the twofold symmetry axis and perpendicular to it. Thus, both refractive indices are large, and Δn is small.

With an applied field $\mathbf{E} > E_{\mathrm{th}}$, the sample switches to the bistable blue surface-stabilized structure with markedly increased birefringence. This texture appears to have the layers normal to the surfaces ($\delta = 0$, parallel to the applied field) (Fig. 5B). The system is driven to this bookshelf layer geometry by the tendency of the polarization to orient parallel to the applied field. Because the polarization is in the layer plane, this preferred orientation of the polarization parallel to the field cannot be achieved with tilted layers. The "straightening" of tilted layers in this case is similar to the formation of quasi-bookshelf alignment with chevron SmC* materials upon application of large electric fields and is not surprising (*20*). The bistable nature of the bookshelf-aligned system is in accord with the "monostable" behavior of the known AFE SmCP phases and is evidence that director alignment parallel to the surfaces is preferred. The birefringence increase is due to the highly biaxial nature of the molecules and the phase. In the bookshelf geometry (Fig. 5B), the conjugated aromatic units contribute to the polarizability only for light polarized along the director.

All of the EO and current response characteristics of known B7 materials are consistent with a simplified model in which the B2 and B7 phases are actually diastereomeric SmCP structures, as shown in Fig. 2. The classic bow-phase mesogens in the B2 phase form an AFE $\mathrm{SmC_SP_A}$ racemate, and other known B7 materials are AFE $\mathrm{SmC_AP_A}$ conglomerates. By using interlayer clinicity as a stereochemical control element, we have created a bow-phase mesogen exhibiting a conglomerate $\mathrm{SmC_SP_F}$ structure with desirable FE order. However, the natural rule requiring at least one twofold symmetry axis normal to the director in smectic liquid crystals remains apparently intact.

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8. One family of such applications requires electronic second-order nonlinear susceptibility $\chi^{(2)}$. Compounds of type **2** in the FE state have been shown to possess the largest $\chi^{(2)}$ yet measured for a liquid crystalline material [R. Macdonald, F. Kentischer, P. Warnick, G. Heppke, *Phys. Rev. Lett.* **81**, 4408 (1998)].
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10. There is, a priori, no electrostatic free energy difference between the macroscopic FE and AFE structures, assuming that the layers are infinite homogeneous dipolar sheets. At the molecular level, one or the other structure could be favored electrostatically, depending on the details of molecule-pair correlations across layers. In the SmCP system, the magnitude of this effect, or indeed which structure should be favored electrostatically, is not known.
11. A SmCP phase with anticlinic methyl-terminated layer interfaces may be considered a smectic bilayer with all anticlinic layer interfaces (one of these layer interfaces cuts the molecules in half and is rigidly anticlinic because of the covalent structure). The polar symmetry of a bilayer smectic with all anticlinic layer interfaces is discussed in P. E. Cladis and H. R. Brand, *Liq. Cryst.* **14**, 1327 (1993).
12. All new compounds in the synthesis gave satisfactory ^{1}H and ^{13}C nuclear magnetic resonance spectra, mass spectra, and combustion analyses.
13. Molecules of triester **3** do not possess twofold symmetry. Such molecules (or indeed twofold symmetrical molecules) may spontaneously organize such that the twofold symmetry of the phase is broken, leading to smectics with C_1 symmetry. For example, the bow-phase system could spontaneously organize to produce tilt in the projection of the director on the polar plane, leading to bow-phases with C_1 symmetry [H. R. Brand, P. E. Cladis, H. Pleiner, *Eur. Phys. J. B* **6**, 347 (1998)]. There is no compelling evidence to date, however, that such symmetry breaking occurs in the bow-phases. Thus, in the smectic phases of triester **3**, molecules are oriented randomly about the axis normal to the director, and the twofold symmetrical symbolic structures shown in Fig. 1 capture the symmetry of the phase rather than of the molecules. The presence of twofold symmetry normal to the director (about **P**), such that properties of the phase are invariant with sign of the director, is the only "symmetry rule" remaining intact in the smectic LC field.
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16. All attempts to prepare freely suspended films of triester **3** failed. Instead, stable freely suspended liquid crystal fibers of $\sim$10-μm diameter are produced. X-ray diffraction from these fibers shows them to consist of smectic layers in the form of concentric cylinders. Although this observation provides additional confirmation of the fluid smectic nature of the B7 phase, such fibers have not, to date, proven useful for determining the FE or AFE nature of the phase. On the basis of a very small number of examples, it appears that the tendency to form fibers instead of films is general for B7 materials. Details of the x-ray scattering observed for triester **3**, and apparently for all B7 materials, are quite unusual and complex. In bulk unaligned samples, there appear to be multiple coexisting phases with slightly different layer spacings that are all close to the extended length of the mesogen. This could result from metastable structures forming from the isotropic melt along with the thermodynamic phase. Additional scattering peaks suggest some kind of periodic order in the plane of the layers, on a very large length scale. A full understanding of the B7 structure requires an explanation of this unusual x-ray scattering behavior. The observed layer spacings, however, prove that no unusual interdigitation occurs in the B7 phase of compound **3**.
17. The LC cells used in the present work are of the same type as those used for characterization of the classic bow-phase materials (*7*). These cells, which are commercially available from Displaytech (www.displaytech.com), have glass substrates with a 3.5- to 4.5-μm cell gap, coated with low-pretilt polyimide alignment layers. The rubbing directions on the two substrates are parallel.
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An Orientational Transition of Bent-Core Molecules in an Anisotropic Matrix

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We report the discovery of an orientational transition of bent-core molecules in a background anisotropic medium, in this case a smectic liquid crystal made of rod-like molecules. The resulting director is apolar in nature, and the medium can be described as an orthogonal biaxial smectic. The detailed phase diagram of mixtures of the two types of compounds revealed the induction of two liquid crystalline phases that are specific to compounds with bent-core molecules. The chemical nature of the bounding surface had a marked influence on the observed textures.

Thermotropic liquid crystals are states of soft condensed matter that exhibit a large variety of orderings of molecules with shape anisotropy (*1, 2*). Nematics (N) exhibit a long-range orientational order of rod-like or disc-like molecules about a common axis called the director, which has apolar symmetry. They are used in practically all commercial flat panel display devices. If the molecules are rod-like, the translational symmetry can be broken along one direction, giving rise to different types of smectic liquid crystals (*1,*

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2). Although in general the molecules are not cylindrically symmetric, both N and smectic A (SmA) liquid crystals are uniaxial, characterized by two principal refractive indices.

Orientational transition of anisotropic molecules can also occur in a background medium. For example, colloidal suspensions like those of long polymeric molecules in isotropic solvents undergo an orientational transition to the N phase as the density is increased beyond a critical value (*3*). The possibility of getting a biaxial nematic liquid crystal (N_b) because of a mutual orientation of rod-like and disc-like molecules has been discussed in a large number of theoretical papers (*1*). However, an experimental investigation of such a mixture (*4*) showed only a coexistence of two uniaxial nematic liquid crystals, one richer in rods than the other, in agreement with the prediction of a molecular theory that properly took into account the chemical potentials of the two species (*5*). N_b and biaxial SmA (SmA_b) phases are characterized by three directors and three refractive indices. They can be expected to have more complex electrooptic responses compared to the uniaxial phases, thus enlarging the potential for applications. The properties of the SmA_b phase have been discussed theoretically (*6*), and the only known example of SmA_b occurs in a polymeric system (*7*) upon cooling from the N_b phase.

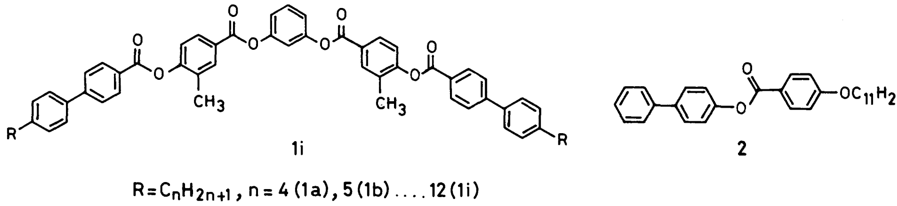
In the past few years, a new type of molecular shape, namely that with a large bent core (with a bend angle of ~120°; see Fig. 1), has been shown to give rise to novel liquid crystalline phases (*8, 9*). The packing of such highly biaxial bent-core (BC) but achiral molecules in smectic layers produces a spontaneous transverse polarization (*8*). Such molecules have also been called banana- or bow-shaped molecules in the literature (*10*). Further, the molecules tilt about the "arrow" directions of the bows, breaking the achiral symmetry of the layers, as was beautifully demonstrated by Link *et al.* (*9*). Thus, chirality and polarization appear to be intimately related in liquid crystals. The different possible relative arrangements of the polarization vectors, the tilting directions, and the chiral sense of successive layers can generate many different structures (*9, 11*), and the discovery of Link *et al.* has led to intense activity in this field. Several hundred compounds with BC molecules have been synthesized (*12*), and up to five different liquid crystalline phases specific to such compounds have been identified. These are the lamellar B_2 phase (*12*) studied in detail by Link *et al.*; the B_1 phase, which exhibits a two-dimensional lattice (i.e., a columnar structure); and B_5, B_6, and B_7, whose structures are not yet established. Studies on many homologous series have shown that the lower homologs (in the case illustrated in Fig. 1, if the end alkyl chains have five to seven carbon atoms, i.e., **1b** to **1d**) exhibit the B_6 phase, a few mid-range homologs (**1e** to **1g**) the B_1 phase, and the higher homologs the lamellar B_2 phase. Most often a given homolog exhibits only one of these phases, with very few known examples of polymesomorphism (*12*) of the B liquid crystalline phases.

Here, we report on a new type of orientational transition of the BC molecules in an anisotropic SmA matrix made of rod-like molecules. Both the compounds were synthesized in our laboratory (*13*), and their molecular structures were engineered for a close matching of both the aromatic cores and the alkyl chains (Fig. 1). We show that rod-like molecules without a highly polar end group such as **2** can exhibit the bilayer SmA_2 phase, and that mixtures of **2** with BC molecules of **1i** exhibit B_2, B_1, and B_6 phases, such that an increase in the concentration of the rod-like molecules is equivalent to a shortening of the length of the alkyl chains in a homologous series of the BC molecules (as in going from **1i** to **1b**). As the concentration is reduced below ~13 mole percent (mol%) of **1i**, there is a rearrangement of the **1i** molecules such that their symmetry axes (i.e., "arrows") point along the layer normal of the SmA_2 structure formed by the rod-like molecules. For mixtures of **2** with ~4 to 13 mol% of **1i**, an orientational ordering transition of the BC molecules in the smectic layers occurs, with the relevant director being orthogonal to that of the rod-like molecules, which gives rise to a biaxial smectic A_2 (SmA_{2b}) phase. There is a marked influence of the boundaries of the cell on the orientation of the BC molecules in the SmA_{2b} liquid crystal, as revealed by its textures.

The rod-like molecule **2** has an alkyl chain only at one end of the aromatic moiety, thus making it biphilic in nature. X-ray scattering studies of the smectic, using an image plate, have shown a weak scattering near $q = \pi/l$ (where q is the wave vector and l is the molecular length), hence it has a bilayer SmA_2 structure (*14*). Obviously the aromatic cores of adjacent layers would like to be in close proximity, giving rise to the SmA_2 structure, which was found earlier only in compounds with the strongly polar cyano or nitro end groups and other dipoles in the aromatic core with an orientation opposite to that of the end-group dipole (*1*).

The compound **1i** exhibits the B_2 phase and shows characteristic textures. Electrooptic studies like those reported by Link *et al.* show that both homochiral and racemic states coexist and the tilt angle is ~40°, which has also been confirmed by x-ray scattering studies. As the phase diagram (Fig. 2) shows, for compositions between 37 and 85 mol% **1i**, the B_1 phase with a two-dimensionally periodic structure is induced (*14*). For compositions between 13 and 37 mol% **1i**, the mixtures exhibit the B_6 phase, which has a typical focal conic texture and is moderately switchable. Increasing the concentration of the rod-like molecules gives rise to phases that are exhibited by compounds with pure BC molecules having shorter chains. The obvious difference in the molecular shapes of the two components is reflected in a fairly large (~10°) depression in the transition temperature to the isotropic phase (I phase) from both ends of the phase diagram (*15*).

For the composition range of ~4 to 13 mol% **1i**, a homeotropically aligned liquid crystal sample can be obtained by treating the glass plates with a polymer having long pendant chains [such as octadecyl triethoxysilane (ODSE)]. The uniaxial nematic presents a dark field of view between crossed polarizers. However, strong fluctuations of the director can be



1i

2

$R = C_nH_{2n+1}$, n = 4 (1a), 5 (1b) 12 (1i)

Fig. 1. Molecular structure of the compounds used in the binary system studied: (**1i**) 1,3-phenylene-bis[4-(3-methylbenzoyloxy)]-4′-*n*-dodecylbiphenyl-4′-carboxylate; (**2**) 4-biphenylyl-4″-*n*-undecyloxybenzoate. Phase transition temperatures are, for **1i**, crystal 114°C B_2 128.5°C I and, for **2**, crystal 98.5°C SmA_2 109.5°C N 125.0°C I.

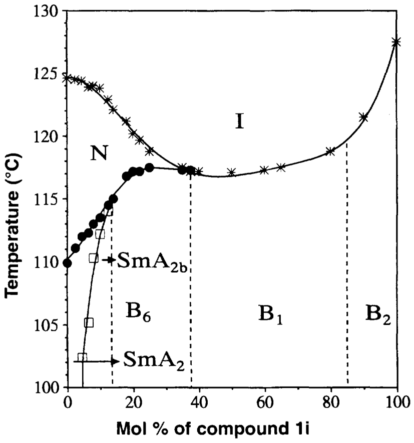


Fig. 2. Phase diagram of mixtures of compounds **2** and **1i**. Note that the B_2-B_1, B_1-B_6, and B_6-SmA_{2b} transition lines are vertical (*15*). First-order transition lines involving N, SmA_2, SmA_{2b}, and B_6 as well as N, B_6, B_1, and I phases appear to meet at two points.

seen, which abruptly cease at the N-SmA$_2$ transition point. As the temperature is further lowered below another transition point, the sample exhibits a schlieren texture [that maps the director field, see (*1*)] between crossed polarizers, in which dark brushes emerge from some "points" (Fig. 3). schlieren textures are normally seen in the smectic C phase and are caused by curvature distortions in the **c**-vector field, which is the projection of the tilted director on the plane of the layers, and the points from which dark brushes emerge are projections of disclination lines (*1, 2*). Because of the polar nature of the **c** vector, only four-brush defects (i.e., of strength ±1, the sign signifying the relative rotation of polarizers and the dark brushes) are seen in that case. In the mixture studied by us, however, we see defects with two brushes (i.e., of strength ±½). This is possible only if the vector field that has curvature distortions (i) lies in planes parallel to the surfaces, and (ii) has an apolar character (*16*). The texture shows that the medium is an orthogonal biaxial smectic liquid crystal. In view of the SmA$_2$ structure of the background medium with rod-like molecules, we designate the biaxial smectic phase in the mixture studied by us as SmA$_{2b}$.

The projected "length" (along the "bow string") of the aromatic core of the BC molecule is ~26 Å, which is comparable to the total length of the aromatic cores of a bilayer of the SmA$_2$ background medium. If bows orient with the "arrows" lying in the smectic planes, they are likely to pack within a bilayer to give rise to a polar rather than an apolar vector field in the smectic planes (Fig. 4A). This is a possible arrangement in the B$_6$ phase occurring in compositions above 13 mol% **1i** (*16*). In the SmA$_{2b}$ phase, which has an apolar vector field, the BC molecules should be oriented with the "arrow" direction along the layer normal (Fig. 4B). The relevant lengths of the aromatic and aliphatic parts of the bows and single rods are "matched" in this configuration also. In view of the bilayer structure of the SmA$_2$ phase, one half of the bilayer favors the "up" while the other favors the "down" orientation of the bows, so that the medium is not longitudinally ferroelectric. Thus, the BC molecules are orientationally disordered above the SmA$_{2b}$-SmA$_2$ transition point (T_{ub}) and become ordered below it. The orientational transition takes place in the background matrix of liquid crystalline SmA$_2$ phase made of rod-like molecules. Differential calorimetric studies (Pyris 1D, Perkin-Elmer) show that when the range of uniaxial SmA$_2$ phase is small, the SmA$_2$-SmA$_{2b}$ transition is weakly first order in nature, with a heat of transition ~200 J/kg for a concentration of 8 mol% BC molecules (*14*).

If the temperature is lowered at a rate of ~1°/min in the SmA$_{2b}$ phase in cells constructed as described above, one can see waves of bright and dark patches moving across the sample. The precise origin of this effect is not clear to us; it may reflect the shear-induced reorientation of the director $\hat{b}$ of the BC molecules due to movements of smectic layers in the sample. The texture is markedly different if the sample is prepared between cleaned but otherwise untreated slide and coverslip. The schlieren texture now has only ±1 defects with four brushes, which remains static when the temperature is lowered. This result shows the strong influence of the boundary conditions on this rather fragile phase. In the untreated cell, the aromatic cores of the BC molecules appear to be attracted to the silicon dioxide surfaces of the glass plates, and they can tilt near the surface to maximize the attractive energy (Fig. 4C). The in-plane director $\hat{b}$ corresponding to the long (or bow-string) axis of the BC molecule is still in the plane of the layer, but the director $\hat{a}$ corresponding to the "arrows" is now tilted. The director deformation in $\hat{a}$ can only give rise to ±1 defects as in smectic C liquid crystals. The attraction of the BC molecules to the glass plates presumably also leads to a higher concentration near the surfaces than at the middle of the sample, which could explain the absence of the wave-like fluctuations arising from any movement of smectic layers near the center of the cell.

The uniaxial-to-biaxial transition of the medium has also been confirmed in a conoscopic study of an oriented sample (*14*). The uniaxial cross clearly splits as the temperature is lowered across the transition point. In cells treated for planar alignment, the SmA$_2$ is reasonably well aligned but with some folds occurring along the rubbing direction. As the temperature is lowered across T_{ub}, the number of folds increases perceptibly.

The biaxial smectic phase can be characterized by three principal refractive indices, μ_a, μ_b, and μ_c, where the suffixes *a*, *b*, and *c* refer to the polarization of the incident light beam being parallel to the "arrow" director $\hat{a}$, the "bow-string" director $\hat{b}$, and the director perpendicular to the *ab* plane, respectively. The biaxiality order parameter is reflected in the nonzero value of $\mu_b - \mu_c$. To measure it, we used a homeotropically aligned sample taken in a cell with one wall consisting of an indium tin oxide–coated transparent conducting glass plate with a gap of ~1 mm. An electric field (~200 V/mm at 5 kHz) applied in the gap aligned the $\hat{b}$ director along the field. We measured $\mu_b - \mu_c$ using a quarter-wave plate compensator as a function of temperature, which was maintained to an accuracy of 10 mK using an INSTEC hot stage (*14*).

The orientational order parameter of the background SmA$_2$ liquid crystal (which is given by $\langle 3\cos^2\theta - 1\rangle/2$, where θ is the angle made by the long axis of the rod with the layer normal) is not expected to vary much with

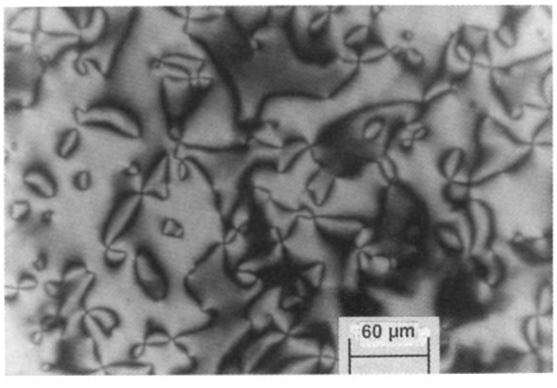


Fig. 3. Schlieren texture of the SmA$_{2b}$ phase exhibited by the binary mixture with 8 mol% of the BC compound, taken between ODSE-coated glass plates with crossed polarizers. Note the large number of defects of strength 1/2.

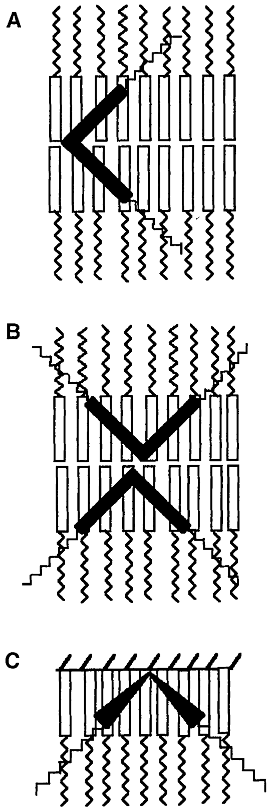


Fig. 4. Schematic diagram of the proposed arrangement of rod-like and BC molecules in (**A**) the B$_6$ liquid crystal, (**B**) the SmA$_{2b}$ liquid crystal, and (**C**) the tilt of the BC molecule in a SmA$_{2b}$ layer adjacent to an untreated glass plate.

temperature. The biaxiality order parameter of the BC molecules can then be written as

$$\eta = \langle \cos 2\phi \rangle \qquad (1)$$

where ϕ is the azimuthal angle made by the long axis of the BC molecule with the $\hat{b}$ director.

For the alignment of the BC molecules as shown in Fig. 4B, we can estimate the expected values of $\mu_b - \mu_c$ using the polarizabilities of the two arms of the BC molecules and those of the background rod-like molecules, and the composition of the mixture. Assuming η to be ~ 0.3, we get $\mu_b - \mu_c \approx 0.007$ for a concentration of 4.5% of the BC molecules, a value close to that measured at $T_{ub} - T \approx 10°C$. However, if the BC molecules are vertically aligned, as in Fig. 4A, the value of $\mu_a - \mu_c$ would be about one-third as great. The birefringence data in the temperature range of T_{ub} to $T_{ub} - 0.15°$ were fitted to the expression

$$\mu_b - \mu_c = C(T_{ub} - T)^{\beta} \qquad (2)$$

using a nonlinear least squares fitting procedure (where C is a proportionality constant and β is the order parameter critical index). We find that $\beta \approx 0.79$ for the mixture with 4.5 mol% BC molecules and 0.56 for the mixture with 8 mol% BC molecules. One would have expected that the ordering transition should follow the *xy* model, in which case β should be ~ 0.35 (*17*). We believe that the higher measured values reflect the fact that the phase diagram of T_{ub} versus concentration (Fig. 2) tends to have an almost vertical slope at lower concentrations of the BC molecules. It is known from studies of systems showing re-entrant phases (*18*) that the critical index could then double for essentially geometric reasons. As the concentration of the BC compound increases, the index β decreases. However, the concentration range over which the SmA_{2b} phase occurs is relatively small, and the slope of the transition line is not small enough to get the expected *xy* value.

It would be interesting to look for this transition in other systems with the hope of widening the range of occurrence of the biaxial smectic phase. It would then be possible to study many physical properties of the system, which has an almost ideal *xy* character. A similar transition could occur in bilayer membranes, in which the strong fluctuations of the two-dimensional system can be expected to have a bearing on the problem.

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15. Note that all the transition lines between different B phases are essentially vertical in Fig. 2. Observations on contact preparations between compositions on either side of the appropriate transition line show two phase regions. The islands of one phase in the background of the other neither grow nor shrink with temperature. The potential energy minima corresponding to the SmA_b, B_6, B_1, and B_2 phases are separated by large barriers.
16. Defects (called dispirations) of strength ½ can also occur if successive bilayers as in Fig. 4A have an antiferroelectric ordering of the BC molecules, and the disclination is associated with a screw dislocation with a Burgers vector of magnitude $2l$ [Y. Takanishi, H. Takezoe, A. Fukuda, J. Watanabe, *Phys. Rev. B* **45**, 7684 (1992)]. In our sample of SmA_{2b}, defects of strength 1 often split to form two defects of strength ½, which is not seen in dispirations. Further, we did not find any switching due to polarization when a dc electric field up to 5 V/μm applied in the layer plane was reversed. Also, we did not see six- and eight-brush defects often seen in antiferroelectrics.
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High-Strength Welds in Metallocene Polypropylene/Polyethylene Laminates

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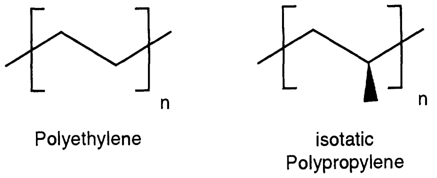
Spectacular advances in organometallic chemistry over the past two decades have resulted in single-site catalysts that are revolutionizing production of polyethylene (PE) and isotactic polypropylene (*i*PP). This report describes an unanticipated benefit of metallocene-catalyzed semicrystalline polyolefins, namely welded joint strengths in PE/*i*PP laminates that can exceed the cohesive strength of the constituents. We propose that interfacial polymer entanglements, established in the molten state and subsequently anchored in chain-folded lamellae upon crystallization, are responsible for this intrinsic property. The poor adhesion exhibited by traditional Ziegler-Natta–catalyzed polyolefins is shown to derive from the accumulation of amorphous polymer, a by-product of the polymerization reactions, at the interface. These results should facilitate fabrication and improve the properties of composites based on materials that dominate the plastics industry.

Polypropylene (PP) is the thermoplastic polymer with the fastest expansion in production in the world, with an average annual growth rate of 9% since 1991 (*1*). Currently, worldwide PP resin production is estimated at over 20 million metric tons (*1*). The vast majority of products are fabricated with *i*PP, a stereoregular macromolecule (Scheme 1) that crystallizes into chain-folded lamellae that melt at about 165°C. This material is used in a plethora of durable and nondurable goods (*2*) such as food packaging, automobile battery cases, and child car seats. PE is the most widely used plastic (*2*), with applications ranging



Scheme 1.

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