

Electrooptical-Responsive Microsphere with Ferroelectric Liquid Crystalline Segments

MASAHIRO YOSHIDA, XINGHE FAN, YOSHIMITSU UEMURA, YASUO HATATE

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

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ABSTRACT: We synthesized a ferroelectric liquid crystalline monomer (4-[4'-(7-octeneloxy)benzoyloxy]benzoate-2-methylbutylester, OBBM) possessing both carboxyl *p*-benzoxlybenzoate and carboxyl (s)-(-)-2-methylbutylester as a mesogenic group in its side chain. The liquid crystalline and styrene monomers were employed to make matrices of microspheres prepared by dispersion, suspension, or emulsion polymerization. In this study, we investigated, in detail, physicochemical properties, thermal responses, and electrooptical responses of the microspheres possessing liquid crystalline abilities. The ferroelectric liquid crystalline monomer OBBM had a thermotropic liquid crystalline ability, two-phase transition temperatures, and a Smectic C* texture, which is characteristic of ferroelectric liquid crystalline substances. The microspheres prepared also exhibited a liquid crystalline ability, and the phase-transition temperatures toward the liquid crystalline segments into the microspheres prepared by copolymerizing the liquid crystalline and styrene monomers could be decreased with increasing of the styrene monomer. Furthermore, we found that the microspheres remarkably exhibited electrooptical responses at about 8 V. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2490–2499, 2001

Key words: ferroelectric liquid crystalline monomer; liquid crystalline microsphere; thermal response; electrooptical response; phase-transition behavior

INTRODUCTION

Recently, a number of liquid crystalline polymer systems have been reported and are drawing much attention from the point of view of typical liquid crystalline polymer science and their applications.^{1–9} In particular, side-chain ferroelectric liquid crystalline polymers have gained practical and fundamental interest as systems which com-

bine the properties of polymers and ferroelectric liquid crystals with a fast electrooptical response.^{10–20} This combination is achieved by attaching the ferroelectric mesogen to a main chain via a flexible spacer. Since the spacer is effectively decoupling the movement of the mesogen from the polymer backbone, a different behavior of the mesogen, spacer, and side chain can be expected in the switching process. In addition, the use of some optically active substituents in the side chains of liquid crystalline polymers has been tried in analogy with low molecular weight liquid crystals.^{21–24} The ferroelectric liquid crystalline polymers are not always restricted in an identical polymer chain. By utilizing the copolymerizing effect that polymers are potentially equipped

Correspondence to: M. Yoshida (myoshida@cen.cen.kagoshima-u.ac.jp).

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with, we can easily control a temperature, giving a liquid crystalline structure. The copolymerizing method is a more effective methodology to improve the properties of a liquid crystalline polymer.^{25–30} The control of the arrangement in the liquid crystalline molecules caused by various outside stimuli can give many newer functions to the property of the original polymer.

To date, the research of polymeric microspheres which have a liquid crystalline response has not been generally reported. We noted that the polymeric microsphere has ferroelectric side-chain liquid crystalline properties, which can be expected to endow high functions such as a low molecular liquid crystal. We first synthesized a ferroelectric side-chain liquid crystalline monomer possessing a chiral structure at the side-chain terminal. As the epoch-making monomer synthesized has a spontaneous polarization, it will be able to respond sensitively to outside stimuli such as to various temperatures and electric fields. We continuously prepared the polymeric microspheres possessing a liquid crystalline character with various diameters by copolymerizing the ferroelectric liquid crystalline and styrene monomers (dispersion, suspension, or emulsion polymerization). In this study, we discuss the physicochemical properties of polymeric microspheres and characterize, in detail, the thermal and electrooptical responses in the microspheres.

EXPERIMENTAL

Reagents and Apparatus

p-Hydroxybenzoic acid, 8-bromo-1-octene, and (s)-(-)-2-methyl-1-butanol was purchased from the Aldrich Chemical Co., Ltd. (Milwaukee, WI). 2,2'-Azobisisobutyronitrile (AIBN) and potassium peroxodisulfate (KPS) as initiators were purchased from Wako Pure Chemical Industries Co., Ltd. (Osaka, Japan). Polyvinylpyrrolidone [PVP (K-30), molecular weight: 40,000, Aldrich Chemical Co., Ltd.] and poly(vinyl alcohol) (PVA, polymerization degree: 1500, Wako Pure Chemical Industries, Co., Ltd.) were employed as dispersion stabilizers. PVP and PVA were used without further purification. Other reagents were of commercially available special grades. H-NMR (JOEL GSX-400, JOEL Datum Co., Ltd.) or FTIR (50F FTIR, Jasco Co., Ltd.) spectroscopy was used to confirm the chemical structures of the liquid crystalline monomer. Thermal analyses were per-

formed with a DuPont 910 thermal analyzer connected to differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) modules. Texture observations on the liquid crystalline character were carried out using a polarizing optical microscope (Nikon Co., Ltd., Eclipse E600POL) fixed with a hot stage. The observation of the microsphere surface was performed using a scanning electron microscope (SEM, Topcpn Model SM-300, Topcon Co., Ltd.). A gel permeation chromatograph (GPC) (Tosho Co., Ltd.) was used to determine an average-weight molecular weight. Particle-size analysis was performed using a Coulter particle analyzer (Coulter LS130, Coulter Electronics, Inc.). A polarized light-transmitting apparatus was constructed by us.

Synthesizing of Ferroelectric Side-chain Liquid Crystalline Monomer

We designed a ferroelectric side-chain liquid crystalline monomer, OBBM, containing both carboxyl *p*-benzoyloxybenzoate (a mesogenic part) and carboxyl (s)-(-)-2-methylbutylester (a terminal group). The monomer was synthesized according to Figure 1. The intermediates and final product were purified using thin-layer chromatography (TLC), and their chemical structures were then confirmed spectrophotometrically.

Synthesis of Compound 1

Compound 1 was synthesized in a flask. *p*-Hydroxybenzoic acid, 1.11 g, and 8-bromo-1-octene, 1.68 g, were placed in the flask and dissolved in 300 mL ethanol. Potassium hydroxide, 0.49 g, was then added to the solution. The reaction mixture was refluxed at 80°C for 24 h. After refluxing, the mixture was cooled to room temperature. The reaction solution was adjusted to pH 2–3 by 1M hydrochloric acid. The solvent was evaporated completely and solid products were obtained. The crude products were purified by recrystallization in ethanol. The purified product was dried *in vacuo* at room temperature. The yields of compound 1 were about 90%.

Synthesis of Compound 2

Compound 2 was synthesized from *p*-hydroxybenzoic acid and (s)-(-)-2-methyl-1-butanol. A cationic-exchange resin (Dow Chemical HCR-W2, Dow Chemical Co. Ltd.) was employed as a catalyst for esterification. *p*-Hydroxybenzoic acid, 1.00 g, (s)-(-)-2-methyl-1-butanol, 1.90 g, and HCR-W2

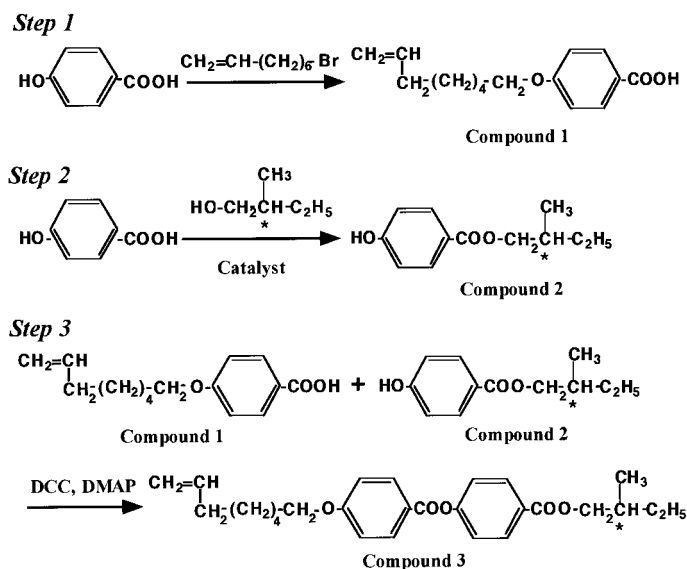


Figure 1 Synthesis scheme of ferroelectric side-chain liquid crystalline monomer.

resin, 10.0 g, in 100 mL toluene were put into a flask equipped with a water separator. The reaction was carried out at 110°C for 3 days. The resins used as a catalyst were filtered off, and the filtrate was concentrated using a rotary evaporator under reduced pressure. The crude products obtained were purified using TLC (eluate: $\text{CHCl}_3/\text{CH}_3\text{OH} = 9/1$, v/v). The yields of compound 2 were about 94%.

Synthesis of Compound 3

In a flask, 1.93 g 7-octeneloxyhydroxybenzoic acid and 1.77 g *p*-hydroxybenzoic acid 2-methylbutylester were dissolved in 30 mL CH_2Cl_2 . 4,4'-Dicyclohexylcarbodiimide (DCC), 1.75 g, and 4-dimethylaminopyridine (DMAP), 0.97 g, were added to the mixture at 25°C.² The reaction mixture was maintained at 25°C under stirring for 24 h. The mixture obtained was filtered to remove solid compounds (hydrated DCC), and the filtrate was concentrated using a rotary evaporator under reduced pressure. The crude products obtained were purified using TLC (eluate: $\text{CHCl}_3/\text{CH}_3\text{OH} = 9/1$, v/v). The yields of the final product were about 84%.

Preparation of Microspheres

The microspheres were prepared in a three-neck round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a condenser. The reactor is illustrated in Figure 2.

Dispersion Polymerization

PVP, 0.31 g, was dissolved in a 30 mL methanol in the reactor. Mixing compounds (0.037M) of

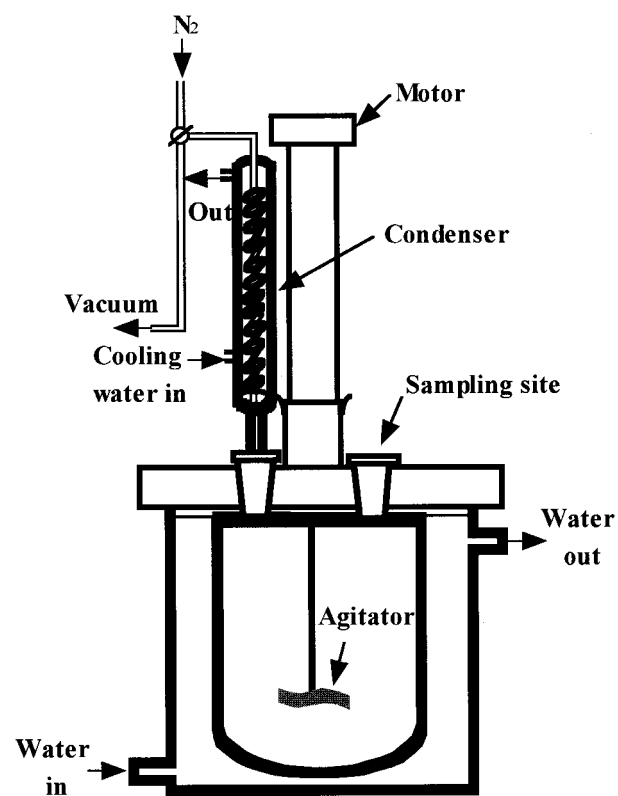


Figure 2 Schematic illustration of polymerization reactor.

OBBM and the styrene monomers (mol ratios: OBBM:styrene = 10:0, 8:2, 6.7:3.3, 5:5, 3.3:6.7, 2:8, 0:10) containing 0.02M AIBN were put into the reactor under a nitrogen atmosphere. The polymerization was conducted at 80°C under stirring (600–650 rpm) for 16 h. After polymerization, the reaction mixture was centrifuged at 1500 rpm for 30 min. The microspheres collected were washed with water and hexane and then dried *in vacuo* at room temperature for 24 h.

Suspension Polymerization

PVA, 0.31 g, was dissolved in 30 mL water in the reactor. Mixing compounds (0.037M) of OBBM and the styrene monomers (mol ratios: OBBM:styrene = 10:0, 8:2, 6.7:3.3, 5:5, 3.3:6.7, 2:8, 0:10) containing 0.02M AIBN were put into the reactor under a nitrogen atmosphere. The polymerization was carried out at 80°C under stirring (600–650 rpm) for 16 h. After polymerization, the microspheres were filtrated and washed with water and hexane and then dried *in vacuo* at room temperature for 24 h.

Emulsion Polymerization

Sodium dodecylsulfate (SDS), 0.31 g, was dissolved in 30 mL water in the reactor. Mixing compounds (0.037M) of OBBM and the styrene monomers (mol ratios: OBBM:styrene = 10:0, 8:2, 6.7:3.3, 5:5, 3.3:6.7, 2:8, 0:10) containing 0.02M KPS were put into the reactor under a nitrogen atmosphere. The polymerization was carried out at 80°C under stirring (600–650 rpm) for 16 h. After polymerization, the microspheres were filtrated and washed with water and hexane and then dried *in vacuo* at a room temperature for 24 h.

Effect of Initiator Concentrations in the Preparation of Microspheres

Microspheres were prepared using various initial concentrations of AIBN or KPS (C_i : 0.01, 0.02, 0.025, 0.03, 0.04, 0.06M). The other preparation conditions in the dispersion, suspension, or emulsion polymerization were performed as mentioned above.

RESULTS AND DISCUSSION

The molecular structures of the monomer OBBM were confirmed using H-NMR and FTIR. Tetramethylsilane (TMS) and chloroform-*d* were used as

Table I Thermal Stability of Ferroelectric Side-chain Liquid Crystalline Monomer OBBM

Temperature (°C)	Weight Loss (wt %)
254	5
283	10
303	15
320	20
333	25

an initial standard substrate and a measurement solvent, respectively. The neat method was employed in the FTIR measurement. Both measurements were carried out at 25°C. The results were as follows:

H-NMR analysis: 0.90–1.00 ppm [m, —COO—CH₂—CH(C₂H₅)—CH₃]; 1.27–1.36 ppm (m, —CH₂CH₃); 1.85–2.10 ppm [m, —(CH₂)₅—]; 4.02–4.07 ppm (m, —COO—CH₂—); 4.10–4.25 ppm (m, —CH₂—O—); 4.90–5.08 ppm (m, CH₂=CH—); 5.78–5.88 ppm (m, CH₂=CH—); 6.98–8.18 ppm (m, aromatic protons). FTIR analysis: 2962–2854 cm⁻¹ (stretch vibration of methylene and methyl groups); 1735 cm⁻¹ (stretch vibration of carbonyl group); 1120 cm⁻¹ (stretch vibration of ether group); 1608 cm⁻¹ (stretch vibration of ester group); 990 cm⁻¹ (stretching vibration of vinyl group).

We succeeded in synthesizing the ferroelectric side-chain liquid crystalline monomer OBBM. Moreover, Table I summarizes the thermal stability of the liquid crystalline monomer OBBM as a fundamental physicochemical property. The thermal stability of the monomer OBBM was investigated by a thermogravimetric analyzer (TGA) at a heating rate of 20°C/min under a nitrogen atmosphere. The sample weight for the measurement was 9 ± 1 mg. The liquid crystalline monomer OBBM was relatively stable up to 250°C; however, the monomer gradually lost molecular weight over 250°C. At an increasing temperature of more than 300°C, the monomer lost 15–25 wt % of its molecular weight. The point is that the liquid crystalline monomer OBBM synthesized is stable enough to exist under a high temperature.

Figure 3 shows SEM photographs of the microspheres prepared by dispersion, suspension, or emulsion polymerization. The volume-average diameters of the microspheres obtained by dispersion, suspension, or emulsion polymerization were 1.5 μm, 45 μm, or 80 nm, respectively. The microspheres prepared were well-defined micro-

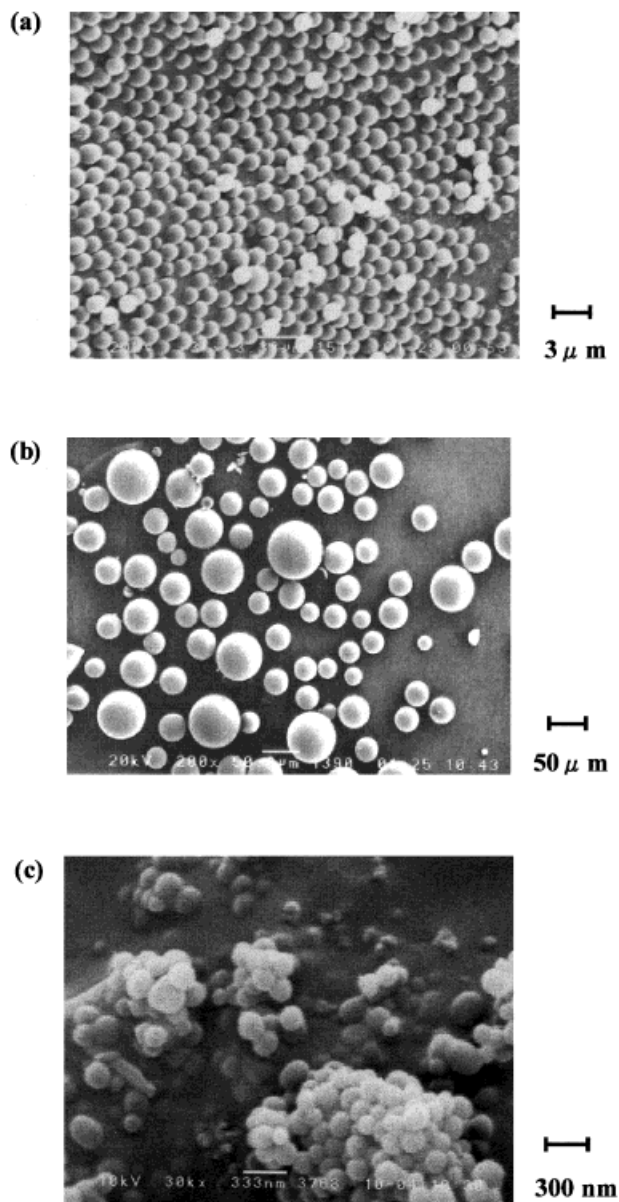


Figure 3 SEM photographs of microspheres: (a) microsphere prepared by dispersion polymerization; (b) microsphere prepared by suspension polymerization; (c) microsphere prepared by emulsion polymerization.

spheres as shown in Figure 3. The surfaces of the microspheres were smooth, and a large number of microspores on the microspheres were not observed.

Texture observations of the monomer and microspheres were carried out using a polarizing optical microscope equipped with a thermoregulator. Microscopic photographs were taken at the temperature where a liquid crystalline response appeared, as shown in Figure 4. The liquid crys-

talline monomer OBBM exhibits a Smectic C* texture, which is characteristic of the ferroelectric liquid crystalline compounds^{14,15,22,30} The microspheres prepared by dispersion, suspension, or emulsion polymerization exhibited liquid crystalline properties; however, we could not accurately identify their textures.

The relationship between the weight-average molecular weight of the microspheres and the initial concentration of the initiator in dispersion, suspension, or emulsion polymerization is shown in Figure 5. As shown in Figure 5, the weight-average molecular weight of the microspheres decreased with increase of the initiator concentration. We found that the initiator concentration depended on the weight-average molecular weight of the microspheres and the value of the weight-average molecular weight toward each initiator concentration is nearly constant without depending on the preparation methods. As the other preparation conditions in the dispersion, suspension, or emulsion polymerization are the same except for the initiator concentration, we found that the difference in the particle size in the microspheres was caused by the polymerizing methods themselves.

Thermal properties of the liquid crystalline monomer or the microspheres were performed by DSC measurement. The DSC measurements were carried out at 5°C/min to the upper-limit temperature under a nitrogen atmosphere. The sample weight was 9 ± 1 mg. Figure 6 shows DSC spectra of the monomer and microsphere prepared by dispersion polymerization (OBBM:styrene = 6.7:3.3). The DSC thermograms of the monomer or microsphere have two endothermic peaks. The mesophase transition temperature (T_m) and the mesophase-isotropic phase transition temperature (T_i) in the monomer appeared at 20 and 37°C, respectively. The transition temperatures (T_m and T_i) in the microsphere appeared at 80 and 100°C, respectively.

The effect of the liquid crystalline monomer concentration on the phase-transition temperatures (T_m and T_i) of the microspheres prepared by dispersion, suspension, or emulsion polymerization is shown in Figure 7. As shown in Figure 7, T_m and T_i increase with an increasing OBBM concentration. It was found that the microspheres containing more than a 50 mol % OBBM concentration possess a liquid crystalline ability. In ad-

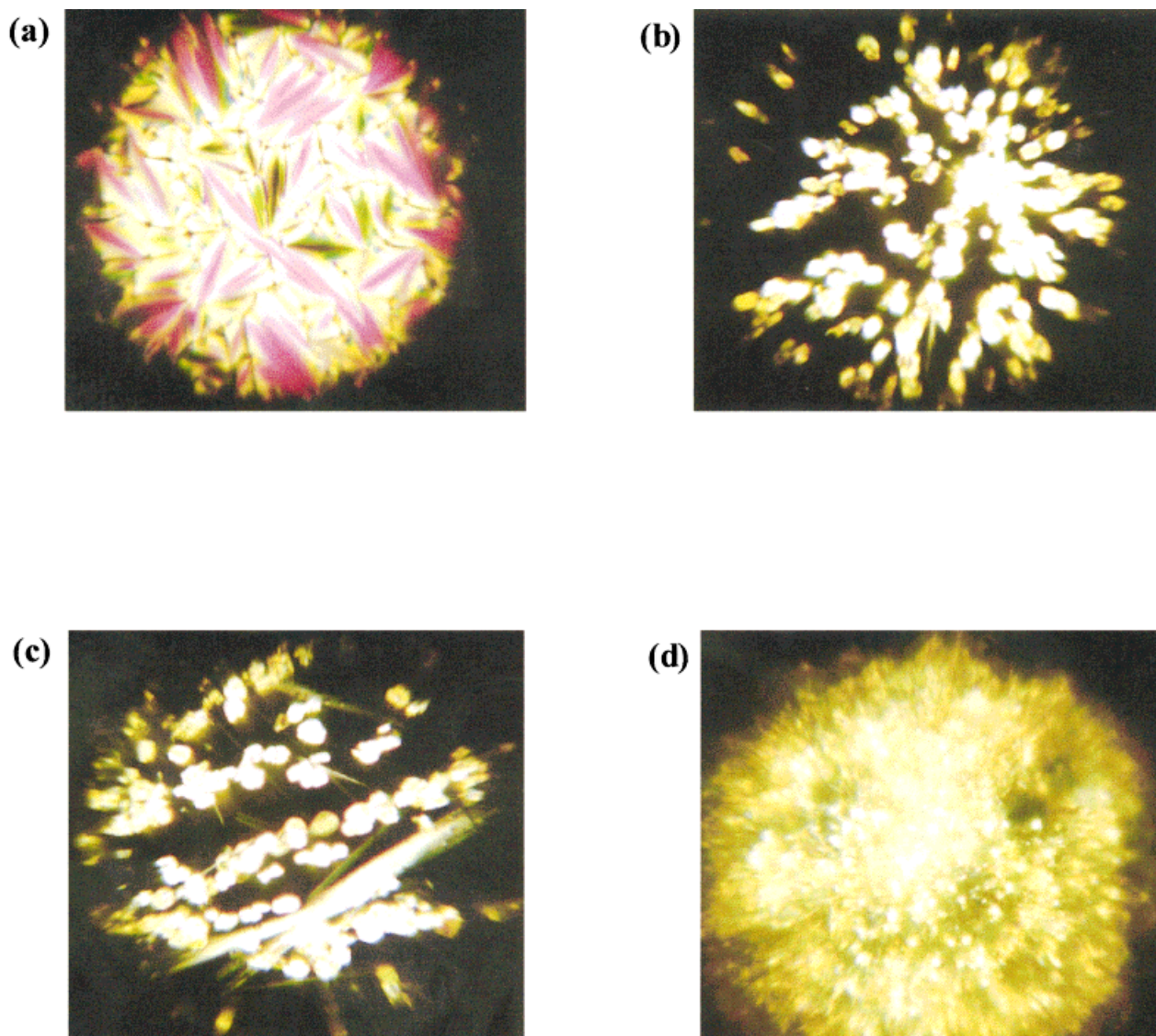


Figure 4 Polarizing microscope photographs of OBBM and microspheres: (a) OBBM; (b) microsphere prepared by dispersion polymerization; (c) microsphere prepared by suspension polymerization; (d) microsphere prepared by emulsion polymerization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

dition, the important point to note is that T_m and T_i could be decreased with an increasing styrene monomer compared to those of microspheres prepared by OBBM homopolymerization.

The relationship between the weight-average molecular weight of the microspheres and the phase-transition temperatures (T_m and T_i) is shown in Figure 8 (OBBM:styrene = 6.7:3.3). The measurement of the weight-average molecular weight employed the GPC (eluate: chloroform; measurement temperature: 30°C). As shown in Figure 8, when the weight-average molecular

weight of the microspheres is approximately less than 1×10^4 , the phase-transition temperatures (T_m and T_i) increase with increasing average-weight molecular weights. On the other hand, when the average-weight molecular weight of the microspheres is more than 1×10^4 , T_m and T_i exhibit constant values without depending on the average-weight molecular weight. Furthermore, we confirmed that the profiles of the microspheres prepared by different compositions of OBBM and styrene monomers show the same tendency.

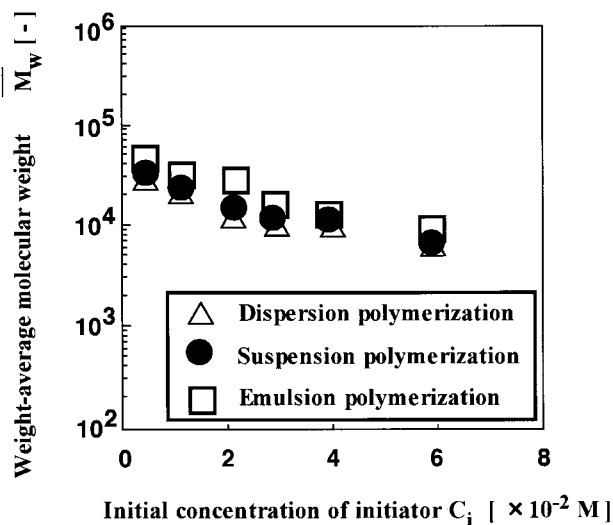


Figure 5 Relationship between initial concentration of initiator and weight-average molecular weight on the preparation of microsphere.

We investigated the liquid crystalline properties in the microspheres with polarized light transmittance. The measurement of polarized light transmittance is quantitatively possible to realize the change of the liquid crystalline response at the appointed temperature and voltage. For the measurement of polarized light transmittance, we measured under various temperatures or voltages using the handmade apparatus shown in Figure 9. A He—Ne laser (wavelength: 632.8 nm) was used as an incident beam. The intensity of the transmitted rays toward the sample was transformed to a voltage. For the measurement of the thermal response in the liquid crystalline microspheres, the temperatures were increased from 30 to 200°C at 3°C/min. The temperature was then reduced from 200 to 30°C at 3°C/min. In addition, the transmitted light intensity was measured under various voltages at a constant temperature (90°C). The voltages were varied in the range of 0–10 V.

Figure 10 shows the change of the transmitted light intensity toward various temperatures in the microsphere prepared by dispersion polymerization (OBBM:styrene = 6.7:3.3). The results of the suspension or emulsion polymerization were similar to the behavior of the dispersion one. In increasing the temperature to about 100°C, the transmitted light intensity suddenly decreased a little over T_i . It follows from this result that the liquid crystalline segments into the microspheres were transferred from the mesophase to the iso-

tropic phase. On the other hand, when temperature was cooled, the transmitted light intensity immediately increased at a little less than T_i . It is considered that the liquid crystalline segments in the microspheres transferred from the mesophase to the solid phase. These thermal responses resulted in hysteresis phenomena on both sides of T_i , because the experiment apparatus used was of our making. It was very difficult for us to detect a true sample temperature in the polarized light transmittance measurement.

Figure 11 shows the change of the transmitted light intensity toward various voltages in the microsphere prepared by dispersion polymerization

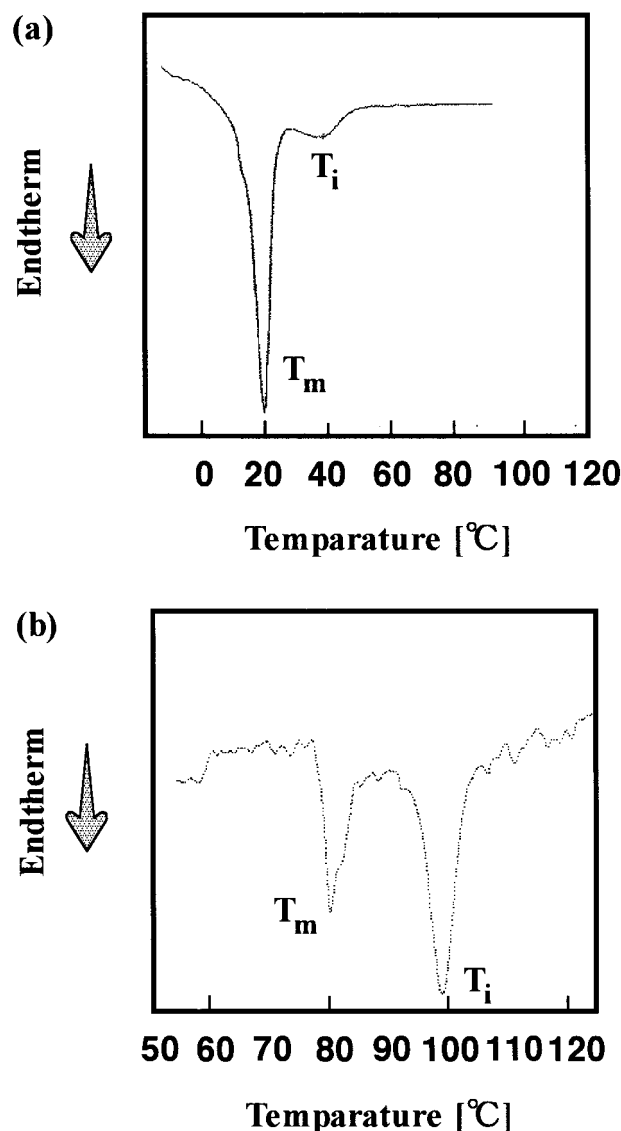


Figure 6 DSC spectra: (a) OBBM; (b) microsphere prepared by dispersion polymerization.

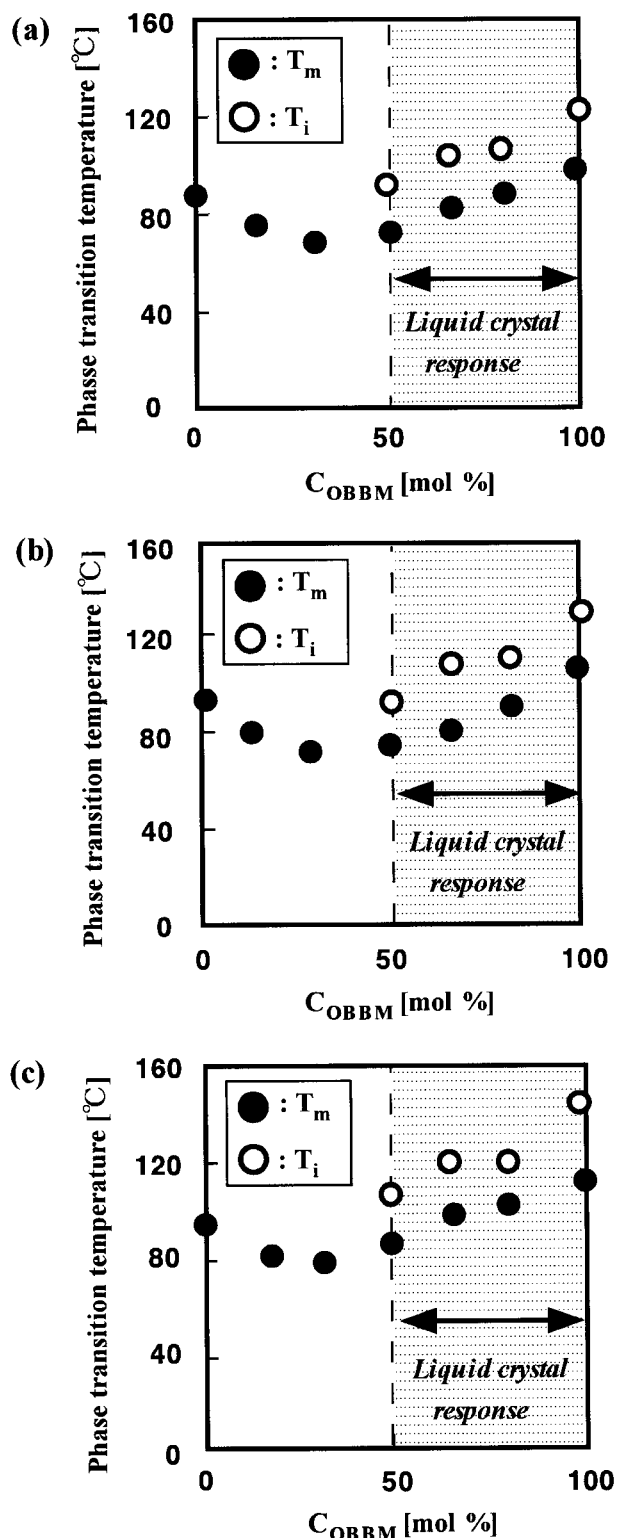


Figure 7 Effect of liquid crystalline monomer concentration on phase-transition temperatures: (a) microsphere prepared by dispersion polymerization; (b) microsphere prepared by suspension polymerization; (c) microsphere prepared by emulsion polymerization.

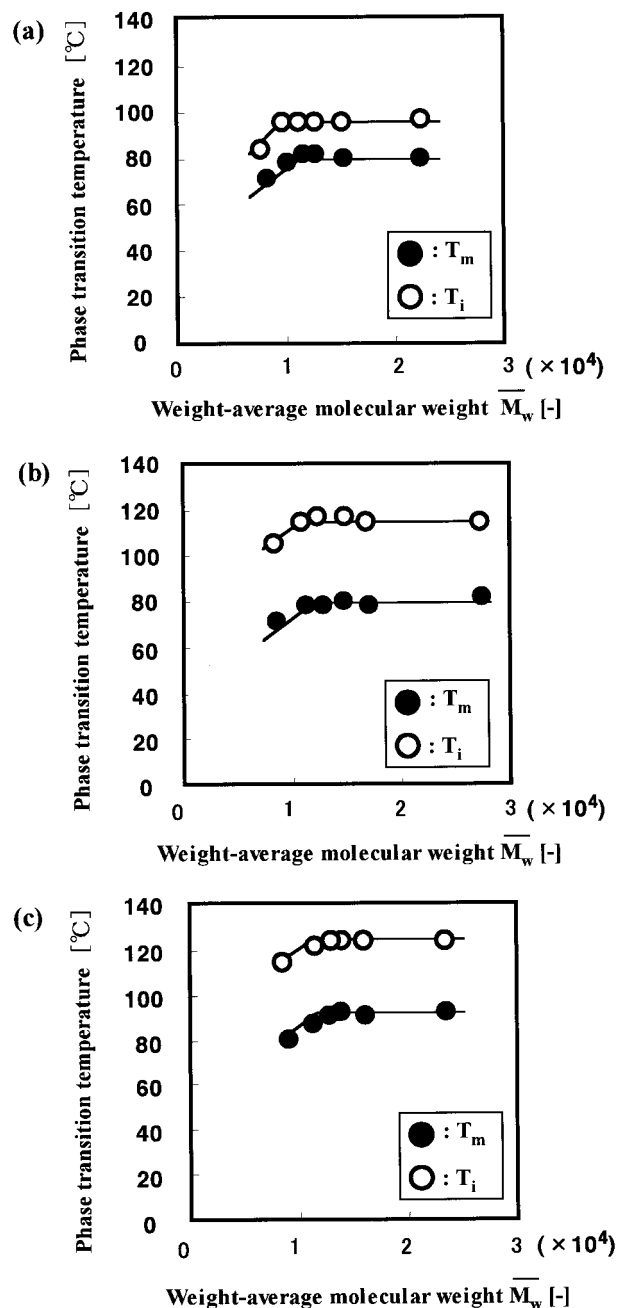


Figure 8 Relationship between average-weight molecular weight and phase-transition temperature: (a) microsphere prepared by dispersion polymerization; (b) microsphere prepared by suspension polymerization; (c) microsphere prepared by emulsion polymerization.

(OBBM:styrene = 6.7:3.3) at a constant temperature (90°C). In increasing the voltages gradually from 0 V, the transmitted light intensity decreased from 1100 to 750 mV at nearly 8.2 V. In slowly reducing the voltage from 10 V, the transmitted liquid intensity increased from 750 to 1100

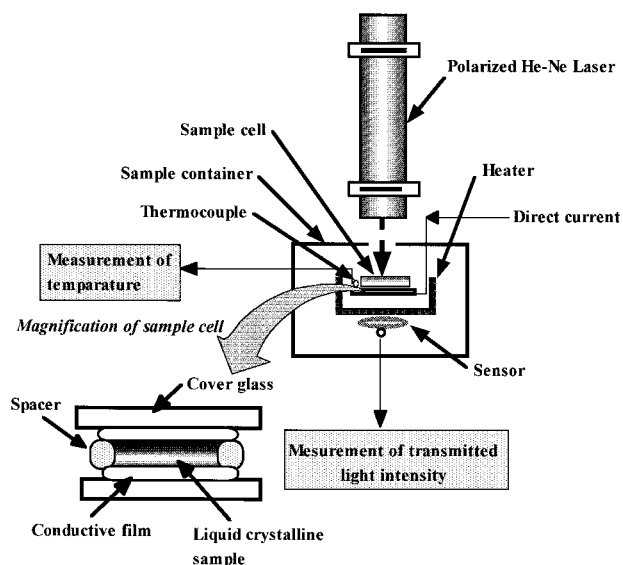


Figure 9 Schematic illustration of polarized light transmittance apparatus.

mV at about 3.8 V, and the transmitted light intensity exhibited the original constant value (1100 mV). The microspheres prepared by suspension or emulsion polymerization also exhibited the same electrooptical responses. We could sufficiently confirm the ferroelectric characterization in the monomer OBBM or the microspheres by the results of the electrooptical response.

CONCLUSIONS

A ferroelectric side-chain liquid crystalline monomer OBBM, possessing both carboxyl *p*-benzoxyl-

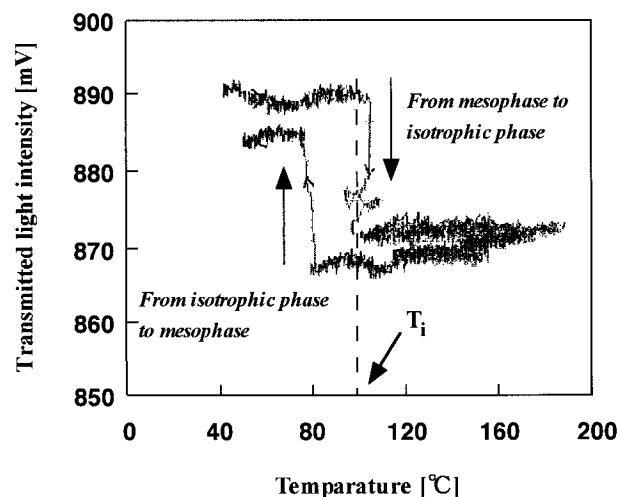


Figure 10 Measurement of transmitted light intensity toward various temperatures in microsphere prepared by dispersion polymerization.

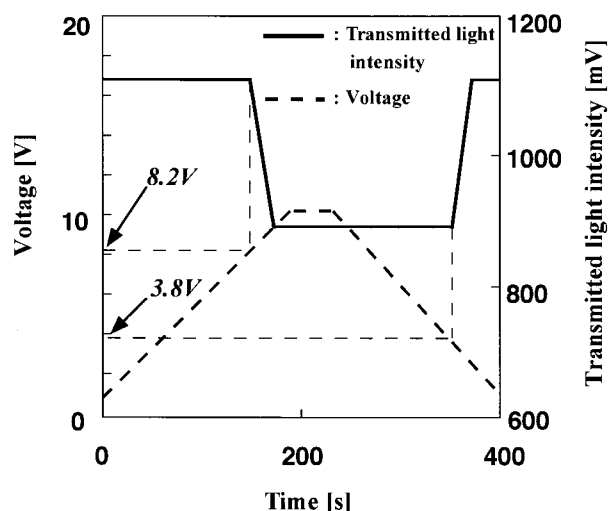


Figure 11 Measurement of transmitted light intensity toward various voltages in microsphere prepared by dispersion polymerization.

benzoate and carboxyl (s)-(-)-2-methylbutylester as a mesogenic group in its side chain, was synthesized. The liquid crystalline and styrene monomers were used to make matrices of the microspheres prepared by dispersion, suspension, or emulsion polymerization. In this study, we particularly investigated, in detail, the physicochemical properties and thermal and electrooptical responses in the microspheres. In conclusion, (1) the ferroelectric side-chain liquid crystalline monomer OBBM had a thermotropic liquid crystalline property, and its phase-transition temperatures determined by DSC measurement were 20°C (from the solid phase to the liquid crystal phase) and 37°C (from the liquid crystal phase to the isotropic phase), (2) the ferroelectric liquid crystalline monomer OBBM was confirmed to exhibit a Smectic C* phase by the thermal polarized light microscopy measurement, (3) the volume-average diameters of the microspheres prepared by dispersion, suspension, or emulsion polymerization were 1.5 μm , 45 μm , or 80 nm, respectively, (4) the microspheres prepared also showed liquid crystalline properties by the thermal polarized light microscopy measurement, (5) the phase-transition temperatures of the liquid crystalline phase in the microspheres prepared by copolymerizing the liquid crystalline and styrene monomers could be decreased with increasing of the styrene monomer, and (6) the microspheres clearly exhibited thermal responses at various temperatures or electrooptical responses at the appointed voltage. It is our belief that the use of

the microspheres possessing liquid crystalline responses will find many applications in the future.

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