

Perpendicular Organization of Macromolecules: Synthesis and Alignment Studies of a Soluble Poly(iptycene)

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The ability to control supramolecular orientation and alignment has become important in many present and emerging technologies, including optical displays, high volume data storage, and dichroic polarizers.¹ There have been many examples of small molecules and polymers aligning in an anisotropic environment, typically, with their long axis parallel to the aspect ratio of the host.^{1b,d,2} Although molecular control has become increasingly important,^{1–3} chemists have been unable to control supramolecular orientations by designing guest molecules that organize within hosts in more unique ways. We have taken an important first step toward this goal by designing a lathe-like ladder polymer that on average prefers to align perpendicularly to a flexible polymer host.

We recently demonstrated that iptycenes incorporating anthracene subunits align with their long axes perpendicular to the director of a nematic liquid crystal (LC) or the stretching direction of a stretch-aligned polymer.⁴ We ascribe this unique sense of alignment to a minimization of local density changes in the polymeric matrix; the host LC or polymer “threads” through the nanometer-scale pores defined by the rigid iptycenes. Polymers in which iptycenes are contained within the main chain (poly(iptycene)s) are very rare.⁵ We now report the hyperbaric preparation of a soluble, shape-persistent, two-dimensional ladder poly(iptycene), which aligns in a contra aspect ratio fashion to a stretched polymeric host, as illustrated in Figure 1.

The synthesis of monomer **1** is illustrated in Scheme 1. The reactive anthracene and epoxy moieties at the ends of the monomer are designed to react via a Diels–Alder transformation to build up the ladder polymer structure. The central iptycene unit becomes part of the polymer main chain upon step-growth polymerization. In addition, the terminal ring of the anthracene moiety bears long alkyl chains that are essential to oligomer solubility during polymerization.

Attempts to polymerize **1** under traditional Diels–Alder conditions (refluxing Decalin at atmospheric pressure for several days) met only with marginal success. Polymerization of **1** under hyperbaric conditions for several hours, however, gave poly(iptycene)s with a higher overall degree of polymerization and fewer degradation products than traditional reactions. Since Diels–Alder reactions have a negative volume of activation, increasing the pressure of the reaction results in an exponential increase of the reaction rate.⁶ Under the conditions used in our laboratory, a theoretical rate enhancement of up to 1.5×10^4 at a pressure of 8800 atm is possible. This allowed for larger polymers while reducing the length of time the reaction mixture was exposed to aggressive thermal conditions. Addition of small amounts of

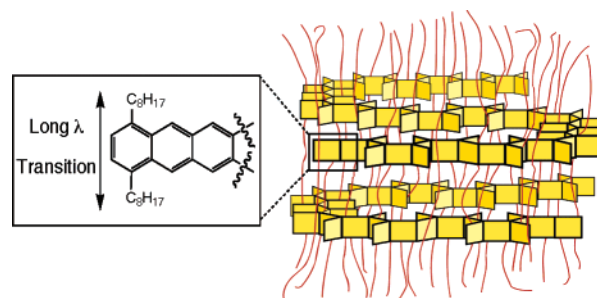
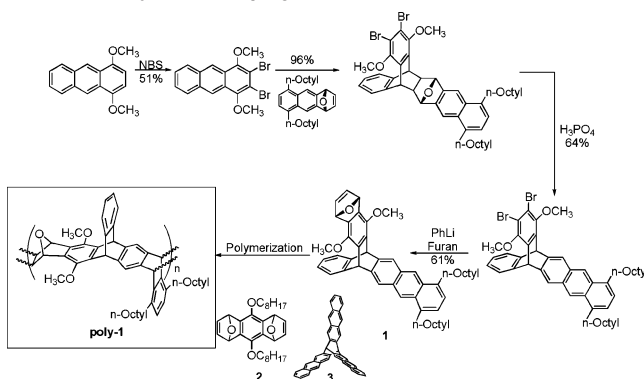


Figure 1. Depiction of stretch-aligned PVC threaded through **poly-1** and the resulting perpendicular orientation of the two polymers.

Scheme 1. Synthesis of **poly-1**

hyperbranching agents **2** and **3** led to even larger polymers, the largest with a number-average molecular weight (M_n) of 42 000 g/mol. These reactions were typically performed on a 30 mg scale. The molecular weights of these polymers, as determined by gel-permeation chromatography (GPC) versus polystyrene standards, are most likely overstated due to the rigid structure of **poly-1**.

The main chain of **poly-1** is not made up of extended chromophores. There are, however, residual anthracene end groups in the main chain that can be identified by solution phase UV/vis and fluorescence spectroscopy. It is known that the transition dipole moment of the lowest energy vibronically coupled absorption of anthracene is short-axis polarized.⁷ More specifically, the 0–0 absorption band of anthracene is purely short-axis polarized.

This inherent anisotropy of anthracene allowed us to characterize the alignment of **poly-1** relative to a uniaxially stretch-aligned polymer host. Solution-cast poly(vinyl chloride) (PVC, $M_n = 99\,000$ Da, PDI = 2.3) thin films containing ~0.5–1 weight-percent **poly-1** were prepared. We had previously found PVC to be a superior host for iptycenes.⁴ Although the limited number of anthracene groups in **poly-1** precluded absorption spectroscopy from reliably detecting the anthracene vibronic transitions in the thin film, fluorescence

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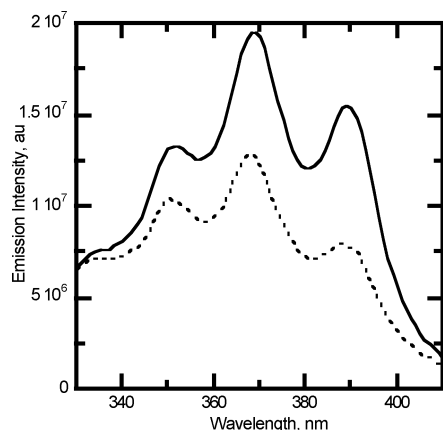


Figure 2. Corrected polarized fluorescence excitation spectra of low PDI ($M_n = 17\,000$ Da, PDI = 1.2) **poly-1** in stretch-aligned PVC. Spectra when the polarizer is oriented parallel (solid line) or perpendicular (dotted line) to the stretching direction are illustrated. The dichroic ratios of the 0–0 bands were independent of film orientation (1.82 and 1.92).

excitation spectroscopy was suitable for reliable observation of the short-axis polarized transitions. These films were uniaxially stretched at 100 °C (draw ratio ~450%) to impart macromolecular alignment of the PVC⁸ and then characterized using polarized excitation spectroscopy. On the basis of pure aspect ratio considerations, the poly(iptycene) should have aligned parallel to the host polymer backbone.

Polarized excitation spectra of a low polydispersity index sample ($M_n = 17\,000$ Da, PDI = 1.2) of **poly-1** in uniaxially stretched PVC are shown in Figure 2. The long wavelength region of the excitation spectra has vibronic patterns in the wavelength range characteristic of anthracene groups. These spectral regions were compared with the excitation light polarized parallel or perpendicular relative to the stretching direction of the film. The spectra have been corrected for instrumental anisotropy by comparison with an analogous film that was not stretched and was therefore isotropic.

The data clearly show enhanced excitation of the long wavelength absorption bands of the anthracene moieties when the excitation light is polarized parallel to the PVC stretching direction. In addition, the short-axis polarized 0,0 transition at 388 nm exhibits the highest dichroic ratio. These data indicate that the short axes of the anthracene groups tend to align parallel to the stretching direction of the PVC. As illustrated in Figure 1, this corresponds to the poly(iptycene) aligning perpendicular to the host PVC. It is also important to note that the observed dichroic ratios of the sample are consistent (6% error) regardless of film orientation.

If only aspect ratios of the two polymers were taken into account, the opposite sense of alignment would be predicted. When anthracene is subjected to similar conditions, it prefers to align with its long axis parallel to the stretched PVC.⁴ We propose that this unique sense of supramolecular alignment, with the two polymers preferring to align normal to one another, stems from the aforementioned threading mechanism. Locally orthogonal chains in an isotropic sample become globally perpendicular upon uniaxial deformation and global alignment of PVC along the force direction. This mechanism not only accounts for the observed anisotropic fluorescence data but also allows for maximum alignment of the stretched PVC host while eliminating the internal molecular free

volume of the poly(iptycene). However, there is surely some distortion from a purely two-dimensional structure, with the stereo-random nature of the polymer causing the poly(iptycene) backbone to bend.⁹ This defect structure will have a limiting effect on the observed dichroic ratio.

The lathe-like form of **poly-1** was confirmed via small-angle neutron scattering (SANS) measurements of a dilute (1.0 mg/mL) solution of the macromolecule in THF-*d*₈. The absence of aggregation at this concentration was confirmed by UV/vis spectroscopy. When the SANS data (q range = 0.0054–0.37 Å^{−1}, included in the Supporting Information) are fit with unconstrained, triaxial form factors (elliptical cylinder, triaxial ellipsoid, or parallelepiped), these rigid body models converge to similar lathe-like aspect ratios. The best (minimal χ^2) form factor is an elliptical cylinder with a thickness of 6 Å, minor radius of 36 Å, and major radius of 170 Å.

In conclusion, we have demonstrated the synthesis of a high-molecular weight, soluble, shape-persistent poly(iptycene) using hyperbaric conditions to accelerate the reaction. In addition, we have shown that the internal molecular free volume presented by iptycene groups in the main chain causes **poly-1** to align perpendicular to stretch-aligned PVC, contradicting the aspect ratio model. To our knowledge, this is the first report of two different polymers aligning perpendicular to each other. We envision similar design principles leading to materials with enhanced impact resistance and auxetic properties.¹⁰

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Supporting Information Available: Experimental details for the synthesis and characterization of **poly-1**; description of polarized fluorescence measurements; neutron scattering data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (a) Bahadur, B. *Mol. Cryst. Liq. Cryst.* **1991**, 209, 39. (b) Montali, A.; Bastiaansen, C.; Smith, P.; Weder, C. *Nature* **1998**, 392, 261. (c) Schadt, M. *J. Chem. Phys.* **1979**, 71, 2336. (d) Grell, M.; Bradley, D. D. C. *Adv. Mater.* **1999**, 11, 895.
- (a) Yang, C. Y.; Heeger, A. J.; Cao, Y. *Polymer* **2000**, 41, 4113. (b) Breen, C. A.; Deng, T.; Breiner, T.; Thomas, E. L.; Swager, T. M. *J. Am. Chem. Soc.* **2003**, 125, 9942. (c) Springer, H.; Kussi, J.; Richter, H. J.; Hinrichsen, G. *Colloid Polym. Sci.* **1981**, 259, 911. (d) Springer, H.; Neuert, R.; Muller, F. D.; Hinrichsen, G. *Colloid Polym. Sci.* **1983**, 261, 800. (e) Heilmeyer, G. H.; Castellano, J. A.; Zannoni, L. A. *Mol. Cryst. Liq. Cryst.* **1969**, 8, 293. (f) He, B.; Li, J.; Bo, Z.; Huang, Y. *Macromolecules* **2005**, 38, 6762.
- (a) Percec, V. et al. *Nature* **2004**, 430, 764. (b) Hudson, S. D.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, V. S. K. *Science* **1997**, 278, 449.
- Long, T. M.; Swager, T. M. *Adv. Mater.* **2001**, 13, 601.
- Perepichka, D. F.; Bendikov, M.; Meng, H.; Wudl, F. *J. Am. Chem. Soc.* **2003**, 125, 10190.
- Van Eldik, R.; Hubbard, C. D. *Chemistry Under Extreme or Non-Classical Conditions*; John Wiley and Sons: New York, 1997.
- (a) Wedel, H.; Haase, W. *Chem. Phys. Lett.* **1978**, 55, 96. (b) Craig, D. P.; Hobbins, P. C.; Walsh, J. R. *J. Chem. Phys.* **1954**, 22, 1616.
- (a) Karacan, I.; Bower, D. I.; Ward, I. M. *Polymer* **1994**, 35, 3411. (b) Thulstrup, E. W.; Michl, J.; Eggers, J. H. *J. Phys. Chem.* **1970**, 74, 3868. (c) Michl, J.; Thulstrup, E. W.; Eggers, J. H. *J. Phys. Chem.* **1970**, 74, 3878.
- The polymerization will necessarily create interpolymer steric congestion that can be relieved by a twisting of the polymer into a structure that resembles a helical “lock washer” structure.
- Evans, K. E.; Alderson, A. *Adv. Mater.* **2000**, 12, 617.

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