Journal of Statistical Physics, Vol. 62, Nos. 5/6, 1991

Applications of Liquid Crystal Polymers

Michael Jaffe[1]

Received May 22, 1990; final October 30, 1990

The science and technology of liquid crystal polymers is selectively reviewed with an emphasis on those aspects key to successful commercial utility. The importance of the low viscosity demonstrated by nematic polymers under commercial processing conditions, coupled with the low volume change on cooling and high thermal stability associated with these nematogens, is identified as the major factor behind the success of the thermotropic copolyester as a high-performance molding resin. The developing area of side-chain liquid crystal polymers as electro-optical media is discussed, stressing the importance of combining function and processibility for ultimate commercial viability. Potential markets and projected commercial growth rates are discussed from the point of view of the enabling science needed to successfully define and implement new commercial applications for liquid crystal polymers.

KEY WORDS: Liquid crystal; liquid crystalline polymer; structure-property relationships; nematic polymer; side-chain liquid crystal polymer; applications; fiber; injection molding.

The liquid crystalline nature of stiff polymer molecules in solution was predicted by Onsager in 1947,[1] further refined by Flory in 1956,[2] and experimentally verified through aramid investigations at duPont in the 1960s (see, e.g., refs. 3). Flory suggested that as the molecular chain becomes more rodlike, a critical aspect ratio is reached, above which the molecules necessarily line up to pack efficiently in three dimensions. All of the symmetries and textures known in low-molar-mass liquid crystals have been shown to possess polymer analogues and a few classes identified in polymers are unique (for example see ref. 4). Liquid crystal polymer concepts have been extended to encompass a vast number of homopolymer and copolymer compositions which exhibit either lyotropic or thermotropic

---

[1] Hoechst Celanese Research Division, Sumit, New Jersey 07901.

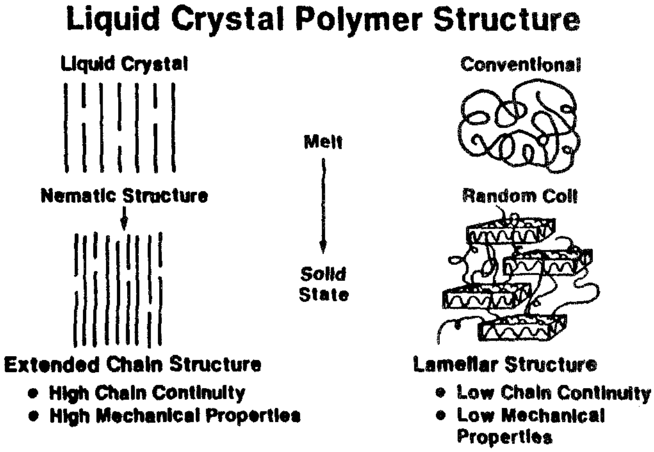


Fig. 1. Schematic comparison of the structures formed during the uniaxial processing of LCP and conventional, crystallizable, random coil polymers.

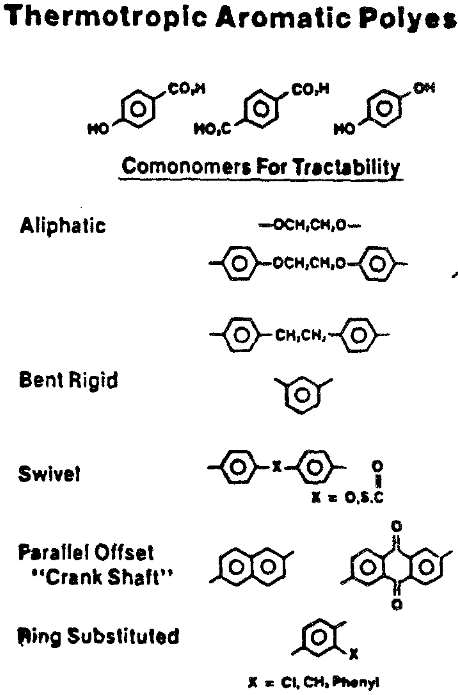


Fig. 2. Copolymer approaches to tractible, thermotropic polyesters based on *para*-phenylene.

behavior. Industrially, most of the research efforts have focused on the main-chain nematic polymers. These molecules combine inherently high thermal and mechanical properties with processing ease and versatility. The reasons for this are illustrated in Fig. 1 which diagrammatically compares the uniaxial processing and resulting structure of a nematic and a crystallizable, conventional polymer. Processing ease originates from the ease with which molecular "rods" can slide past one another; the very high mechanical properties come from the "extended chain" morphology present in the solid state. First, best known, and most important commercially of the LCPs is the lyotropic all-aromatic polyamide developed by the duPont Company under the Kevlar trademark. The most versatile of the main-chain nematics are the thermotropic copolyesters, which are amenable to both uniaxial processing such as fiber formation and three-dimensional processing such as injection molding. Commercial examples of thermotropic copolyester resins are Vectra(TM), developed by Hoechst Celanese, and Xydar(TM) currently marketed by Amoco.(5,6)

Since the 1970s, the laboratories of Carborundum, Hoechst Celanese, duPont, Eastman Kodak, and others have produced hundreds of composi-

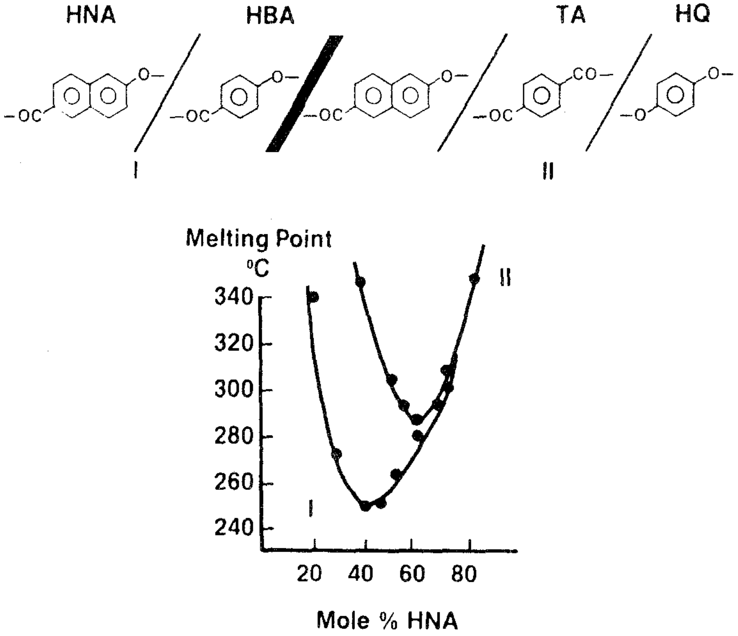


Fig. 3. Effect of substituting A–A, B–B monomers for an A–B monomer on the transition behavior of a typical thermotropic copolyester.

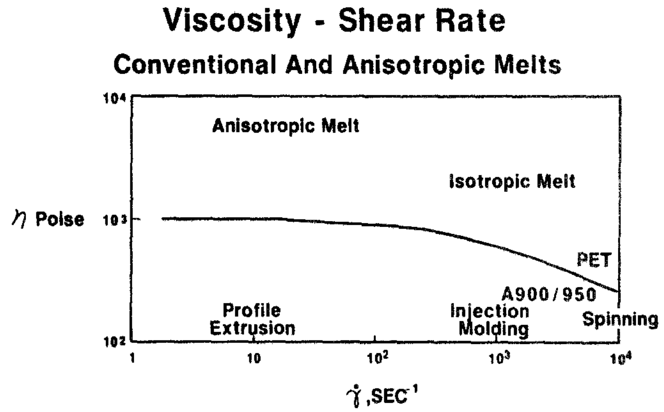


Fig. 4. A comparison of typical rheological behavior of thermotropic and conventional polyesters.

tion of matter and processing patents related to nematogenic polyamides and polyesters.(5,6) Almost all of these are based on a basic *para*-phenylene chain structure which, in the case of the polyesters, is chemically modified with comonomers, chain substitution, molecular swivels, etc., to drive the mesogenic transition temperature of the polymer far enough below the

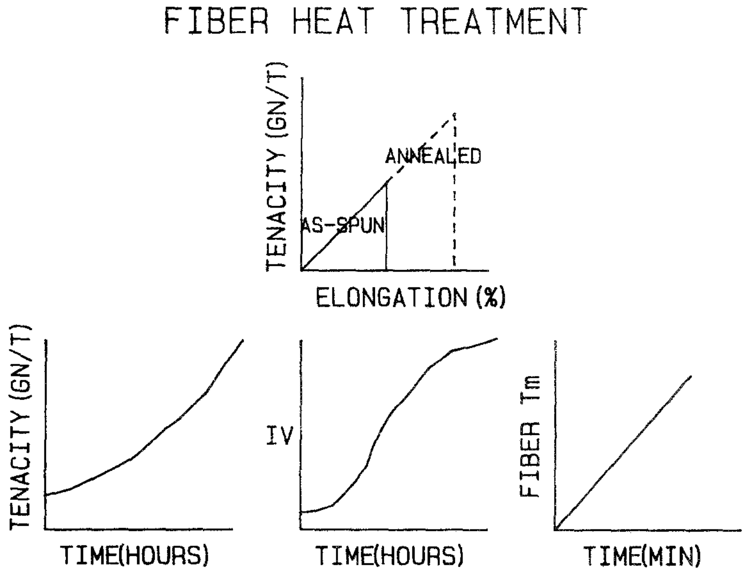


Fig. 5. Structure–property response of highly oriented, thermotropic copolyester fiber to annealing close to the crystal to nematic transition temperature.

decomposition temperature of the chains to allow melt fabrication. Copolymerization breaks up the inherent rigidity of these molecular chains; comonomers are chosen to retain the linearity, hence the mesogenicity of the resulting copolymer. A summary of the molecular approaches is shown in Fig. 2, and the effects of relatively subtle backbone changes (substitute hydroquinine and terephthalic acid for *p*-hydroxybenzoic acid) on transition temperature behavior is shown in Fig. 3.

As in the case of the lyotropic nematic polymers, thermotropic copolyesters orient easily in an elongational flow field, producing highly oriented uniaxial structures with moduli as high as 140 GPa (20 MSI) in melt spinning, extrusion, and similar processes. An example of typical LCP rheological behavior is shown in Fig. 4. Drawdown is the critical extrusion variable and low drawdowns (3–20) are sufficient to achieve almost perfect molecular orientation. Surprisingly, some die swell is noted during LCP extrusion, as determined by real time measurements of the spinning fiber diameter and X-ray orientation.(5) While the origin of this die swell is typically attributed to disorientation of "domains," a vigorous treatment of the effect has not been defined. The extrusion processes employed are almost identical to those used for conventional thermoplastics, with the exception that full molecular orientation is achieved during the spinning process and no further orientation through drawing in the solid state is

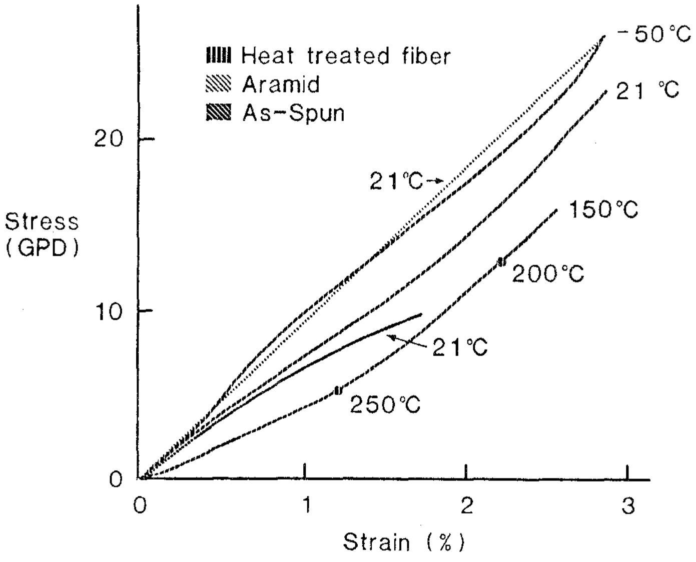
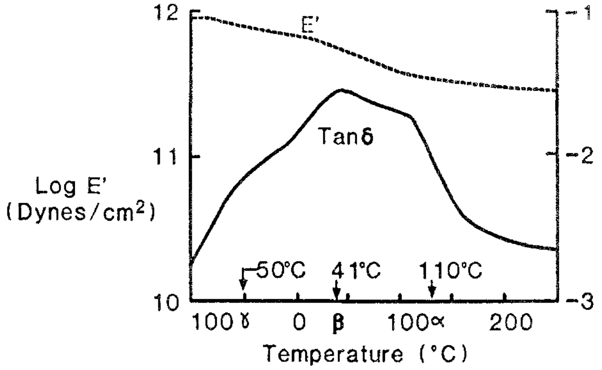


Fig. 6. Stress–strain behavior of highly oriented, thermotropic copolyester fiber as a function of temperature. Typical aramid performance is included as a comparison.

possible (or required). Property improvement in extrudates, most notably tensile strength increases up to 5–6 times the as-spun values, may be achieved by annealing close to the melting point. This process combines structural perfection with solid-state polymerization. Key changes observed during heat treatment are illustrated in Fig. 5. Heat treatment improves strength, elongation, melting point, chemical stability, and thermal retention of properties. Figure 6 shows the changes noted in an LCP fiber stress-strain curve as a function of heat treatment and test temperature. Property dropoffs at elevated temperature are the result of a series of secondary transitions, as illustrated in the dynamic mechanical spectrum shown in Fig. 7. The molecular origins of these processes have been defined by Yoon and Jaffe(7) and Green *et al.*(8) Typical fiber properties for thermotropic copolyesters include a tensile modulus of 65–124 GPa (9–18 MSI) at a strength of ~3 GPa (435 KSI). The broad modulus range reflects differences in molecular architecture within the known thermotropic copolyesters. Morphologically, it has been shown by Sawyer and Jaffe(9) that the fiber is composed of a hierarchy of fibrillar structures,



Summary

γ
- Transition (~ -70°C)
- Reorientational motion of phenylene groups
- Ea~11 Kcal/mole

β
- Transition (~ 60°C)
- Reorientational motion of naphthalene groups
- Ea~28 Kcal/mole

α
- Transition (100°~150°C)
- Rotational motion of several monomer units
- Ea~~110 Kcal/mole

Fig. 7. Dynamic mechanical spectra of a typical thermotropic copolyester (*p*-hydroxybenzoic acid/6-hydroxy-2-naphthoic acid 73/27).

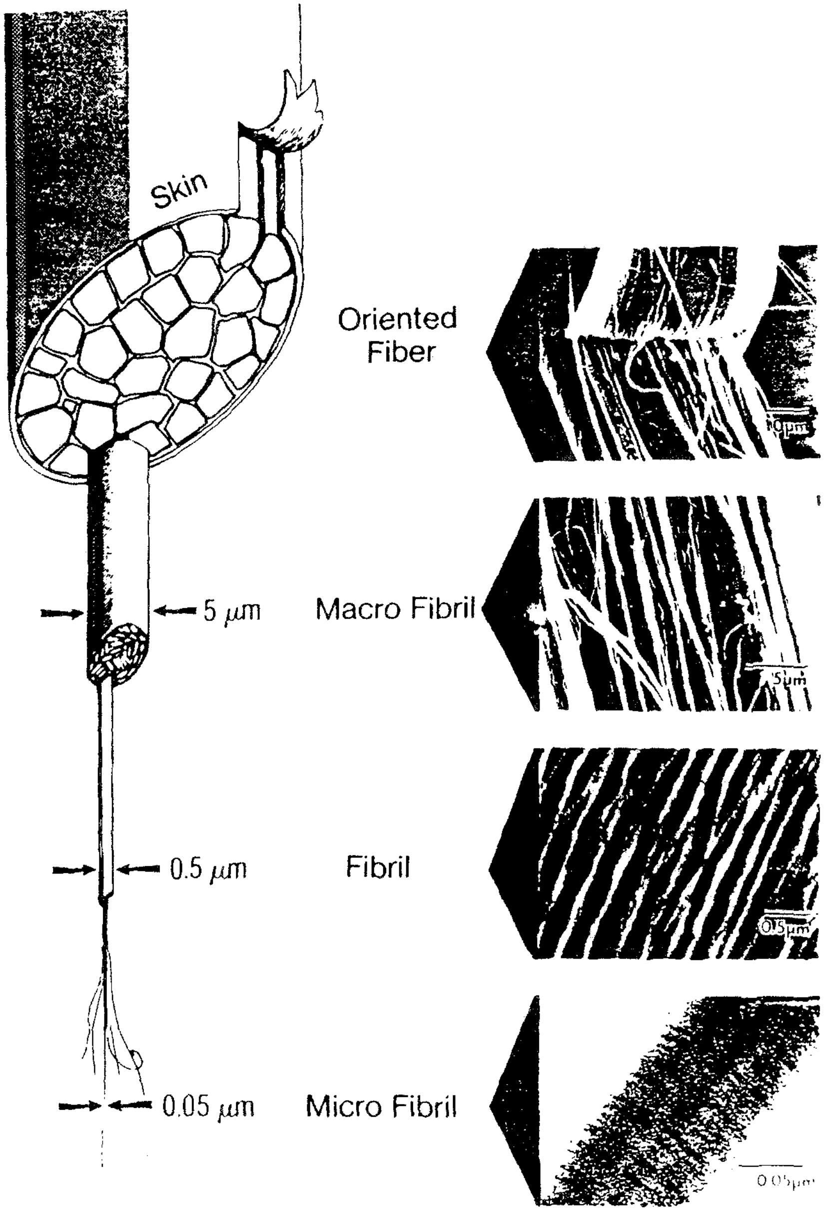


Fig. 8. Hierarchial structure of uniacially oriented thermotropic copolyester extrudate.

covering several orders of magnitude in diameter from angstroms to microns, as illustrated in Fig. 8. Fiber utility is limited by relatively poor performance in compression (typically, compressive strength is on the order of 10–40 MPa). A vigorous debate continues in the literature as to whether the origin of the poor compressive properties is molecular or morphological in origin (see, e.g., ref. 10).

High-modulus thermotropic copolyesters can be thermally fabricated into three-dimensional articles by all methods of conventional melt processing. The resulting structure and orientation distribution is reminiscent of that seen in short-fiber-reinforced plastics. For example, molded articles appeared "layered" and it can be shown that these layers are a manifestation of varying orientation. Sawyer and Jaffe(9) have shown that molding comprises similar morphological units to those noted in fiber, with the local orientation of the hierarchy reflecting the local orientation of the molded part. The thermotropic molding resins offer a balance of properties unobtainable with any other materials, including:

1. Moderate density.
2. Excellent mechanical properties.
3. Controllable range of melting points.

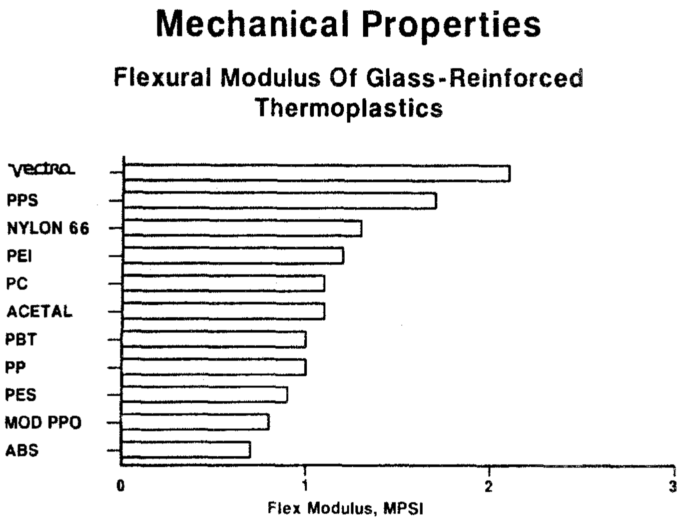


Fig. 9. A comparison of the flex modulus of a series of molded, glass-filled thermoplastics: PPS, polyphenylene sulfide; PEI, polyetherimide; PC, polycarbonate; Acetal, polyoxymethylene; PBT, polybutyleneterephthalate; PP, polypropylene; PES, polyethersulfone; MOD PPO, modified polyphenylene ether; ABS,....

4. Low melt viscosity.
5. Easy orientation.
6. Low shrinkage.
7. Controllable thermal expansion.
8. High use temperatures.
9. Excellent cryogenic property retention.
10. Excellent solvent resistance.

The major deficiency of molded LCP parts is the relative weakness exhibited at weldlines (formed by the impinging of two or more flow fronts in multiple gated molds) and reflecting the lack of diffusion and entanglements noted for stiff polymer chains in the transverse direction. This effect can be mitigated through mold design and the use of inorganic or fibrous fillers. A comparison of LCP [Vectra(TM)] molded properties in comparison to other plastics is illustrated in Figs. 9–11.

Acceptance of nematic LCPs in the marketplace is being led by performance-oriented applications, especially in the areas of[11,12] consumer goods and appliances, electrical devices and electronics, telecommunications, transportation, industrial uses, fiber optics, aircraft and aerospace applications, chemical and hostile environments, military uses and ordinance. These applications exploit the ease with which the LCP fills complex molds (low viscosity), the high dimensional integrity of the molded part (low volume change on cooling), and the ability to design parts with very thin walls (high mechanical properties).

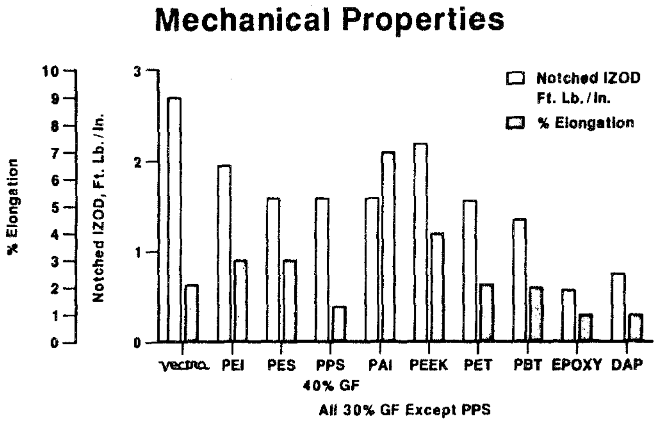


Fig. 10. A comparison of the toughness and elongation of a series of molded, glass-filled thermoplastics. PAI, polyamideimide; PEEK, polyetherether ketone; PET, polyethyleneterephthalate; DAP,....

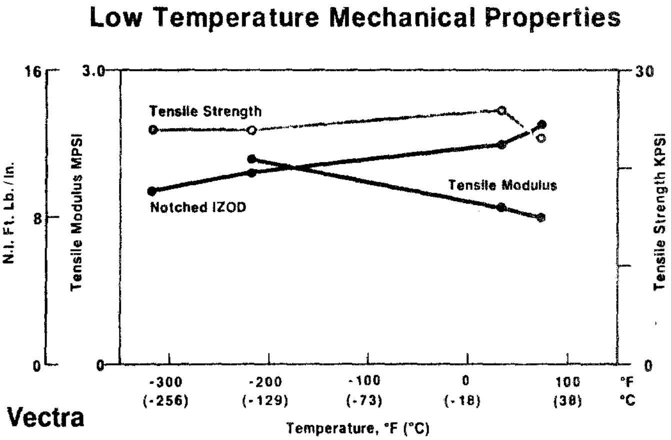


Fig. 11. Behavior of a typical molded thermotropic copolyetser [Vectra(TM)] at cryogenic temperatures.

More recently, the potential for polymeric liquid crystals in device rather than structural applications has been recognized. The combination of inherent order, environmental stability, and ease of processing has led to interest in LCPs in applications as diverse as nonlinear optics, optical data storage, and "orienting carriers" for conducting polymers. As structural parameters are of secondary importance in these applications, all LCP textures, including some known to exist only in polymers, are under active investigation. Both main-chain and side-chain LCP approaches are of interest with the goal of tailoring orientational and transitional states to the specific end use desired. Emerging problems include achieving sufficient density of active species to produce materials with competitive figures of merit (i.e., dipole concentration for NLO applications) and balancing mesogenicity effects with high and stable use temperatures. The incorporation of mesogenicity into polymers opens vast possibilities for molecular design, which will ultimately lead to the creation of materials with highly specific and unique property sets.(4)

The growth of LCP usage in the marketplace is expected to be broad based and rapid from today to the mid-1990s and beyond, with the total expected to exceed 10 million pounds for the thermotropic copolyesters alone. This expansion will be fueled partly by the replacement of current materials, i.e., ceramics, metals, composites, etc., but mostly by the design of LCPs into the next several generations of devices and systems where the performance of LCPs will overshadow competing materials.

REFERENCES

1. L. Onsager, *Ann. N. Y. Acad. Sci.* **51**:627 (1949).
2. P. F. Flory, *Proc. R. Soc. Lond. A* **234**:73 (1956).
3. P. W. Morgan, *Macromolecules* **10**:1381 (1977); T. I. Bair *et al.*, *Macromolecules* **10**:1396 (1977); M. Panar *et al.*, *Macromolecules* **10**:1401 (1977).
4. C. B. McArdle, ed., *Side Chain Liquid Crystal Polymers* (Chapman and Hall, New York, 1989).
5. M. Jaffe *et al.*, in *High Technology Fibers*, Part B, M. Lewin and J. Preston, eds. (Marcel Dekker, New York, 1989).
6. G. Calundann, in *High Performance Polymers: Their Origin and Development*, R. B. Seymour and G. E. Kirshenbaum, eds. (Elsevier, New York, 1986).
7. H. Yoon and M. Jaffe, *Polymer Preprints* (1984).
8. D. I. Green, G. R. Davies, I. M. Ward, M. H. Alhaj-Mohammed, and S. A. Jaward, *Polym. Adv. Technol.* **1**:41 (1990).
9. L. C. Sawyer and M. Jaffe, *J. Mat. Sci.* **21**:1897 (1986).
10. C. Y.-C. Lee and C. S. Wang, *Proc. Polym. Mat. Sci. Eng.* **62**:81 (1990).
11. J. R. Dole, *Chemtech* **17**:242 (1987).
12. C. E. McChesney and J. R. Dole, *Modern Plastics* (1988).