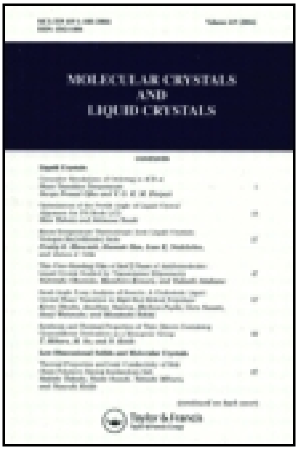


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Investigation of Photo-Responsive Chiral Polyisocyanates

Jie Li [a] , Gary B. Schuster [b] & Mark M. Green [b]

[a] School of Chemistry and Biochemistry, Georgia Institute of Technology Atlanta, GA, 30332-0200

[b] Herman F. Mark Polymer Research Institute Polytechnic University, Six Metrotech Center Brooklyn, NY, 11202

Version of record first published: 24 Sep 2006

To cite this article: Jie Li, Gary B. Schuster & Mark M. Green (2000): Investigation of Photo-Responsive Chiral Polyisocyanates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 344:1, 7-13

To link to this article: http://dx.doi.org/10.1080/10587250008023808

Mol. Cryst. Liq. Cryst., 2000, Vol. 344, pp. 7-13
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Investigation of Photo-Responsive Chiral Polyisocyanates

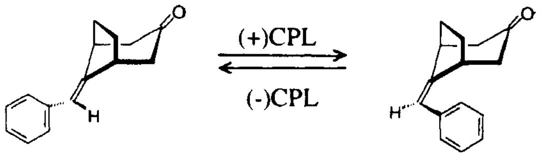
JIE LI[a], GARY B. SCHUSTER[b] and MARK M. GREEN[b]

[a]*School of Chemistry and Biochemistry Georgia Institute of Technology Atlanta, GA 30332–0200 and* [b]*Herman F. Mark Polymer Research Institute Polytechnic University Six Metrotech Center Brooklyn, NY 11202*

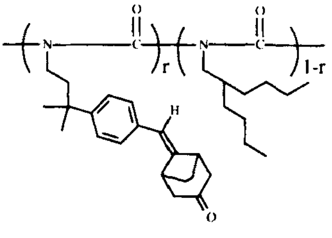
A new class of polyisocyanates incorporating the 8-phenylmethylenebicyclo [3.2.1]octan-3-one chromophore through three different linkage patterns to the polymer backbone was synthesized. Photoresolution and photoracemization experiments were conducted to test its response to circularly polarized light (CPL). Irradiation of the polymers with CPL leads to the partial photoresolution of the bicyclicketone chromophore. This enantiomeric excess causes the polyisocyanate chain to favor one helical sense over the other. The handedness of the polymer chain can be switched with the sense of the circularly polarized light, leading to novel photoresponsive polyisocyanates.

Introduction. Polyisocyanates are an unusual class of macromolecules, since they are one of the few types of synthetic polymers that adopt a stable helical chain conformation in solution as well as in the solid state.[1-3] In the absence of chiral pendants, the polyisocyanate chain exists as a racemate with dynamically interconverting equal populations of P and M helical backbone conformations.[4] However, when a stereogenic center is present in a pendant group, the polymer helices are related as diastereomers with different energy, and the helical sense with the lower free energy will predominate, leading to an optically active polyisocyanate.[5,6] For this case, Green and coworkers have shown that, due to the highly cooperative helix structure of the polyisocyanate, the equilibrium between the M and P helices of the polyisocyanate shows a nonlinear response to the concentration of chiral pendant groups of different types.[7-10] The helical excess of copolyisocyanates formed from a mixture of (*R*)- and (*S*)-enantiomers responds strongly to slight differences in the concentrations of the enantiomers and the net helical sense is controlled by the enantiomer that is in the majority.[11] More recently, it was shown that terpolyisocyanates composed of as little as 1.6 % of a chiral unit with only a 2.8 % enantiomeric excess and 98.4 % of achiral units shows a strong preference for one helix sense of the polymer, resulting in a striking amplification of the chiral information of the chiral pendant group.[12] The helical excess can be detected by circular dichroism (CD) spectroscopy in the absorption range of the polymer's amide backbone (ca. 255 nm).[13] The magnitude of the induced optical activity of the polyisocyanates is interpreted by statistical physics based on the one-dimensional Ising model,[14-17] which offers insight on the control of chiral amplification.

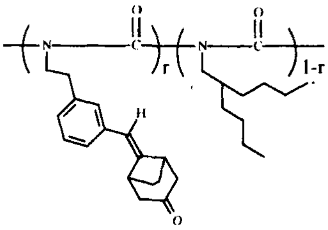
The potential of using CPL to switch between binary states of organic photochromic material has been recognized previously.[18,19] This goal requires the reversible photoresolution and photoracemization of a chiral



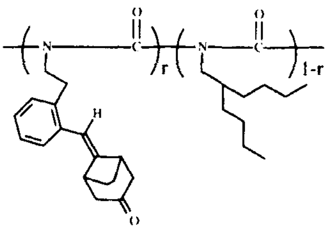
photochromic compound in a photochemical reaction. The excited state of the photochromic compound causes interconversion between the R and S enantiomers. Due to the different absorption of these enantiomers with CPL, a photostationary state develops with the enantiomer having the smaller absorption predominating. The enantiomeric excess at photostationary state (γ_{pss}) of the chiral photochromic compound is determined by the Kuhn anisotropy factor[20,21] ($g_\lambda = \Delta\varepsilon/\varepsilon$), according to: $\gamma_{pss} = \frac{1}{2} g_\lambda$. Unfortunately, the enantiomeric excess at the photostationary state for most organic photochromic compounds is ca. 10^{-4}.[22-24] Chemists have been trying to improve the enantiomeric excess from photoresolution by designing photoresolvable compounds with unique structures.[25-28] Schuster and coworkers discovered a new photochromic compound, axially chiral bicyclo[3.2.1]octan-3-one, **1**, which can be photoresolved to ca. 1.5% enantiomeric excess upon irradiation with CPL.[29]



para-terpolymer (r = 0.06)
Mw = 226,000



meta-copolymer (r = 1) Mw = 27, 000
meta-terpolymer (r = 0.02) Mw = 623, 000



ortho-copolymer (r = 1) Mw = 16, 000
ortho-terpolymer (r = 0.02) Mw = 405, 000

The discovery of the stereochemical amplification of polyisocyanates and the development of photoresolvable ketone **1** presents an opportunity for the generation of novel photoresponsive chiral polyisocyanates by the incorporation of the photoresolvable bicyclo[3.2.1]octan-3-one moiety into a polyisocyanate. This must be accomplished without the sacrifice of the required photochemical properties of the chromophore. Such systems may be of interest for optical data storage.[31-34,35]

Results. Three types of polyisocyanates were synthesized having the bicyclo[3.2.1]octan-3-one moiety incorporated through different linkage patterns to the polymer backbone (Chart 1). The chiroptical properties of the polymers were investigated to learn the effect of the chiral bicyclicketone pendants on the polymer chain conformations.

Polymerization of the isocyanate monomers followed Shashoua's method[36,37] using NaCN as the initiator. The molecular weights of the polymers were determined by gel permeation chromatography (GPC). The compositions of the terpolymers were determined by ^{1}H NMR spectroscopy.

The photoresolution of the bicyclicketone pendants on the polyisocyanate was accomplished by exposing N_2-saturated solutions of the polymers to circularly polarized light. CPL having wavelength >300 nm was generated by passing the light from a 1000W Hg (Xe) lamp through a cutoff filter, a Glan-Taylor linear polarizer, and a Fresnel rhomb. CD spectra in the amide backbone absorption region (ca. 255 nm)[13] were used to detect the shift in equilibrium between the M and P helices of the polyisocyanate chain caused by the photoresolution.

The *meta* and *ortho*-terpolymers show a CD signal around 255 nm region while the *para*-terpolymer does not have a measurable CD spectrum after irradiation with CPL. The appearance of a CD band in the *meta*-terpolymer and *ortho*-terpolymers indicates the successful chirality transfer from bicyclicketone pendants to the polymer main chain, leading to one hand of the helix dominating the other. It is interesting to observe that the sign of the CD for the *meta*-terpolymer is opposite to that of the *ortho*-terpolymer although both polymers were irradiated with the same circularly polarized light. The opposite CD sign of *meta*-terpolymer and *ortho*-terpolymer indicates an opposite twisting sense of the polymer chains.

The *meta*-terpolymer was employed to test the photo-switching of the helical sense of the polymer with circularly polarized light. Rotation of the linear polarizer by 90° converts (+)CPL to (-)CPL. Racemic *meta*-terpolymer in an *n*-hexane solution was irradiated with (+)CPL and (-)CPL alternatively, and the reaction was followed by CD spectroscopy.

The samples show a mirror image relationship in their CD spectra demonstrating that the *meta*-terpolymer is capable of being switched. The helical sense of the polymer chain changes with the handedness of the circularly polarized light. Furthermore, irradiation of this solution with unpolarized light racemizes the ketone and causes the polymer to return to its racemic state. Similar results were observed for the *meta*, and *ortho*-copolymers and the *ortho*-terpolymer.

Discussion. Previous studies by Green and coworkers showed that a predominant helix sense in polyisocyanates can be detected by CD measurements in the polymer main chain absorption region at ca. 255 nm.[7,9,10] However, a complication might arise in the systems studied here. The appearance of the CD signal at ca. 255 nm in the sample may not represent that of the polymer's amide backbone since the absorption of the backbone overlaps with the absorption of bicyclicketone monomer. Thus, the CD signal at ca. 255 nm of the irradiated polymer might be due to the bicyclicketone pendants or the polymer backbone.

The oppositely signed CD spectra observed for the *meta*-terpolymer and *ortho*-terpolymers after irradiation with the same CPL sense shows that the CD signal at 255 nm come from the polymer backbone. The sign of the

CD spectrum of the bicyclicketone pendants generated from irradiation with the same handed CPL will be the same.

Chirality transfer from the bicyclicketone chromophore to the polymer backbone. The transfer of chirality from the bicyclicketone pendants to the polymer backbone is determined by the diastereomer free energy difference between (M-helix + *R*-pendant) and (P-helix + *R*-pendant) interactions.[14-17] This free energy difference is highly dependent upon the distance between the chiral pendants and polymer backbone. One can expect that with a large distance between the bicyclicketone chromophore and the polymer backbone (i.e. the *para*-polymer case) the bicyclicketone chromophore chirality will be independent of any interaction with the polymer backbone, leading to a zero free energy difference of the diastereomers.

Conclusion. Chiral bicyclicketone chromophores have been successfully incorporated into the polyisocyanate system through different linkage pattern to build novel photoresponsive polymers. Photoresolution of the bicyclicketone chromophore in the polymer by circular polarized light has been achieved. The chirality transfer from the chiral bicyclicketone pendants to the polymer backbone is found dependent upon the distance between the chiral pendants and the polymer main chain. Upon irradiation of the polymers having as little as 2% of *ortho*-linked or *meta*-linked bicyclicketone pendants with circularly polarized light, the small enantiomeric excess that results in the ketone is able to induce one helix sense in the polymer. The handedness of the helical polyisocyanate with *ortho*- or *meta*-linked bicyclicketone pendants is switchable with the sense of the circularly polarized light. The *ortho*-linked bicyclicketone pendants in the terpolymer system are found to have an opposite helical preference than the *meta*-linked system. Irradiation of the photoresolved polymer with the unpolarized light results in the racemization of the bicyclicketone group, returning the helical polymer to its racemic state.

Acknowledgement: This work was supported by the grants from the National Science Foundation, the Office of Naval Research and Molecular Design Institute, for which we are grateful.

References

[1] Shmueli, U.; Traub, W.; Rosenjeck, K. *J. Polym., Part A-2* **1969,** *7,* 515.

[2] Troxell, T. C.; Scheraga, H. A. *Macromolecules* **1971,** *4,* 528.

[3] Itou, T.; Chikiri, H.; Teramoto, A.; Aharoni, S. M. *Polymer J. (Tokyo)* **1988,** *20,* 143.

[4] Tonelli, A. *Macromolecules* **1974,** *7,* 628.

[5] Goodman, M.; Chen, S. *Macromolecules* **1970,** *3,* 398.

[6] Goodman, M.; Chen, S. *Macromolecules* **1971,** *4,* 625.

[7] Green, M. M.; Andreola, C.; Munoz, B.; Reidy, M. P.; Zero, K. *J. Am. Chem. Soc.* **1988,** *110,* 4063.

[8] Lifson, S.; Andreola, C.; Peterson, N. C.; Green, M. M. *J. Am. Chem. Soc.* **1989,** *111,* 8850.

[9] Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Willson, G. *J. Am. Chem. Soc.* **1989,** *111,* 6452.

[10] Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cooks, R. G.; Lifson, S. *Science* **1995,** *268,* 1860.

[11] Green, M. M.; Garetz, B. A.; Munoz, B.; Chang, H.; Hoke, S.; Cooks, R. G. *J. Am. Chem. Soc.* **1995,** *117,* 4181.

[12] Green, M. M.; Selinger, J. V.; Jha, S. K.; Cheon, K.-S. *J. Am. Chem. Soc.* **1999,** *121,* 1665.

[13] Deutsche, C. W.; Lightner, D. A.; Woody, R. W.; Moscowitz, A. *Ann. Rev. Phys. Chem.* **1969,** *20,* 407.

[14] Selinger, J. V.; Selinger, R. L. B. *Phys. Rev. Lett.* **1996**, *58,* 76.

[15] Selinger, J. V.; Selinger, R. L. B. *Mol. Cryst. Liq. Cryst.* **1996**, *33*, 288.

[16] Selinger, J. V.; Selinger, R. L. B. *Phys. Rev. E* **1997**, *55(2),* 1728.

[17] Selinger, J. V.; Selinger, R. L. B. *Macromolecules* **1998,** *31,* 2488.

[18] Stevenson, K. L.; Verdieck, J. F. *J. Am. Chem. Soc.* **1968,** *90,* 2974.

[19] Stevenson, K. L.; Verdieck, J. F. *Mol. Photochem* **1969,** *1,* 271.

[20] Kuhn, W.; Knopf, E. Z. *Phys. Chem.* **1930,** *7,* 292.

[21] Kuhn, W. *Naturwissenschaften* **1930,** *18,* 183.

[22] Buchardt, O. *Angew. Chem. Int. Ed. Engl.* **1974,** *13,* 179.

[23] Rau, H. *Chem. Rev.* **1983,** *83,* 535.

[24] Inoue, Y. *Chem. Rev.* **1992,** *92,* 741.

[25] Feringa, B. L.; Huck, N. P. M.; Jager, W. F.; de Lange, B. *Science* **1996,** *273,* 1686.

[26] Feringa, B. L.; Huck, N. P. M.; Schoevaars, A. M. *Adv. Mater.* **1996,** *8,* 681.

[27] Zhang, M.; Schuster, G. *B. J. Am. Chem. Soc.* **1994,** *116,* 4852.

[28] Zhang, Y.; Schuster, G. B. *J. Org. Chem.* **1994,** *59,* 1855.

[29] Zhang, Y.; Schuster, G. B. *J. Org. Chem.* **1995,** *60,* 7192.

[30] Turro, N. J. *Modern Molecular Photochemistry* **1978.**

[31] Eigler, D. M.; Lutz, C. P.; Rudge, W. E. *Nature* **1991,** *352,* 600.

[32] Ball, P.; Garwin, L. *Nature* **1992,** *355,* 761.

[33] Feringa, B. L.; Jager, W. F.; de Lange, B. *Tetrahedron* **1993,** *49,* 8267.

[34] Burnham, K.; Schuster, G. B. *J. Am. Chem. Soc.* **(submitted).**

[35] Green, M. M.; Selinger, J. V. *Science* **1998,** *282,* 880–881.

[36] Shashoua, V. E. *J. Am. Chem. Soc.* **1959,** *81,* 3156.

[37] Shashoua, V. E.; Sweeney, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960,** *82,* 866.