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A LIQUID CRYSTAL BASED POLYMER FOR APPLICATIONS IN MMW MODULATION DEVICES

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Abstract A new liquid crystal monomer, the diacrylate of a bis phenyl diazene, was synthesized. It was polymerized to form both unoriented and oriented polymer solids -- the latter in the presence of a magnetic field. The millimeter wave birefringence was measured for a polymeric rod, whose macroscopic orientation was perpendicular to its long axis, using a waveguide version of the Mach-Zehnder interferometer, and the measured Δn was 0.075 at 30 GHz. The mechanical strength of oriented and unoriented polymer plates was measured. The tensile modulus in the direction parallel to the oriented axis was 6.8×10^8 N/m^2, which was about 4 times that of the same material without macroscopic orientation. The torsional rigidity modulus of a thin rod (orientation perpendicular to its length) was measured to be of the order 10^7 N/m^4. Both the large dielectric anisotropy and high mechanical strength make the oriented polymer potentially suitable for application in a novel class of millimeter wave modulation devices.

INTRODUCTION

Many microwave (MW) and millimeter wave (MMW) modulation devices such as phase shifters and scanning antennas use some form of mechanical articulation motion to modulate the propagating electromagnetic waves. The mechanical articulation can make a device quite bulky; as an example, to scan a microwave beam with a parabolic antenna, the whole antenna is physically rotated to redirect the beam direction. In the coming decades, as more wireless telecommunications applications are anticipated in the MW and MMW range, development of compact and simple to operate phase shifters, antennas, etc. will become more urgent.[1]

A novel method to reduce the bulk of mechanical modulation devices is to use electromagnetically anisotropic materials as modulation media; these materials can be used in the new class of more compact mechanical modulation devices described in this paper. In the case of the birefringence materials, the propagating speed depends on the relative angle between the propagation vector and the optical axis; the propagation speed can thus be modulated by changing the angle.[2] Such birefringent materials (e.g. liquid crystals) have been used extensively in the visible light range to modulate electromagnetic waves for displays; however, this simple idea has not been used in the MW and MMW range extensively, partly because of the dearth of anisotropic solid materials.

Many polymeric materials are electromagnetically anisotropic but prove to be difficult to fabricate into large anisotropic volumes uniformly because of difficulty in controlling the polymer molecular alignments. Although the production of anisotropic crystals and films on a very small scale (about mm size) through crystallization and mechanical shear has been successfully reported, most of the present methods have proven to be difficult to scale up. The inability to produce large uniformly anisotropic polymeric solids has impeded the development of anisotropic optics in the MW and MMW range.

While liquid crystals have been used extensively as a birefringence modulation media for visual displays in the visible light range, the possibility of combining the orientation order of low molar mass liquid crystals with that of high molecular weight compounds to create new polymer materials for new applications (e.g. processing of high strength materials, birefringence materials in the MMW range) has led to the relatively new science of liquid crystal polymers. The liquid crystal can be incorporated into the polymer in two ways. In the first approach, the mesogenic groups are joined head-to-tail with suitable spacer groups to form a main-chain liquid crystal polymer.[3,4] These materials form basic structural units of systems reproducing high modulus fibers. The second method is to link the mesogenic groups to an existing polymer backbone to form a side-chain polymer or comb-like polymeric system.[5,6] In the comb-like polymer, the liquid crystal side chain can be aligned to provide the anisotropy.

The common method for preparing aligned thermotropic liquid crystal polymers is to create macroscopic ordering in the liquid crystalline phase of the polymer by applying external force fields such as a surface steric alignment force, an electric field or a magnetic field. The polymer is then cooled to below the glass transition temperature to freeze the macroscopic ordering. However, in practice, it is difficult to create very high ordering for the thermotropic liquid crystal polymers, and also difficult to retain a high order in the glass state without gradual relaxation and loss of macroscopic ordering.[7-10]

A different approach to the preparation of highly ordered polymer materials is *in* *situ* polymerization of oriented liquid crystal monomers.[11-19] By using this approach, macroscopic ordering and the optical anisotropy of oriented polymeric materials might be permanently retained after the polymerization. In addition, it is much easier to align liquid crystal monomers than polymers using external fields. Therefore, this is a promising approach to produce polymeric materials that require macroscopic ordering.

Liquid crystal monomers containing diacrylates with carboxylate bridges have been found suitable for *in situ* polymerization, either thermally[11-15] or photochemically.[16-19] However, they do not have high birefringence in the microwave region. In order to further increase the birefringence and widen the nematic ranges, we have synthesized new liquid crystal diacrylates containing diazene bridges.

This report contains a description of the synthesis of these new liquid crystal monomers, the preparation of oriented polymer by *in situ* polymerization in the presence of an external magnetic field, the measurements of their MMW birefringence, and their mechanical strength, which are important for device applications. The MMW birefringence of these oriented polymers, placed in a waveguide sample cell, was measured in a waveguide version of a Mach-Zehnder interferometer. In addition, we show conceptually that the sample cell can be used as a novel mechanical phase shifter and can be further modified to a very compact version of a mechanical scanning array antenna.

EXPERIMENTAL

The diacrylate liquid crystal monomers were synthesized and then thermally polymerized *au naturelle* or in the presence of a magnetic field. They were polymerized in the required shapes to measure their birefringence in a 30 GHz Mach-Zehnder interferometer, and to measure their mechanical strength. To render the description of the three experimental tasks clearly, this section is divided into three parts: synthesis; the measurement of MMW birefringence; and the measurement of the tensile and torsional stress modulus.

Synthesis of Liquid Crystal Polymers

Three diacrylate liquid crystals with the diazene bridges were synthesized from the liquid crystal in five main steps. Figure 1 ($X = H, F, CH_3$) shows the schematic steps of the synthesis, and the details are described elswhere.[20] The diacrylate with $X = H$, 4,4'-(3,3'-dimethylbiphenyl) bis{4-6[(acryloyxy)hexyloxy]-phenyl diazene}, has the widest nematic range, and was thus used to prepare the oriented polymers.

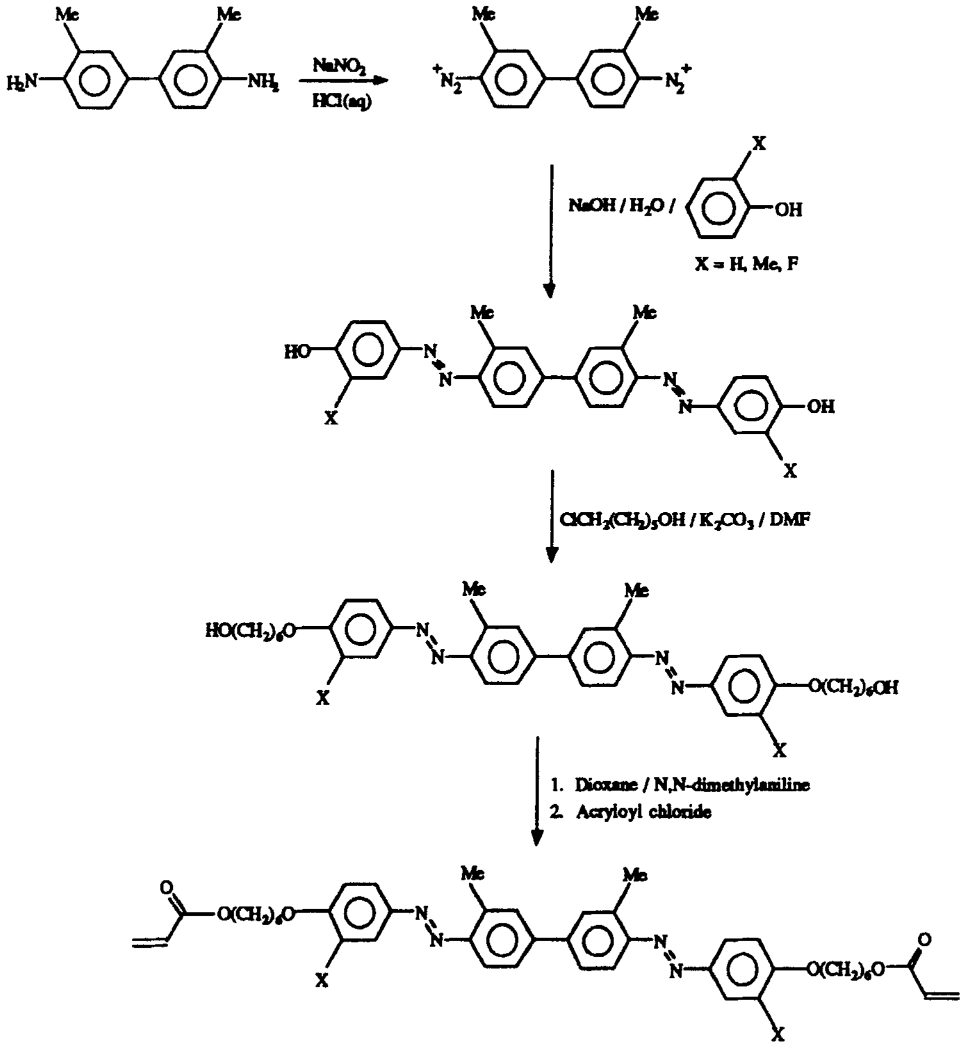

FIGURE 1 Synthetic scheme for the diazene diacrylate monomers.

An appropriate amount of the monomer was mixed with 2 wt. % of an initiator, dicumyl peroxide, and dissolved in chloroform. The solvent was evaporated and dried in a vacuum overnight. The mixture was gradually introduced either into a long cylindrical sample tube or a rectangular container, with stepwise melting at 100 °C to avoid air bubbles being trapped in the sample. After the sample container was filled, it was put inside a magnet and heated up to 110 °C for 30 minutes to ensure macroscopic alignment. Finally, the sample was polymerized by raising the temperature to 130 °C for 2 hours. Samples for the microwave experiment were polymerized in the cylindrical tube which was placed inside a 1.8 tesla electromagnet; its optical axis (along the magnetic field direction) was parallel to one of its diameters and perpendicular to its length. Samples for mechanical strength measurements (tensile stress modulus) were polymerized in a rectangular container placed inside a 7 tesla superconducting magnet; its optical axis was parallel to the long side of the rectangle. The rectangular shaped samples were further cut into dogbone shape with the optical axis parallel to the bone axis, which was the direction of the stress.

MMW Birefringence

A rectangular waveguide version of a Mach-Zehnder interferometer,[21] shown schematically in Figure 2 , was used, for its simplicity and flexibility in accommodating solid samples, to measure the birefringence. For the most common and simple TE_{10} mode of propagation inside a rectangular waveguide, the E-field vectors of the propagating MMW are well-defined and are perpendicular to both the axis of the waveguide and the broad sides of the waveguide.[22] In our experiment, a MMW beam in TE_{10} mode, generated by a 30 GHz Gunn oscillator, passed through an isolator and an attenuator, was divided into two arms through a 10 db directional coupler. One arm had a variable attenuator while the other had a mechanical 360° phase shifter and a sample cell. The beam from the two arms were recombined through another 10 db directional coupler and the resultant field strength measured by a diode detector. The 360° phase shifter and the attenuator were used to match the relative phase and power between the two branches to obtain a null output from the diode detector. The sensitivity of the interferometer was about ±0.25° of the phase shift.

The rectangular waveguide sample cell was simply a vertical section of the 30 GHz WR28 (internal dimension 0.711 x 0.355 cm) waveguide with a teflon insert. The axis of the insert was hollow with a diameter that was slightly larger than the diameter of the sample to accommodate snugly the cylindrically shaped polymer sample. The length of the insert was the same as that of the sample. In this experiment, to accommodate a polymer sample of diameter 0.22 cm and length 6.1 cm, the diameter of the center hole in the insert was 0.23 cm and the length of the insert was 6.1 cm.

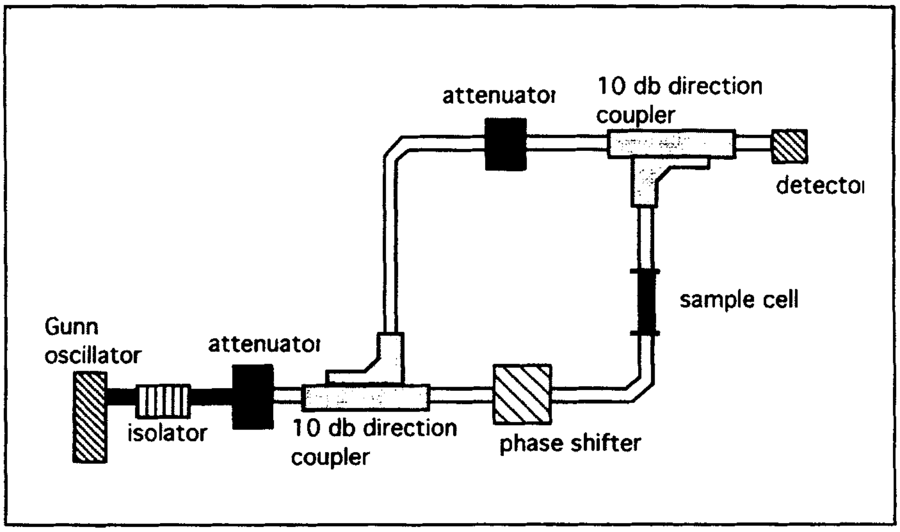

FIGURE 2 The 30 GHz waveguide Mach-Zehnder interferometer.

To measure the phase shift introduced by a sample, with the sample inside the sample cell, the phase angles of the two arms were matched by adjusting the 360° phase shifter and the attenuator until the detector reading was minimum. The phase angles of a polymer rod (diameter 0.22 cm, length 6.1 cm) with its orientation directions parallel and perpendicular to the E-field were measured.

Tensile and Torsional Rigidity Modulus

The tensile properties for both the oriented and unoriented samples were tested using an Instron type TT-C-L Tensile Tester with a home-built computerized data acquisition system. Dogbone shaped samples were prepared with a width of 4 millimeters and a thickness of 1.25 mm. The length of the oriented sample was 17.8 mm, and the unoriented sample was 20.6 mm long. The samples were uniaxially extended at a rate of 0.25 mm per minute. Figure 3 shows the experimental stress (kPa) versus percentage elongation curve for the unoriented sample; the oriented sample showed similar behavior.

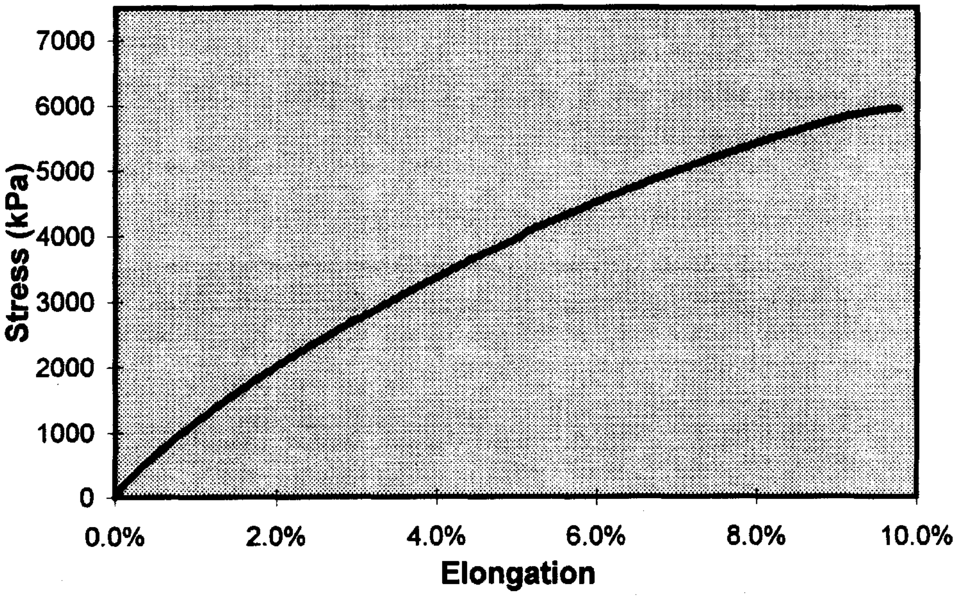

FIGURE 3 Stress versus strain of the unoriented polymer sample.

The torsion rigidity modulus was measured with a simple home-built apparatus. A polymer sample, in a long cylindrical shape, was clamped between a fixed clamp at one end and a rotating clamp with a wheel at the other end. A torque was applied by adding weight to the wheel, and the corresponding angular deflection of the twist in the sample was measured from the angular deflection of the wheel. An angular deflection of 1 degree was obtained with an applied torque of 1.08×10^{-4} N·m for the polymer sample (diameter 0.22 cm, and length 4.0 cm); this sample was also used for the MMW measurements.

RESULTS AND DISCUSSION

Liquid crystal monomers containing diacrylates, commonly with three-ring mesogenic core and two flexible chains, have been found suitable for *in situ* polymerization, either photochemically or thermally.[17-19] However, they are not the most ideal candidates for MMW applications because of limited birefringence and nematic ranges. For the purpose of *in situ* thermal polymerization to produce oriented samples, the nematic range has to be wide enough to cover the thermal polymerization temperature. Therefore, we have synthesized three liquid crystal diacrylate monomers containing diazene bridges, with X = H, X = F, and X = CH_3 (Figure 1), and all have wide nematic range, as shown in Table I.

TABLE I Nematic ranges of the diazene diacrylate monomers.

Liquid crystal	Nematic range (°C)
X = H	100 - 214
X = F	91 - 190
X = CH_3	90 - 161

Because the compound with X = H has the widest nematic range, it was polymerized for the MMW and mechanical properties measurements. After the polymerization, the samples did not retain their liquid crystalline properties, and cannot be regarded as liquid crystal polymer.

Table II shows the phase angles of the 360° phase shifter in the MMW interferometer as a function of the parallel and perpendicular orientation of the polymer sample.

TABLE II Phase angles for polarized MMW measurements.

Sample orientation	Parallel	Perpendicular
Phase angle	380°	230°

As a first order estimation, the birefringence Δn of the material could be calculated from the equation, $\delta\theta = 360° \cdot \Delta n \cdot d \cdot C / \lambda_o$, where the relative phase angle shift $\delta\theta = 380° - 230° = 150°$, the length of the sample d = 6.1 cm, the correction factor C = 0.91 was determined from calibration with known samples, and the wavelength $\lambda_o = 1.00$ cm at 30 GHz. The birefringence of the sample was then $\Delta n = 0.075$. Most of the MMW birefringence of pure liquid crystals measured at 30 GHz was in the range of 0.07 to 0.12; thus the measured birefringence of 0.075 was reasonable considering that the liquid crystal monomers were polymerized. Since commercial liquid crystals generally have higher Δn,[23] it is possible that by selecting liquid crystal monomers with higher birefringence and also by using more refined polymerization techniques, its Δn could be improved. This is desirable as many practical applications such as scanning antennas require $\Delta n > 0.1$.

For application in mechanical modulation devices, such as the mechanical phase shifter and scanning slot array antennas described below, the polymer needs to have sufficient mechanical properties to maintain its integrity under mainly rotational stress. The tensile modulus, elongation at break, and the ultimate strength were determined, and the results are summarized in Table III.

TABLE III Mechanical properties of the polymer samples.

Sample	Tensile modulus	Elongation at break	Break strength
Oriented	$6.8\text{x}10^8$ N/m^2	2.1 %	$6.9\text{x}10^6$ N/m^2
Unoriented	$1.8\text{x}10^8$ N/m^2	9.8 %	$5.9\text{x}10^6$ N/m^2

The measured tensile modulus of the oriented polymer sample was 6.8×10^8 N/m^2, and the modulus of the sample polymerized in the absence of a magnetic field was $1.8\text{x}10^8$ N/m^2, which differ by a factor of about four. The much larger tensile modulus of the oriented sample along its anisotropic direction than the unoriented sample is probably the result of chain alignment in the former. The anisotropic sample was more brittle than the unoriented sample, as evidenced by the difference in elongation at break, even though the break strengths of the two samples were the same within experimental error.

The torsional rigidity modulus was calculated from $G = (2\, M_t\, L)/(p\, R^4\, f)$,[24] where the torque $M_t = 1.08\text{x}10^{-4}$ N·m, length $L = 0.04$ m, $R = 0.0011$ m, and $f = 1$ degree; the vaule was then $G = 6.7 \times 10^6$ N/m^4. This is a reasonably high value, indicating a more than sufficient mechanical robustness for its intended applications.

The birefringence, at $\Delta n = 0.075$, of the above polymer was quite high for a bulk polymer, indicating that this particular *in situ* polymerization technique for oriented polymer sample was effective in preserving liquid crystal orientation order. By selecting liquid crystal monomers with higher initial birefringence, the polymer birefringence might be further improved using the same polymerization method. With improved birefringence, the polymer could be effectively used in a proposed mechanical phase shifter and a mechanical scanning antenna. Brief descriptions of the conceptual designs of the modulation devices are as follow.

Mechanical Phase Shifter

The waveguide sample cell that was designed to measure the birefringence can be modified to act as a mechanical phase shifter. Our experiment showed that even though a highly anisotropic birefringence material was used to modulate the propagating MMW inside the waveguide, the MMW still retained its TE_{10} mode after passing through the sample cell (or phase shifter) with an effective phase delay $\delta\theta$ determined by[25]

$$\delta\theta = 360 \cdot d \cdot \left(\sqrt{\frac{n^2}{\lambda_o^2} - \frac{1}{4a^2}} - \sqrt{\frac{1}{\lambda_o^2} - \frac{1}{4a^2}} \right)$$

where n is the effective refractive index of the polymer sample, d is the length of the polymer sample, λ_o is the wavelength of the microwave in free space, and a is the waveguide broad side dimension. The effective refractive index n is a function of the angular position of the oriented polymer sample. The phase delay of a propagating MMW inside the phase shifter can thus be effectively controlled by rotating the cylindrical birefringence core.

Mechanical Scanning Array Antennas

The sample cell, with its rotating birefringence core, can also be modified into a mechanical scanning slotted array antenna. By making the waveguide sufficiently long with matching length of the core, and by cutting an array of slots on the narrow side of the waveguide,[26] it acts as an antenna. Since for such antenna, the beam angular direction depend on the effective propagating constant of the MMW inside the slotted waveguide, the beam can be scanned back and forth by rotating the birefringence core. Because there is no external moving parts, such antenna is extremely compact.

In reporting the above experimental results, only one set of data was presented for each measurement to simplify the reporting; however, quite a number of samples was synthesized and measured, and most of the good samples (well aligned) yielded consistently similar data. Our data show that because of their reasonably high birefringence (with potential improvement) and mechanical robustness, the oriented diacrylate polymers are potentially applicable in the new class of compact mechanical MMW modulation devices.

REFERENCES

1. For general information on MMW devices: D. G. Bodnar in ***Principles and Applications of Millimeter-wave Radar***, Chapter 11, edited by N. C. Currie and C.

E. Brown (Artech House, Massachusetts, 1987).
2. G. R. Fowles, *Introduction to Modern Optics*, second edition, Chapter 6 (Holt, Rinehart and Winston, New York, 1975).
3. A. Sirigu, *Liquid Crystallinity in Polymers: Principles and Fundamental Properties*, p. 261, edited by A. Ciferri (VCH Publishers, Inc., New York, 1991).
4. S. S. Skorokhodov, in *Liquid Crystal Polymers*, p. 163, edited by N. A. Plate (Plenum Press, New York, 1993).
5. H. Finkelmann, in *Liquid Crystallinity in Polymers: Principles and Fundamental Properties*, p. 315, edited by A. Ciferri, (VCH Publishers, Inc., New York 1991).
6. C. B. McArdle, *Side Chain Liquid Crystal Polymers* (Chapman and Hall, New York, 1989).
7. W. R.Jackson and H. F. Huhfuss, *J. Polym. Sci,.* **14**, 2043 (1976).
8. W. R. Krigbaum, H. J. Lader and A. Ciferri, *Macromolecules*, **13**, 554 (1980).
9. W. R. Krigbaum and H. J. Lader, *Mol. Cryst. Liq. Cryst.*, **62**, 87 (1980).
10. D. A. McL. Smith and H. J. Coles, Liq. Cryst., **14**, 937 (1993).
11. C. M. Paleos and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **11**, 385 (1970).
12. L. Strzelecki and I. Liebert, *Bull. Soc. Chim. Fr.*, 597 (1973).
13. L. Strzelecki and I. Liebert, *Bull. Soc. Chim. Fr.*, 603 (1973).
14. L. Strzelecki and I. Liebert, *Bull. Soc. Chim. Fr.*, 605 (1973).
15. E. Perplies, H. Ringsdorf and J. H. Wendorff, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 243 (1975).
16. D. J. Broer, H. Finkelmann and K. Kondo, *Makromol. Chem.*, **189**, 185 (1988).
17. D. J. Broer, R. A. M. Hikmet and G. Challa, *Makromol. Chem.*, **190**, 3201 (1989).
18. R. A. M. Hikmet, *Liq. Cryst.*, **9**, 405 (1991).
19. R. A. M. Hikmet and B. H. Zwerver, *Liq. Cryst.*, **10**, 835 (1991).
20. M.-S. Ho, Ph. D. Dissertation (University of Oklahoma, 1994).
21. M. N. Afsar and K. J. Button, in *Infrared and Millimeter Waves*, Vol. 12, p. 12, edited by K. J. Button (Academic Press, New York, 1984).
22. J. D. Jackson, *Classical Electrodynamics*, p. 235 (John Wiley and Sons, New York, 1962).
23. K. C. Lim, J. D. Margerum, A. M. Lackner, L. J. Miller, E. Sherman and W. H. Smith, Jr., *Liq. Crystals*, **14**, 327 (1993).
24. T. H. Hsu, Stress and Strain Data Handbook (Gulf Publishing Co., Houston, 1986).
25. M. L. Sisodia and G. S. Raghuvanshi, *Microwave Circuits and Passive Devices*, Chapter 4 (John Wiley and Sons, New York, 1987).
26. M. M. Brady, in *Advances in Microwaves*, Vol. 7, p. 131, edited by L. Young (Acdemic Press, New York, 1971).

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