Synthesis of Two-Dimensional Polymers

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A synthetic pathway is described to construct "in bulk" two-dimensional (2D) polymers shaped as molecular sheets. A chiral oligomeric precursor is used that contains two reactive sites, a polymerizable group at one terminus and a reactive stereogenic center near the middle of the molecule. The bulk reaction yields bilayer 2D polymers of molecular weight in the order of millions and a monodisperse thickness of 50.2 angstroms. The 2D molecular objects form through molecular recognition by the oligomers, which self-organize into layers that place the reactive groups within specific planes. The oligomers become catenated by two different stitching reactions involving the reactive sites. At room temperature, stacks of these molecular objects can organize as single crystals and at higher temperatures melt into smectic liquid crystals. Nonlinear optical experiments reveal that solid films containing the 2D polymers form structures that are thermally and temporally more stable than those containing analogous 1D polymers. This observation suggests that the transformation of common polymers from a 1D to a 2D architecture may produce generations of organic materials with improved properties.

For six decades, polymer science has focused on the linear chain and its derivatives, which include nonlinear extensions such as branched polymers and the 3D network. Derivatives of the linear chain common in contemporary polymer science include macromolecular rings, stars, combs, and ladders. Polymers that would form molecular objects of well-defined shape represent a significant departure from the linear chain and its derivatives; molecular tubes, large diameter rods, and sheets would be examples of such objects. The use of these molecular objects is an intriguing future approach to materials chemistry for various reasons. One reason is the inevitable self-ordering these objects would exhibit in the condensed state because of their shape. Other reasons are the possibilities for molecular design of properties (for example, tubes for transport), and the changes in molecular motion modes when monomers are catenated to form these objects rather than linear chains. Such changes would certainly impact on the physical properties of solid materials containing the objects. The great synthetic challenge is to find "bulk" pathways for these supramolecules that do not require preorganization of the small precursor molecules by external means and that catenate the atoms of the object by covalent bonds. This new dimension of polymer science would benefit from our understanding of the principles behind self-assembly of molecules into large aggregates. Generally, the synthesis of such nanostructures from stable aggregates presents a great challenge to chemistry today (*1*).

We have discovered a bulk pathway for 2D polymers that does not rely on the externally controlled preorganization of monomers to form molecular sheets. Preorganization of monomers to form 2D polymers has been investigated previously with Langmuir troughs, vesicles, or surfaces. In one example, a bifunctional monomer that can polymerize into a cross-linked structure was confined in a bilayer membrane (*2*) and the product obtained was claimed to be a 2D network. This system is in fact reminiscent of the 2D gel spectrin found in cell membranes, which has been linked to changes in erythrocyte shape (*3*). Bifunctional monomers have also been polymerized in monolayers spread at the water-gas interface (*4*, *5*). Other previous work describes the concept of 2D polymerization in which monomers are catenated in confined geometries (dissolved in bilayers) or ordered configurations resulting from adsorption on solid surfaces (*6*–*9*). However, once isolated from the confining environments and dissolved, the covalent structure and conformations of these polymers are similar to those of linear chains and the 2D shape is lost. There is also an example in the literature claiming the formation of planar structures from the polymerization of diacetylenes containing hydrogen-bonded substituents, but again this material has a 1D covalent structure (*10*).

Molecular precursor of 2D polymers. In this work we have synthesized oligomers that organize into layered structures as the precursors for 2D polymers. These molecules are designed to experience molecular recognition so that not only do their termini segregate in space but also their two reactive functions become confined to specific planes in the layered structure. A reactive group is present only on one surface of the layer, and a different reactive group attached to a chiral center is buried in a distant plane from the top surface (see Fig. 1). Chemical reaction among groups in this configuration catenates oligomers through two types of stitching into a bilayer 2D polymer. The concept is illustrated schematically in Fig. 2, which shows that co-reaction among the surface groups of two layers builds the bilayer. Comb linear polymers would form if chemical reaction would only occur among functions segregated at the surface of the layer. However, 2D polymers will not necessarily form when chemical reaction occurs within two different planes in each layer. The critical factor is the distance between both planes, because spatial correlation of the paths followed by the two reactions could yield ladder polymers. Formation of 2D polymers through catenation of oligomers in entire layers requires some extent of decorrelation among the directions followed in space by different stitching reactions.

The oligomeric molecule contains three different fragments, and their chemical structures are shown in Fig. 3. Fragment **1** is an enantiomerically enriched chiral compound in which the strongly dipolar cyano group substitutes the stereogenic center. The synthesis of fragment **1** (*11*) and that of the oligomer (*12*) were previously reported by our laboratory. The cyano group is

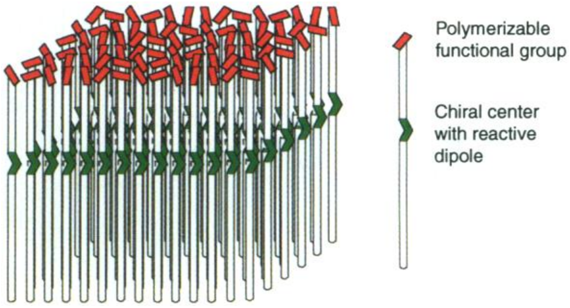

Fig. 1. Schematic representation of oligomers organized in a layer with reactive groups confined to specific planes by molecular recognition. One plane contains polymerizable acrylate groups and another contains chiral centers with a reactive strong dipole moment.

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potentially reactive given the well-known chemistry involved in the pyrolysis of poly(acrylonitrile) to form carbon fibers (*13–17*). At the same time, appending this strong molecular dipole with preferred handedness to the backbone of the fragment provides a mechanism for molecular recognition based on ferroelectric ordering. Fragment 2 has the basic structure of well-known smectogens (*18*) and should therefore promote the formation of layers among oligomers. This fragment and its junction with fragment 1 provide the 2D polymer with a rigid skeleton that maintains its shape in solution or at elevated temperatures. Fragment 3 contains a second reactive group, namely an acrylate group, which can stitch oligomers on the layer's surface through polymerization. Finally, all fragments contain the proper carboxyl and hydroxyl functions to connect them into the precursor oligomer through ester bonds. A minimum energy conformation of an isolated oligomeric molecule is shown in Fig. 4.

An important result in this work was to find that the molecules of oligomer 4 indeed self-organized into layered structures. The micrograph between crossed polarizers (Fig. 5A) captures the oligomeric compound in the midst of a smectic to isotropic phase transition near 100°C. The catenation of smectogens through a molecular backbone to form a comb polymer raises the smectic to isotropic phase transition temperature (*19*). This increase is understood as the result of a lower specific volume in the mesophase due to polymerization, and it is known not to be very sensitive to the length of the catenating backbone. The oligomer in question does not fully transform to the isotropic state as it nears its transition, and isothermal annealing just above the transition (110°C) for less than 1 hour causes the system to reorder fully into a layered structure. This behavior is a signature for the occurrence of spontaneous reaction leading to formation of a 2D polymer (compound 5 in Table 1).

Additional evidence for reaction is provided by differential scanning calorimetry scans that reveal an exotherm above the isotropization temperature of the oligomer. Spectroscopic evidence for the reactions was obtained from ^{1}H and ^{13}C nuclear magnetic resonance (NMR) as well as infrared spectra that indicate the consumption of C=C and C≡N bonds (*20*). The reaction among nitriles forms imine bonds (C=N) that connect two or more oligomers in a plane near the center of a molecular layer. Maintaining the oligomer at temperatures ranging from 125° to 140°C for periods of 14 to 20 hours results in a compound that melts into a layered mesophase (see Fig. 5B) and becomes sharply isotropic near 230°C. This compound is 90% by weight soluble in chloroform, and therefore the main molecular transformation of the system is not random cross-linking of oligomers into a 3D network. Because one terminus of the oligomer is free of reactive groups, the formation of an infinite covalent network is prevented in favor of finite 2D polymers. The nature of defects and their concentration in the layered mesophase should be important in determining the planar dimensions of these polymers.

Model compounds. A number of molecules were synthesized to understand the transformation of the oligomer to a 2D polymer (Fig. 6). Their phase transition temperatures are summarized in Table 1. One was the 1D analog 6 synthesized by free-radical polymerization of the oligomer in dilute solution. The compound exhibits an isotropization transition at 150°C, which is consistent with polymerization of the oligomer because the latter undergoes its phase transition at 100°C. The same transition occurs at 230°C in compound 5, which results from heating oligomer 4 in the absence of a solvent. The observed difference in phase transition temperature between compounds 5 and 6 cannot be attributed simply to degree of polymerization. As mentioned above, the transition is

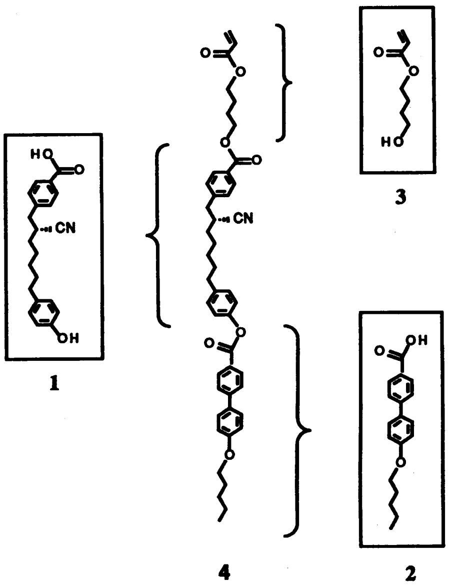


Fig. 3. Chemical structure of the oligomeric precursor and its three basic fragments. The role of fragment **1** is to promote molecular recognition and reactivity for one of the stitching reactions. Fragment **2** is a known smectogen and promotes layering of the oligomers, and fragment **3** contains a polymerizable group for the layer's surface. The rod shape used in the schematics of Figs. 1 and 2 does not imply that oligomers have a fully extended conformation.

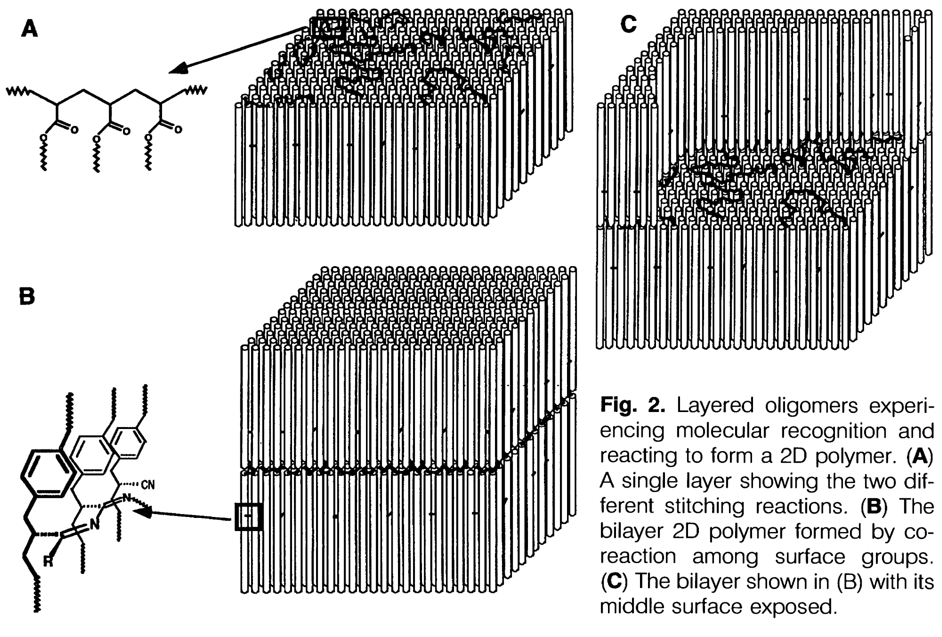


Fig. 2. Layered oligomers experiencing molecular recognition and reacting to form a 2D polymer. (**A**) A single layer showing the two different stitching reactions. (**B**) The bilayer 2D polymer formed by coreaction among surface groups. (**C**) The bilayer shown in (B) with its middle surface exposed.

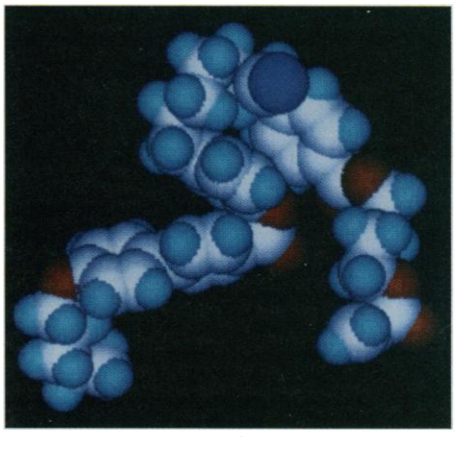


Fig. 4. Minimum energy conformation for an isolated molecule of oligomer **4**.

known to be fairly insensitive to degree of polymerization and, in fact, varied only within a range of 20°C in compounds synthesized in the laboratory to demonstrate this point. The large difference in phase transition temperature observed between compounds **5** and **6** must therefore reflect a transformation in molecular architecture. We conclude that compound **6** is a 1D analog of the 2D polymer and can be described as a comb-ladder polymer because spectroscopic analysis indicates consumption of both acrylate and nitrile groups; ~53% of the nitrile groups are consumed based on the infrared spectrum and acrylate groups are not detected by ^{1}H NMR. Oligomer **7** lacks acrylate groups and is also a smectogen. In this compound, we observed reaction upon heating that leads to the formation of a higher molar mass compound **8** (see Table 1). This observation demonstrates the feasibility of catenating oligomers through the reaction of nitriles to form imine bonds. A third molecule, **9**, contained only fragments **2** and **3** of oligomer **4** and thus had only the polymerizable acrylate group. Interestingly, this monomeric smectogen polymerized in dilute solution to form a comb polymer (compound **10**) or polymerized in bulk (compound **11**) yields products with identical phase transition temperatures (within experimental error). This observation demonstrates that the transformation to a 2D polymer requires additional stitching provided by the CN groups in fragment **1**.

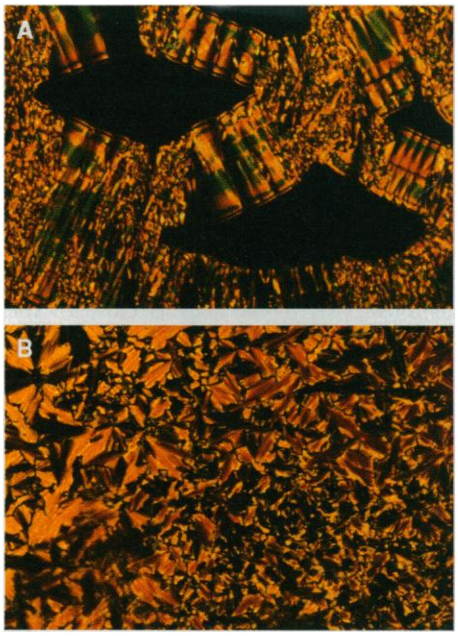
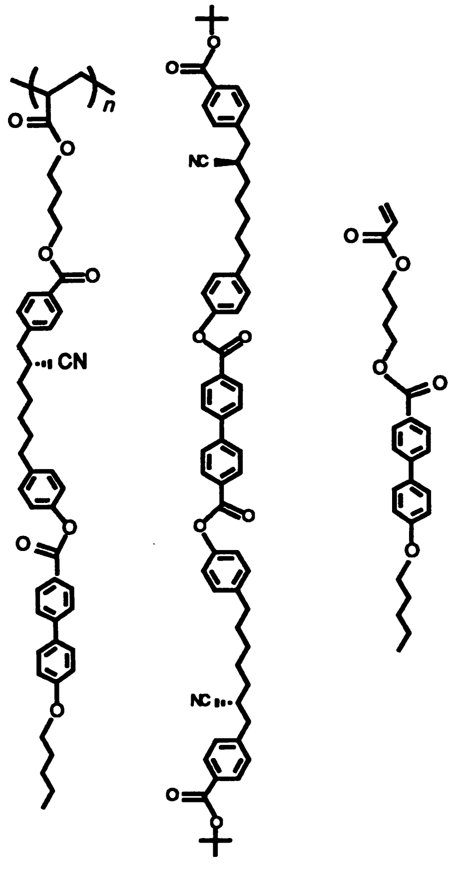


Fig. 5. (**A**) Optical micrograph between crossed polarizers showing the smectic to isotropic phase transition of oligomer **4** near 100°C. (**B**) Optical micrograph between crossed polarizers showing the smectic texture above 200°C of the oligomer transformed to 2D polymer.

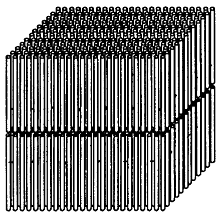
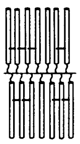
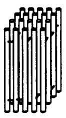
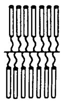
Homochiral molecular recognition. The molecular recognition that places reactive dipoles in a common plane of the layers is possibly linked to homochiral interaction among nitriles. Other interactions among similar molecular sectors of the oligomer may be important as well, such as π-π overlap of biphenyl units located near one terminus. In very recent work we learned about the importance of homochiral interaction among the strong dipoles through synthesis of linear chains (*11*) that resulted from the polycondensation of hydroxyacid **1** and its derivatives (see Fig. 7). Linear chain **12** was obtained from the enantiomerically enriched monomer, chain **13** from the racemate, and chain **14** from the achiral hydroxyacid lacking the nitrile function. We found remarkable differences in molecular organization among the linear chains in the solid state. When the dipole substitutes the repeat with random handedness, one observes total frustration of ordering in the system and a glass is obtained. On the other hand, polymer **14**, which lacks the strong dipole in its repeat, is a highly crystalline material in which chains have boardlike shapes and pack face-to-face (*21*). Interestingly, if the dipole substitutes the backbone with preferred handedness, a highly crystalline solid forms and the boardlike chains pack both face-to-face and edge-to-edge as well (see schematic illustration in Fig. 8). Polymeric chain **12** with its highly organized boardlike chains is effectively polymerized fragment **1** of our oligomeric precursor. Furthermore, we found that a racemic mixture of the oligomer does not yield the same compound obtained from the enantiomer. Instead, the product exhibits a broad biphasic (smectic-isotropic) thermal range from 185° to 237°C. One concludes from observations on the linear chain compounds and the oligomeric racemate that homochiral interactions



6 **7** **9**

Fig. 6. Chemical structures of model compounds synthesized with the objective of understanding the transformation of oligomer **4** to 2D polymers.

Table 1. Smectic-isotropic phase transitions of model compounds that were synthesized to understand the transformation of the precursor oligomer into 2D polymers.

Parameter	Molecule						
	4	5	6*	7	8	9	10 + 11
Architecture							
Isotropization temperature (°C)†	98	230	150	135	190	55	150
Smectic-isotropic biphasic range (°C)	3	10	40	5	60	3	20

*Reaction among nitriles is also observed in this compound. †Peak maximum of isotropization endotherm measured by DSC.

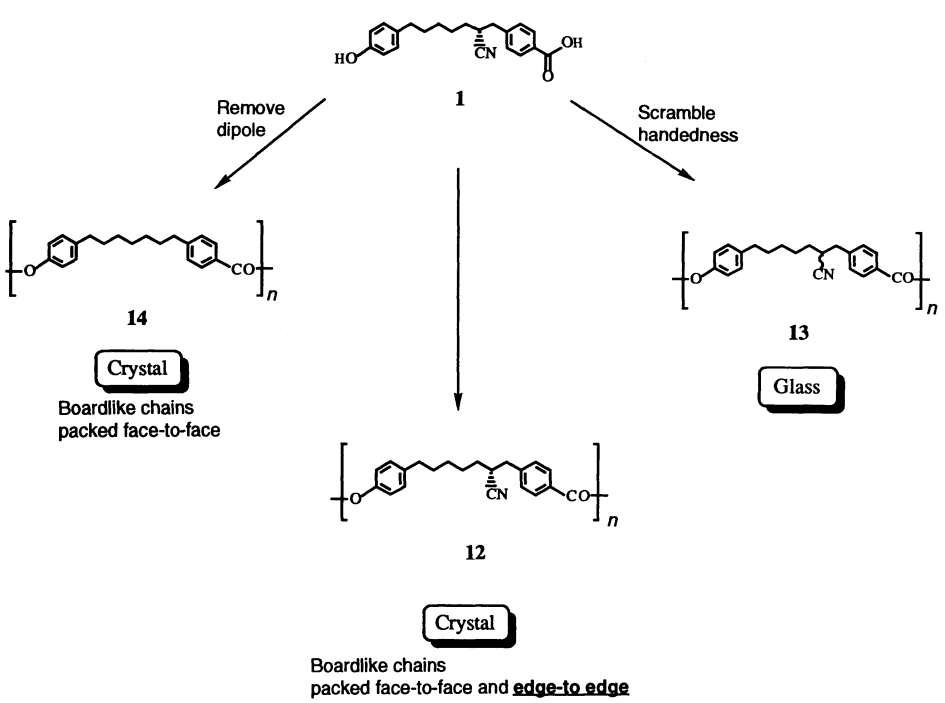


Fig. 7. Monomeric and polymeric compounds which demonstrated that organization of molecules in the solid state is strongly affected by the relative stereochemistry of CN dipoles.

Fig. 8. Schematic representation of chain shape and packing in solid materials as affected by the relative stereochemistry of the strongly dipolar C≡N group. Glassy materials are obtained when dipoles have random handedness, whereas chains are boardlike and pack both face-to-face and edge-to-edge when dipoles have common handedness. In the absence of the dipole, edge-to-edge packing is not observed.

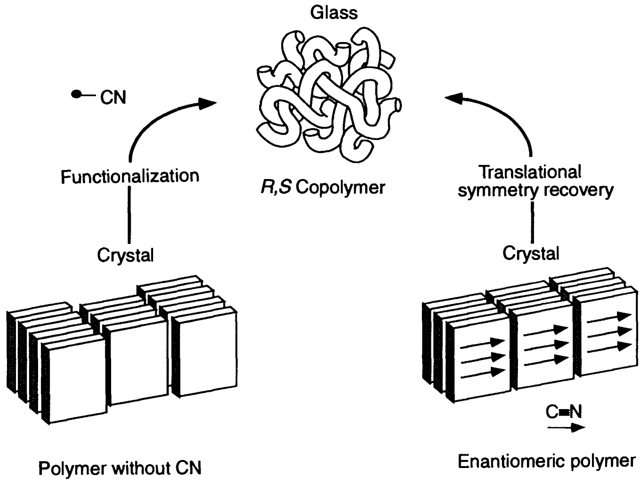


Fig. 9. Transmission electron micrograph showing stacked 2D polymers. The flat objects are less than 100 Å thick and can self-assemble into single crystals as revealed by the electron diffraction pattern in the upper right-hand corner. The arrows point to supramolecules that are fractions of a micrometer in planar dimension and nanometers in thickness.

among nitriles must be an important factor in the molecular recognition that leads to 2D polymers.

The favorable homochiral interaction among nitriles that experiments suggest is also supported by recent calculations published by Andelman and DeGennes (22). In this work, the preference for heterochiral versus homochiral interactions among chiral surfactant molecules shaped as tripods is predicted on the basis of the nature of groups present at the base of the tripod. This simple model predicts that the difference between homochiral and heterochiral partition functions is greater than zero when full charges or dipoles are present at the corners of the tripod defined by the stereogenic center. In this context, the model would predict "facile" homochiral recognition given the strong dipole moment of CN groups in fragment 1. This recognition may catalyze the reaction among nitriles which leads to 2D polymers.

Microstructure and properties. A thin film of 2D polymers analyzed by electron microscopy reveals stacked flat objects (see Fig. 9). Small-angle x-ray diffraction data on thin films with macroscopically oriented layers indicate that the *d*-spacing corresponding to the (001) reflection is 50.2 Å. It is specially interesting that these flat molecular objects formed by in situ polymerization of an oligomeric film can self-assemble into single crystals. This structure is revealed by the electron diffraction pattern in Fig. 9 consisting of the (*hk*0) reciprocal lattice. The remarkable registry among the flat molecular objects suggests that their top and bottom surfaces have the same chemical structure. This observation, as well as their thickness as measured by x-ray diffraction, indicate that the 2D polymers indeed form bilayers containing two covalently linked monolayers of the precursor oligomer (23).

Relative to polystyrene standards, gel permeation chromatography (GPC) using tetrahydrofuran is used as the solvent indicates that the molar mass of dissolved molecular objects can be as high as 17 million daltons. This molar mass is close to the resolution limit of GPC and therefore there are likely to be larger objects in solution and also in the 10% by weight of the product which remains insoluble. As mentioned above, the 2D polymers melt into a smectic fluid (above 100°C). The organization of the system into a smectic fluid at high temperatures is physically logical because the flat objects should naturally form layered mesophases in the condensed state and are therefore ideal smectogens. In this regard, it is interesting to consider the nature of the fluid's isotropization transition; the 2D backbone of the sheets may remain flat while isotropization of the pendant side chains occurs. However, some degree of crumpling in the sheets themselves or other fluctuations could contribute

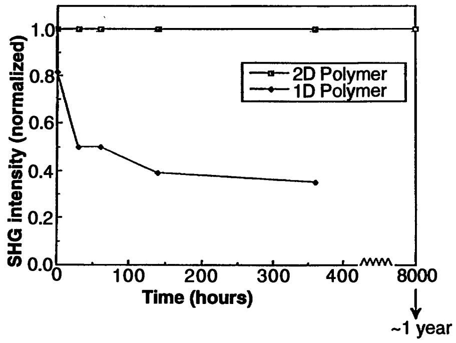


Fig. 10. Intensity of the second-harmonic laser beam (534 nm) as a function of time in two films, one composed of 2D polymers and the other composed of their 1D analogs.

to the loss of detectable birefringence. These are clearly issues to be addressed by subsequent experiments.

Second-harmonic generation. We conclude by reporting on an interesting physical property of solid films containing 2D polymers (compound **5**). Films $\sim$10 μm in thickness were exposed to an electric field of 67 KV/cm at 80°C in order to create a macroscopic noncentrosymmetric medium. This is accomplished by first etching a trough in a chromium film sputtered on fused silica by photolithography. The sample is then placed within the 150-μm gap, and opposite sides of the metal film serve as poling electrodes. Details of this method have been described elsewhere (24). After the poling procedure, one observes changes in the optical microscopic texture of the sample suggesting that some molecular reorientation takes place in the electric field. The experiment performed next was the measurement of second-harmonic generation when an infrared laser beam passed through the film. Poled polymers containing the appropriate chromophores for frequency doubling of laser beams lack temporal stability in a noncentrosymmetric configuration (25). The noncentrosymmetric configuration, which may disappear gradually through molecular relaxations, is essential if the system is to exhibit a finite second-order nonlinear optical susceptibility. The intensity of the green light generated by the film from an infrared laser beam remains unchanged for periods exceeding 1 year (Fig. 10). In contrast, a similar film containing the 1D comb-ladder polymer synthesized exhibits loss of the second harmonic signal within periods of hours. The observed difference could be significant in the use of polymers to prepare future photonic devices.

Observations on phase transitions and nonlinear optical properties described here suggest that molecular motions of identical monomers could be different within 2D polymers relative to those in 1D isomers. The different state of connectivity among monomers in 2D polymers could impact on many physical properties of organic materials including mechanical behavior, adhesion, aging, rheology, and others. These are all questions that should be explored as we learn to polymerize common monomers into 2D structures.

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