Ceram. Soc. **76**, 1788 (1993).

10. K. T. Miller and F. F. Lange, *Proc. Mater. Res. Soc. Symp.* **155**, 191 (1989).
11. K. T. Miller, C.-J. Chan, M. G. Cain, F. F. Lange, *J. Mater. Res.* **8**, 169 (1993).
12. M. C. Cain and F. F. Lange, *ibid.* **9**, 674 (1994); K. T. Miller and F. F. Lange, *ibid.* **6**, 2387 (1991); A. Seifert, F. F. Lange, J. S. Speck, *J. Am. Ceram. Soc.* **76**, 443 (1993); P. K. Narwankar, J. S. Speck, F. F. Lange, *J. Mater. Res.* **10**, 1756 (1995).
13. P. A. Langjahr, T. Wagner, M. Rühle, F. F. Lange, *Mater. Res. Soc. Symp. Proc.* **401**, 109 (1996).
14. K. Okuwada, S-I. Nakamura, M. Imai, K. Kakuno *Jpn. J. Appl. Phys.* **29**, 1153 (1990).
15. D. Heimann, T. Wagner, J. Bill, F. Aldinger, F. F. Lange, in press.
16. J. Livage, M. Henry, C. Sanchez, *Prog. Solid State Chem.* **18**, 259 (1988).
17. C. J. Brinker and G. W. Scherer, *Sol-Gel Science* (Academic Press, New York, 1990).
18. C. D. Chandler, C. Roger, M. J. Hampden-Smith, *Chem. Rev.* **93**, 1205 (1993).
19. R. W. Vest, in *Ceramic Films and Coatings*, J. B. Wachtman and R. A. Haber, Eds. (Noyes, Park Ridge, NJ, 1993), pp. 303–341.
20. J. V. Mantese, A. L. Micheli, A. H. Hamdi, R. W. Vest, *MRS Bull.* **14**, 48 (1989).
21. E. Leroy, C. Robin-Brosse, T. P. Torre, in *Ultrastructure Processing of Ceramics, Glasses, and Composites*, L. L. Hench and D. R. Ulrich, Eds. (Wiley, New York, 1984), pp. 219–231.
22. J. D. Birchall, *Trans. J. Br. Ceram. Soc.* **82**, 153 (1983).
23. R. M. Laine and F. Babonneau, *Chem. Mater.* **5**, 260 (1993); J. Bill and F. Aldinger, *Adv. Mater.* **7**, 775 (1995); Y. Saito, S. Koyama, Y. Sugahara, K. Kuroda, *J. Ceram. Soc. Jpn.* **104**, 143 (1996).
24. J. B. Blum and S. R. Gurkovich, *J. Mater. Sci.* **20**, 4479 (1985).
25. A. D. Polli, F. F. Lange, C. G. Levi, unpublished work.
26. A. D. Polli and F. F. Lange, *J. Am. Ceram. Soc.*, in press.
27. D. E. Bornside, C. W. Macosko, L. E. Scriven, *J. Imaging Technol.* **13**, 122 (1987).
28. A. G. Evans, M. D. Dory, M. S. Hu, *J. Mater. Res.* **3**, 1043 (1988); G. Gille, in *Current Topics in Materials Science*, E. Kaldis, Ed. (North-Holland, Amsterdam, 1985), vol. 12, chap. 7.
29. J. W. Hutchinson and Z. Suo, in *Advances in Applied Mechanics*, J. W. Hutchinson and T. Y. Wu, Eds. (Academic Press, New York, 1991), pp. 63–191.
30. D. K. Leung, C. J. Chang, M. Rühle, F. F. Lange, *J. Am. Ceram. Soc.* **74**, 2786 (1991).
31. M. L. Balmer, F. F. Lange, C. G. Levi, *ibid.* **75**, 946 (1992).
32. A. P. Sutton and R. W. Balluffi, *Interfaces in Crystalline Materials* (Clarendon, Oxford, 1995), pp. 129–131.
33. P. A. Langjahr, T. Wagner, M. Rühle, F. F. Lange, unpublished results.
34. C. V. Thompson, *Annu. Rev. Mater. Sci.* **20**, 245 (1990); ———, J. Floro, H. I. Smith, *J. Appl. Phys.* **67**, 4099 (1990).
35. D. J. Srolovitz and S. A. Safran, *J. Appl. Phys.* **60**, 247 (1986).
36. K. T. Miller, F. F. Lange, D. B. Marshall, *J. Mater. Res.* **5**, 151 (1990).
37. K. T. Miller and F. F. Lange, *ibid.* **6**, 2387 (1991).
38. A. Seifert, A. Vojta, J. S. Speck, F. F. Lange, *ibid.*, in press.
39. T. Yogo, Y. Takeichi, K. Kikuta, S.-I. Hirano, *J. Am. Ceram. Soc.* **78**, 1649 (1995).
40. N. L. Jeon, P. G. Clem, R. G. Nuzzo, D. A. Payne, *J. Mater. Res.* **10**, 2996 (1995).
41. A. Kumar and G. M. Whitesides, *Appl. Phys. Lett.* **63**, 2002 (1993).
42. W. J. Dawson, *Am. Ceram. Soc. Bull.* **67**, 1673 (1988).
43. K. Osseo-Asare, F. J. Arriagada, J. H. Adair, *Ceramic Transactions*, G. L. Messing, E. R. Fuller, Jr., H. Hausner, Eds. (American Ceramic Society, Wester-ville, OH, 1988), pp. 47–53.
44. E. Lilley and R. R. Wusirika, U.S. Patent 4 764 493 (1988).
45. D. Henning and S. Schreinemacher, *J. Eur. Ceram. Soc.* **9**, 41 (1992).
46. Y. M Yoshimura, S. E. Yoo, M. Hayashi, N. Ishizawa *Jpn. J. Appl. Phys.* **28**, 2007 (1989).
47. E. B. Slamovich and I. A. Aksay, *J. Am. Ceram. Soc.* **79**, 239 (1996).
48. A. T. Chien, J. S. Speck, F. F. Lange, A. C. Daykin, C. G. Levi *J. Mater. Res.* **10**, 1784 (1995).
49. A. T. Chien, J. S. Speck, F. F. Lange, unpublished results.
50. Q. Chen *et al.*, *Appl. Phys. Lett.* **66**, 1608 (1995).
51. Q. Chen, Y. Qian, Z. Chen, Y. Zhang, *Mater. Lett.* **22**, 93 (1995).
52. This review was supported by the Air Force Office of Scientific Research under grant F49620-93-1-0358DEF. Research concerning hydrothermal epitaxy was supported by the National Science Foundation to the UCSB/Materials Research Laboratory under the award, DMR-9123048.

Device Applications of Side-Chain Ferroelectric Liquid Crystalline Polymer Films

K. M. Blackwood

Side-chain ferroelectric liquid crystalline polymers are currently used in a number of applications, including displays and electrical sensors. Comparisons with existing technologies and materials indicate that relative to ceramics, such polymers have lower figures of merit but offer greater durability in sensor applications.

Side-chain liquid crystalline polymers (SCLCPs) may be thought of as having normal polymeric backbone architectures with pendant groups that show LC properties. In 1978, Ringsdorf and co-workers conducted systematic studies of SCLCPs (*1, 2*) and showed that, in order to preserve the LC phase behavior of the mesogen, it was necessary to insert a flexible spacer between the main chain and the core. Schematically the structure of a SCLCP can be represented as in Fig. 1.

The response time of a ferroelectric LC material can generally be related to its viscosity as

$$\tau \approx \eta/(EP_s) \qquad (1)$$

where τ is the response time (the response time of a LC device is typically taken to be the time required for a 90% change in the amount of light transmitted through the device), E is the applied field, P_s is the spontaneous polarization of the sample, and η is the bulk viscosity. In a polymer that, even above its glass transition temperature T_g, is more of a viscoelastic solid, the response time will be exceptionally slow in comparison with traditional LC materials. Given this, one may wonder what drives the study of SCLCPs other than mere academic interest. The answer arises from developments in the low molecular weight area. In 1974, Meyer *et al.* showed mathematically that, if one could unwind the helical su-perstructure of a chiral smectic C–phase LC, then the low degree of symmetry would lead to the development of ferroelectricity (*3*). This phenomenon can be understood by considering the arrangement of the mesogens within the smectic C phase. LC materials can exhibit many phase structures between the isotropic melt and the solid crystal. Of these mesophases, the best known is the nematic phase, in which the mesogenic units have a degree of long-range ordering not present in the isotropic melt. This ordering causes the rod-like mesogens to adopt a preferred orientation. This preferred orientation is known as the director, and the movement of this director by electric fields (Fig. 2) is the basis for the present generation of LC displays.

In their quest for better, faster displays, researchers turned their attention to the smectic mesophases. Here, the mesogens arrange themselves into distinctive layers, although there is little positional ordering
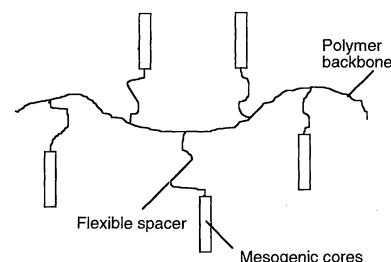
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Fig. 1. Schematic diagram of SCLCP architecture.

within the layers. In the smectic C phase, the mesogens within each layer are tilted to one side at a constant tilt angle. If the mesogen has a chiral center near the core, then this tilt will align the chirally induced dipoles within each layer. Each layer will therefore have a degree of polarization even when no external field is present. This is known as the spontaneous polarization (P_s) and is responsible for the appearance of ferroelectricity. However, the chirality causes each layer to become twisted with respect to its neighboring layers; when summed over many layers, the result is a helical superstructure, which in turn cancels out the P_s vector from each layer. Hence, the sample as a whole has no P_s.

In 1980, Clark and Lagerwall succeeded in unwinding this helical structure and used a rubbed polymer surface to stabilize it in a very thin cell (2 μm) (4). This "surface-stabilized ferroelectric LC" did indeed show a P_s, but of greater interest to Clark and Lagerwall was the fact that the direction of the P_s vector could be switched with the use of electrical pulses. As the mesogens shown in Fig. 3 switch around a cone with a cone angle (θ), they can be made to interact with polarized light in the same way as a birefringent slab,

$$I = I_0 \sin^2(2\alpha) \sin^2[(\pi \Delta n_{eff} d)/\lambda] \quad (2)$$

(5), where I is the fraction of the incident light I_0 transmitted through the device, α is the angle between the mesogens and the plane of polarization of the incident light, Δn_{eff} is the effective in-plane birefringence of the material, d is the device thickness, and λ is the wavelength of the incident light. Thus, if the mesogens are aligned parallel to the plane of polarization, then $\alpha = 0$, $\sin^2(2\alpha) = 0$, and no light is transmitted. When the molecules switch to the other side of the cone, α becomes equal to 2θ, that is, twice the cone angle. If $2\theta = \pi/4$ rads, then $\sin^2(2\alpha)$ is equal to unity and the transmitted light is therefore only limited by the optical retardation of the device. In addition, because of the less disruptive

reorientation processes involved, the electrooptic response time is orders of magnitude faster than that of the best nematic devices. Also, as far as the mesogens are concerned, either side of the cone is of equal internal energy and the device is therefore bistable. Voltage is only required to switch between the states. In contrast, in nematic devices a constant field must be applied to maintain the switched state.

The stability of this unwound helical structure was questionable, and researchers reasoned that polymers, with their higher viscosity, should be more stable in this unwound state. In 1984, Shibaev et al. (6) reported the first example of a ferroelectric SCLCP. Unfortunately, because of the higher viscosity, achieving the unwound state was found to be much more difficult with polymers than with low molecular weight LCs. However, in 1987, Uchida et al., reported the first measurements of electrooptic response time and P_s in a ferroelectric SCLCP (7).

Display Applications

Because polymers have a far higher viscosity than low molecular weight LCs, the molecular design of SCLCPs for display applications must be approached carefully. In general, the material must allow for flexibility of the mesogens. Thus, polymer backbones with inherently low T_g values are chosen. Siloxanes and acrylates are preferred, as these systems have inherently low T_g values. Also, as the work of Ringsdorf and co-workers (1, 2) has shown, it is necessary to incorporate a flexible spacer group between the mesogen and the main chain to preserve the LC phases. Simplistically, this can be thought of as decoupling the mesogen from the main chain. Since 1976, several hundred low molecular weight LC materials have been prepared that exhibit the chiral smectic C phase (S_C^*) (8). Generally, the mesogenic core contains at least two aromatic groups that may or may not be laterally substituted with various halogens. There is a chiral cen-

ter, usually located in the terminal alkyl chain, and the structure typically contains only one asymmetric carbon. To produce the desired smectic phases for ferroelectric display applications in SCLCPs, researchers have tended to follow the design rules classified for low molecular weight LCs.

Despite this apparent wealth of materials, there are still stringent requirements for any materials that might find application in LC displays. First, they must show a good operating temperature range, preferably around room temperature. Second, they require a reasonable response time, although this requirement is quantified by the type of display to which they are applied. For video rate displays, response times in the microsecond region are preferred. At this time, it is difficult to envisage any polymeric material offering this sort of response speed, as even the fastest polymeric materials show switching times of hundreds of microseconds. However, for other less complicated displays, response times of up to hundreds of milliseconds are acceptable. Finally, the SCLCP display must offer some advantage over existing technology. Nevertheless, the nature of polymer science is such that we have many variables that we can adjust, such as spacer length, mesogen type, or backbone type, but there is also the possibility of using copolymers (9–12), elastomers (13–18), cyclic polymers (19–22), and combined main-chain and side-chain LC polymers (23).

Despite all these design parameters, in 1993 Idemitsu Kosan demonstrated the first ferroelectric LCP display (24). This consisted of a layer of ferroelectric SCLCP (2 μm) constrained between two plastic substrates (each 100 μm thick). Indium-tin oxide electrodes (0.05 μm thick) were patterned on one side of each of the substrates, and alignment of the SCLCP was achieved by the shearing of the device according to Idemitsu's own patented technique (25). This type of display offers levels of robustness and flexibility that are found in no other display type, as well as advantages in the ease of processing.

Sensor Applications

A ferroelectric material has a certain degree of inherent polarization, even when no external field is applied (Fig. 4). In the case of a normal dielectric material, as the applied field is increased the degree of polarization increases (Fig. 4A). This relation continues until the level of applied field exceeds the dielectric strength of the material; then dielectric breakdown occurs. However, for a ferroelectric material, a residual polarization is present. If the material is perfectly aligned, this value will remain constant despite the increasing field (Fig. 4B). However, if the
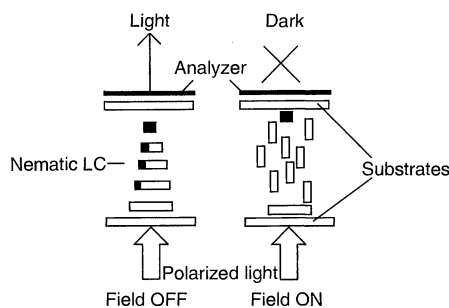

Fig. 2. Diagram of a traditional nematic display device.

Table 1. Piezoelectric and pyroelectric properties of ferroelectric polymers. The PVDF data are from (26); the data on SCLCPs are from (27–30). Labels p_{33} and d_{33} indicate how the measurements were made.

System	Pyroelectric coefficient (p_{33}) (nC cm^{-1} K^{-1})	Piezoelectric coefficient (d_{33}) (pC N^{-1})
PVDF		
Uniaxial	2.74	31.5
Biaxial	1.25	12.4
SCLCP		
Current	5 to 18	16
Expected	65	40

material is not perfectly aligned, then the level of this polarization increases up to a maximum value (Fig. 4C). This represents the further aligning of the P_s vectors within the material. When the field is reversed, the perfectly aligned ferroelectric will switch from one state to the other once a threshold field is exceeded. In the case of the less well-aligned material, the polarization will fall gradually as the material reorients into the other stable state.

Both of these systems will therefore exhibit a hysteresis effect in the polarization response to a sinusoidal field. This hysteresis shows the presence of P_s. Moreover, the magnitude of this polarization is clearly a function of the degree of alignment within the material. This is what makes ferroelectric materials so interesting. Clearly, any external stimulus that alters the degree of internal ordering within the material will change the value of polarization; examples of such stimuli are heat and pressure. The resultant change in the value of P_s can be recorded as a small voltage set up across the material. Ferroelectric materials thus have been termed "smart" materials because they have the ability to respond to their environments and in so doing produce some detectable effect. The obvious application for these ferroelectric materials is as pressure and temperature sensors, termed piezoelectric and pyroelectric devices, respectively.

The piezo- and pyroelectric sensor market has for a long time been dominated by inorganic materials, initially with unusual crystal structures such as that found in quartz, but later with more esoteric ceramic materials such as lead zirconic titanate. Although the design and production of these ceramic materials represent major challenges to the scientists involved, there are still inherent problems with the physical properties of ceramics, particularly brittleness. Moreover, the effects of temperature and pressure on the molecular structure of materials must be related to the mechanical properties of the system. In order to cover the broad range of possible applications, there is a need for materials with the pyro- and piezoelectric properties of these ceramics but with the mechanical compliance of polymers. An organic polymer system, poly-

(vinylidene difluoride) (PVDF), was found to form a noncentrosymmetric crystal structure and to have ferroelectric properties. The PVDF system has an enormous P_s but a very low order parameter; that is, although the crystal unit cell has a very large value of polarization, the relative orientation of these unit cells is poor. Nevertheless, PVDF still finds applications where the unique mechanical parameters of polymers are required. One such application is in ultrasound detectors for medical imaging.

Ferroelectric SCLCPs offer an as yet relatively unexplored route to pyro- and piezoelectric sensors. Because of the molecular architecture of SCLCPs, the values of P_s in these materials will be significantly lower than that of PVDF and well below those of ceramic materials. However, the LC nature of these materials means that the order parameter will be much larger than that found even in uniaxially oriented PVDF. Also, because of these LC properties, these systems have a natural tendency to self-order. Unlike ordering in PVDF, ordering in SCLCPs does not need to be imposed by high thermal and electrical poling fields. SCLCPs have been shown to offer performance close to that of PVDF (Table 1). Because the piezo- and pyroelectric properties are related to the product of P_s and the order parameter, we can speculate, on the basis of our knowledge of the magnitude of P_s in some ferroelectric LC systems combined with the expected order parameter values, about values for the piezo- and pyroelectric coefficients that we may reasonably expect from SCLCP devices.

Clearly, ferroelectric SCLCPs could represent serious competitors for PVDF, although they are still, like PVDF, behind the best ceramics. Nevertheless, this technology is still young and the materials currently under study have not been optimized for this application. Therefore, a challenge to inorganic ceramic materials may yet come from organic polymers.

Future Uses

Ferroelectric SCLCPs were developed as a result of the work by Clark and Lagerwall (4) in the development of low molar mass

ferroelectric LC displays. Ferroelectrics are considered to represent the next generation of LC displays, offering superfast response times and low power bistability, but at present they suffer from poor mechanical shock resistance. On the other hand, SCLCPs have notoriously slow response times but are not as sensitive to mechanical damage. Over the past few years, these two technologies have combined to produce ferroelectric SCLCPs. Thus, the high speed of the ferroelectric switching process compensates for the slow response time of the polymers, and the high dimensional stability of the polymers compensates for the mechanical sensitivity of the ferroelectric mesogens. However, the response time of a SCLCP device is still far too slow for such applications as laptop computers, and improvement of more than an order of magnitude is required for applications involving real-time video displays. It is unclear whether this degree of improvement will ever be achievable, but there are still many markets, such as advertising boards, personal data assistant displays, and public information displays, that do not require a fast response time. These applications would benefit from the advantages of a SCLCP device but would not be hindered by the drawbacks.

This wealth of research into both materials and devices is now being focused into prototype devices. Generally, these displays consist of plastic film with the SCLCP sandwiched between. The display is therefore lightweight, flexible, and rugged. This research area is now coming to fruition, and the first applications are now being considered.

Research into this area produced a spin-off, ferroelectric polymers. These polymers were naturally ferroelectric and therefore exhibited piezo- and pyroelectric properties. However, because of the inherent self-assembly of LC mesogens, ferroelectric properties could be observed without the intricate poling processes involved with materials such as PVDF. Although the sensor market is dominated by the ceramics and it is very difficult to imagine a SCLCP challenging the dominance of the ceramics in the hydrophone devices, there may well be niche markets where, as with PVDF in medical sensors, SCLCPs can find a position.

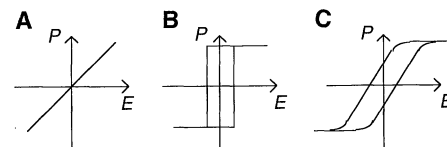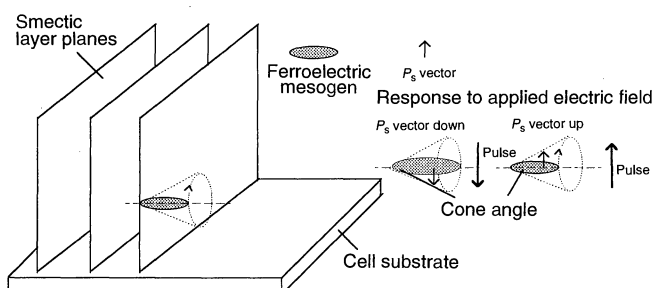**Fig. 3.** Diagram of a surface-stabilized ferroelectric LC display.

Fig. 4. Polarization (P) response to an applied electric field (E) for (**A**) a linear dielectric, (**B**) an idealized ferroelectric, and (**C**) a typical ferroelectric material.

REFERENCES AND NOTES

1. H. Finkelmann, M. Happ, M. Portugall, H. Ringsdorf, *Makromol. Chem.* **179**, 2541 (1978).
2. H. Finkelmann, H. Ringsdorf, W. Siol, J. H. Wendorff, in *Mesomorphic Order in Polymers and Polymerization in Liquid Crystal Media*, A. Blumstein, Ed. (American Chemical Society, Washington, DC, 1978).
3. R. B. Meyer, L. Liebert, L. Strzelecki, P. Keller, *Mol. Cryst. Liq. Cryst.* **38**, L-69 (1975).
4. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).
5. J. C. Jones, M. J. Towler, J. R. Hughes, *Displays* **14**, 86 (1993).
6. V. Shibaev, M. Kozlovsky, L. Beresnev, L. Blinov, A. Platé, *Polym. Bull.* **12**, 299 (1984).
7. S. Uchida, K. Morita, K. Miyoshi, K. Hashimoto, K. Kawasaki, *Mol. Cryst. Liq. Cryst.* **155**, 93 (1988).
8. H. Kelker, R. Hatz, C. Schumann, *Handbook of Liquid Crystals* (Verlag Chemie, Weinheim, Germany, 1980), p. 111.
9. B. P. Griffin and M. K. Cox, *Br. Polym. J.* **12**, 147 (1980).
10. A. N. Semenov, *Mol. Cryst. Liq. Cryst.* **209**, 191 (1991).
11. M. V. Kozlovsky, L. Bata, K. Fodor-Csorba, V. P. Shibaev, *Cryst. Res. Technol.* **27**, 1141 (1992).
12. S. Hanna, A. Romo-Uribe, A. H. Windle, *Nature* **366**, 546 (1993).
13. H. Finkelmann, H. J. Koch, G. Rehage, *Makromol. Chem. Rapid Commun.* **2**, 317 (1981).
14. N. R. Barnes, F. J. Davis, G. R. Mitchell, *Mol. Cryst. Liq. Cryst.* **168**, 13 (1989).
15. C. Degert, H. Richard, M. Mauzac, *ibid.* **214**, 179 (1992).
16. C. Degert, P. Davidson, S. Megtert, D. Petermann, M. Mauzac, *Liq. Crystals* **12** (no. 5), 779 (1992).
17. R. A. M. Hikmet and J. A. Higgins, *ibid.*, p. 831.
18. A. J. Symons, F. J. Davis, G. R. Mitchell, *ibid.* **14** (no. 3), 853 (1993).
19. F. H. Kreuzer, *Proc. 11. Freiburger Arbeitstagung Flüssigkristalle* (University of Freiburg, Freiburg, Germany, 1981), p. 5.
20. _____, M. Gawhary, R. Winkler, H. Finkelmann, European Patent EP0060335 (1981).
21. R. D. C. Richards *et al.*, *J. Chem. Soc. Chem. Commun.* **1990**, 95 (1990).
22. F. H. Kreuzer *et al.*, *Mol. Cryst. Liq. Cryst.* **199**, 345 (1991).
23. B. Reck and H. Ringsdorf, *Makromol. Chem. Rapid Commun.* **6**, 291 (1985).
24. Idemitsu Display demonstrated at Fourth International Conference on Ferroelectric Liquid Crystals, 28 September to 1 October 1993, Tokyo, Japan.
25. K. Yuasa *et al.*, U.S. Patent 5,069,533 (1991).
26. R. G. Kepller and R. A. Anderson, *J. Appl. Phys.* **49**, 4490 (1978).
27. L. M. Blinov, L. A. Beresnev, N. M. Shtykov, Z. M. Elashvili, *J. Phys. (Paris)* **40** (no. 4), C3 (1979).
28. L. A. Beresnev and L. M. Blinov, *Ferroelectrics* **33**, 129 (1981).
29. A. Kokot, R. Wrzalik, J. K. Vij, R. Zentel, *J. Appl. Phys.* **75**, 728 (1994).
30. J. W. O'Sullivan, Y. P. Panarin, J. K. Vij, *ibid.* **77**, 1201 (1995).
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Structure in Thin and Ultrathin Spin-Cast Polymer Films

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The molecular organization in ultrathin polymer films (thicknesses less than 1000 angstroms) and thin polymer films (thicknesses between 1000 and 10,000 angstroms) may differ substantially from that of bulk polymers, which can lead to important differences in resulting thermophysical properties. Such constrained geometry films have been fabricated from amorphous poly(3-methyl-4-hydroxy styrene) (PMHS) and semicrystalline poly(di-*n*-hexyl silane) (PD6S) by means of spin-casting. The residual solvent content is substantially greater in ultrathin PMHS films, which suggests a higher glass transition temperature that results from a stronger hydrogen-bonded network as compared with that in thicker films. Crystallization of PD6S is substantially hindered in ultrathin films, in which a critical thickness of 150 angstroms is needed for crystalline morphology to exist and in which the rate of crystallization is initially slow but increases rapidly as the film approaches 500 angstroms in thickness.

A synthetic polymer exhibits substantial interdependence among its chemical composition, processing protocol, and morphological structure and among its resulting mechanical, thermal, optical, and electrical properties. Typically, the bulk physical parameters depend on the macromolecular nature of the material, with the character-

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istic molecular dimension being the radius of gyration R_g, which is proportional to the square root of the molecular weight. For typical commercial polymers having molecular sizes in the range of 100,000 daltons, R_g might be on the order of 100 Å. In the bulk state, a particular "test chain" such as might be isolated through selective deuteration and measured by neutron scattering, exhibits a Gaussian distribution of the distances of one chain end from the other. About 1% of the volume within the roughly spherical domain encompassing this test chain is occupied by the chain itself, with the remainder being occupied by many other intertangled chains. This picture of the amorphous solid state, first predicted by P. J. Flory in 1953 and subsequently verified by neutron scattering, is well accepted for the bulk state. However, relatively recent simulations indicate that the picture must be

modified for regions near solid substrates and for polymer films of constrained geometry, such as those whose film thickness is comparable to a small multiple of R_g (*1*).

Such constrained geometry films may be classified as "ultrathin" for thicknesses <1000 Å and as "thin" for thicknesses between 1000 and 10,000 Å (1 μm). Ten Brinke (*2*) performed lattice Monte Carlo (MC) simulations on a polymer melt confined between parallel plates and found variations in chain conformation when the distance between the plates was comparable to $2R_g$. In off-lattice MC simulations, Kumar (*3*) found two correlation length scales: Single-chain properties were disturbed over a distance comparable to $2R_g$, whereas many chain properties were screened out at a length three times the monomer segment size. Molecular dynamics simulations of confined chains showed that the solid-melt interface is approximately two segment diameters thick and the segment mobility is highly anisotropic in the interfacial region (*4*). Finally, self-consistent field lattice model calculations (*5*) of polypropylene on graphite showed an enrichment of the interface with polymer ends, some flattening of the chains parallel to the substrate, and anisotropic molecular mobilities.

Application Issues for Polymer Thin Films

Although mechanical applications of polymers take advantage of their bulk properties, there are numerous technologies in which ultrathin and thin polymer films are found. For example, they are used as resists and interlayer dielectrics in microelectronics fabrication, as alignment layers in liquid crystal displays, and as lubricants in magnetic information storage devices. In each of these applications, the polymer chain orientation and state of organization play important