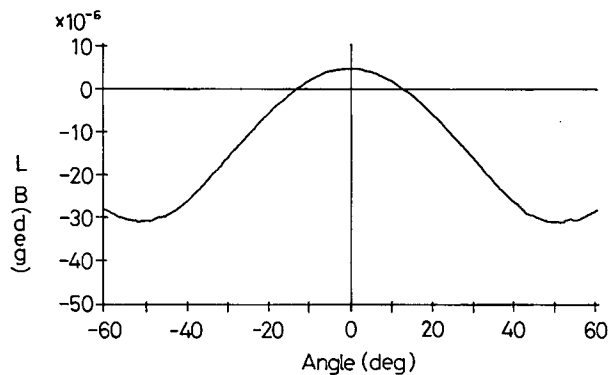


Figure 8 Change in LB of CR-39 specimen 4 with rotation around *x* axis.

to room temperature. For “fast cool,” specimens were taken out of the air oven to cool rapidly in deionized water of room temperature.

Figure 3 shows a flowchart of procedures for sample preparation and LD measurements. Experimental conditions of LB measurements are as follows: Temperature, $21 \pm 3^\circ\text{C}$; wave length, 632.8 nm. LB measurements of specimens were carried out along the lines shown in Figure 4.

RESULTS AND DISCUSSIONS

CR-39

The results of LB measurements are illustrated in Figures 5 and 6. We recognize that both sides of all specimens have large residual birefringence. This is due to the effect of cutting, which results in the residual stress. Specimens without annealing have more unequal distribution of LB than those with annealing. Annealing is very effective in reducing LB of all samples, and results in equal distribution of LB. We also know that the samples prepared from raw material 2 have smaller LB than those from raw

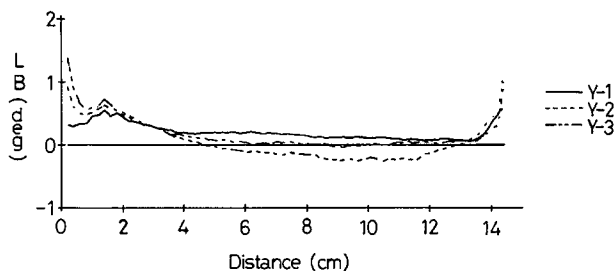


Figure 10 LB of epoxy fast-cool specimen.

material 1. This indicates that oligomers play a role as plasticizer, inducing random orientation of polymer chains, which reduces the residual LB of the specimens.

To write and read data on the disk, it is necessary to focus the laser beam on a tiny spot by lens as shown in Figure 7. We realize that α and θ are related to the rotation of specimens around *z* and *x* axes. So, we must investigate the LB change of specimens with the rotation around *z* and *x* axes, and the change of LB with *x* axis rotation must be small to be used as optical-disk substrates.

For this purpose, we determined first the apparent optical axis in *x*-*y* plane of specimens by measuring the change of LB with the rotation around the *z* axis, and then carried out LB measurements with the *x* axis rotation. Table I illustrates the apparent optical axes of the specimens. Figure 8 shows the change of LB in specimen 4 with the rotation around *x* axis. We also found that the apparent optical axes in *x*-*y* plane of specimens differ from place to place. These results indicate that CR-39 polymer forms a three-dimensional network structure in which polymer chains have three axes orientation, and the orientation direction of polymer chains are different greatly in place.

Since LB for optical-disk substrates should be less than 5 nm (double pass),² annealed samples prepared from raw material 2 satisfy this requirement.

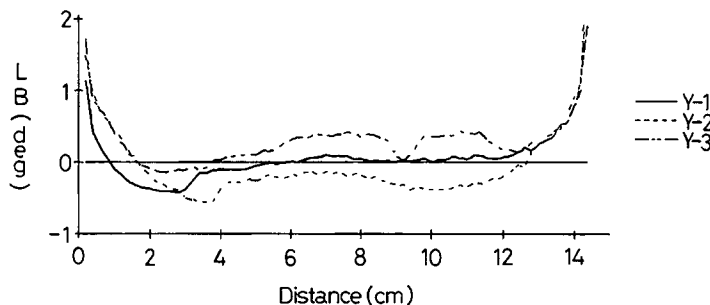


Figure 9 LB of epoxy specimen without second curing.

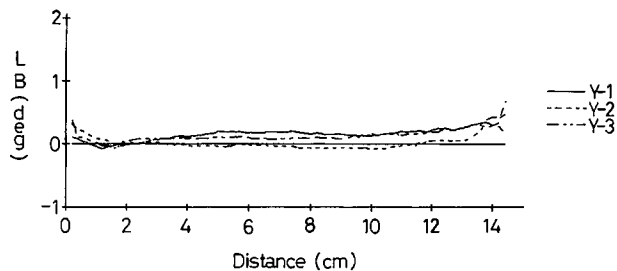


Figure 11 LB of epoxy slow-cool specimen.

Epoxy Resin

Figures 9–12 show the results of LB measurements. We notice that epoxy samples have much smaller birefringence than CR-39. We found that there are considerable differences in the value of birefringence between four specimens without second curing, which were prepared from the same cast-molded sheet. This should be due to unequal temperature distribution in the mold, heterogeneity of mold shrinkage, and a heterogeneous residue of mold pressure. Both sides of specimens have fairly large residual birefringence due to the residual stress resulting from cutting.

Second curing largely reduces LB of samples, and results in uniform distribution of LB. Slow cooling is more effective in reducing LB of samples than fast cooling. Fast cooling may induce some residual stress during cooling. After the second curing, cutting does not induce any residual stress birefringence in both slow- and fast-cooled samples, as illustrated in Figure 12. This finding is not what we expected. We think the second curing results in a rigid three-dimensional network structure that is not influenced by cutting.

Table II illustrates the apparent optical axis in *x*-*y* plane for a disk prepared from the slow-cooled specimen. Figure 13 shows the change of LB with

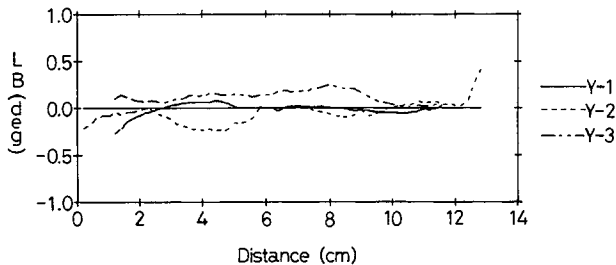


Figure 12 LB of epoxy disk prepared from slow-cool specimen.

Table II Apparent Optical Axis in *x*-*y* Plane for Disk Prepared from Slow-Cool Specimen at Different Locations

Measuring Point	Apparent Optical Axis in <i>x</i> - <i>y</i> Plane
1	69° right from <i>x</i> axis
2	20° right from <i>x</i> axis
3	61° right from <i>x</i> axis
4	47° right from <i>x</i> axis
5	76° left from <i>x</i> axis
6	58° left from <i>x</i> axis

the rotation around *x* axis at the point 3. The change in LB by both *x* and *z* axes rotation is very small. These results imply our epoxy polymer forms a three-dimensional network structure in which polymer chains are randomly oriented, although they have three axes orientation and their orientation directions differ from place to place.

Although the physical properties of the epoxy samples, such as the affinity for water, heat resistance, creep, solvent resistance, and glass transition temperature, are left uninvestigated, slow-cooled samples have good birefringence property necessary for optical-disk substrates. Productivity, measured as production time and cost, is also left as a problem that should be examined in the future.

CONCLUSION

We can summarize the results obtained as follows. For CR-39 resin: (1) Annealing is very effective in reducing LB of samples; (2) the samples prepared



Figure 13 Change in LB of epoxy disk with *x* axis rotation.

from raw material 2 have smaller LB than those from raw material 1. This indicates that oligomers play a role as plasticizer, resulting in random orientation of polymer chains; (3) annealed samples prepared from 2 satisfy the requirement on LB for optical-disk substrates.

For epoxy resin: (1) Second curing largely reduces LB of samples, and results in uniform distribution of LB; (2) slow cooling is more effective in reducing LB of samples than fast cooling; (3) after the second curing, cutting does not induce any residual stress birefringence in samples; and (4) slow-cooled samples have good optical properties to be used as optical-disk substrates.

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Received April 23, 1990

Accepted December 3, 1990