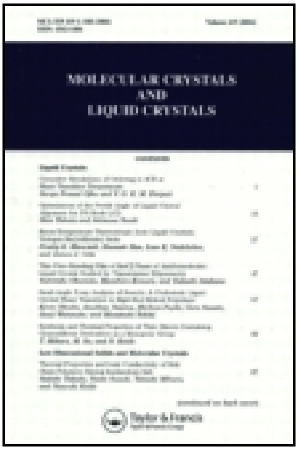


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Designed 2-Substituted Butadiene Structures

Brian Dinkelmeyer [a], Joseph W. Lauher [a] & Frank W. Fowler [a]

[a] Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY, 11794

To cite this article: Brian Dinkelmeyer, Joseph W. Lauher & Frank W. Fowler (1998): Designed 2-Substituted Butadiene Structures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 313:1, 259-264

To link to this article: http://dx.doi.org/10.1080/10587259808044285

Mol. Cryst. Liq. Cryst., 1998, Vol. 313, pp. 259–264
Reprints available directly from the publisher
Photocopying permitted by license only

Designed 2-Substituted Butadiene Structures

Brian Dinkelmeyer, Joseph W. Lauher, and Frank W. Fowler, Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY, 11794.

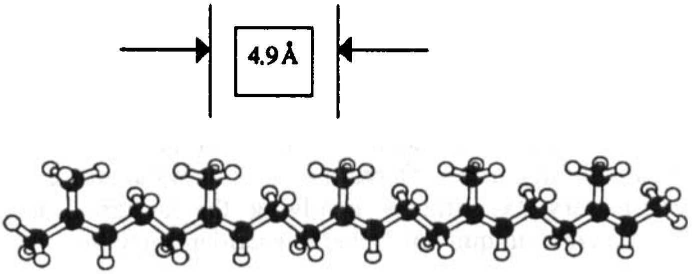
When 1,3-butadienes are irradiated in the solid state they may undergo [2+2] cycloadditions or 1-4 polymerizations with neighboring molecules. In order to control the reaction topochemically of it is essential to bring the desired reactive centers into close contact at a distance and orientation suitable for the desired reaction. A series of 2-substituted butadienes that contain the oxalamide functionality have been designed. Oxalamides are known to form one dimensional hydrogen bonded networks with a repeat distance similar to the intermolecular distance needed for a butadiene polymerization. We anticipate that the diene functionalities will be able to rotate freely around the 2-substituted center, thus allowing a 1-4 polymerization to proceed without a major interruption of the crystal lattice. The results of preliminary experiments involving the designed topochemical preparation of a unique polybutadiene ladder polymer are described.

Keywords: butadiene; ladder polymer; topochemical polymerization

INTRODUCTION

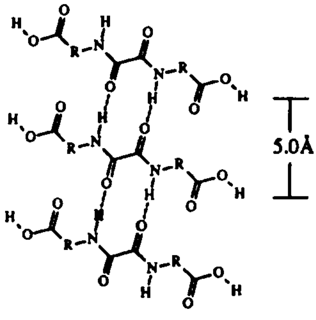
There are many examples of solid state reactions involving 1,3-butadienes in the literature. When irradiated these compounds may undergo [2+2] cyclizations[1], or 1-4 polymerizations with neighboring molecules via a radical mediated process[2]. The topochemical 1-4 polymerization of terminally substituted butadienes has been found to occur in perovskite type layered structures[1], in mono and multilayers[3] and in inclusion compounds[4]. In order to achieve a 1-4 butadiene polymerization by design, control of the topochemistry of the reaction is essential. The desired C1 and C4 reactive centers must be brought into close contact at a distance and orientation suitable for the desired reaction. Ideal systems should also be capable of maintaining their structural integrity during the polymerization process. This last property is essential if topochemical control is to be maintained at high conversion.

The most important polybutadienes are isoprene polymers. An examination of an ideal isoprene polymer reveals that the polymer substituents are about 4.9Å apart. For a topochemical reaction, the butadiene monomers must be in a transoid configuration, spaced at this 4.9Å distance with the C1 and C4 carbon atoms of adjacent molecules in van der Waals contact.



We wish to report the design and preparation of a new series of compounds that may fulfill these requirements for a topochemical butadiene polymerization.

Oxalamide Hydrogen Bonded Structures



Oxalamide dicarboxylic acids form persistent and predictable hydrogen bonded structures[5]. In the solid state the molecules have a characteristic repeat distance between hydrogen bonded neighbors of approximately 5.0Å[5]. It should be possible to prepare ester derivatives of these dicarboxylic acids using the alcohol, 2-(hydrox-ymethyl) 1,3-butadiene.[6] The diester products produced would be expected to self assemble in the solid state with intramolecular distances similar to those necessary for a topochemical polymerization. The resulting polymers would be unique butadiene ladder polymers, Fig. 1.

As mentioned previously, topochemical control may be lost due to the lattice distortions that accompanies polymerization. Our strategy is to minimize these distortions that occur during topochemical reactions by using 2-substituted dienes. The 2-substituent gives the diene monomers a 'pivot' point on which they can rotate. This point of rotation should allow diene monomers to span the distances between nearest neighbors and may minimize the contraction often associated with topochemical processes.

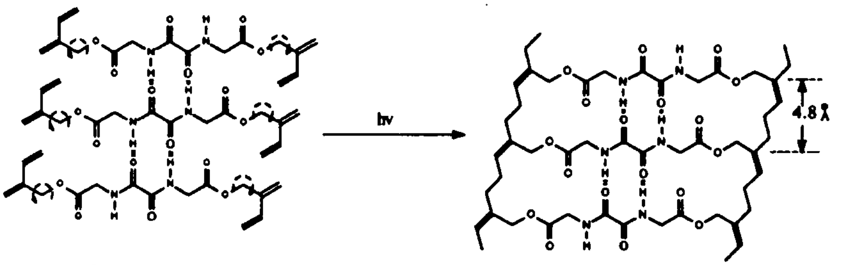
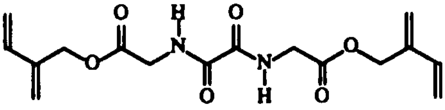


FIGURE 1. The designed topochemical reaction.

Initial Results

The first member of the proposed series, the 2-(hydroxymethyl) 1,3-butadiene[6] diester of the oxalamide of glycine,[7] 1, was prepared. Recrystallization of the compound from methanol/ethylacetate mixtures produced clear thin elongated plates. The crystal quality was poor, but a limited X-ray data set sufficient for single crystal analysis was obtained.[8] As expected the crystallagraphic unit cell has a short b axis of 4.764(2)Å, however, the predicted hydrogen bonded network shown in Fig. 1 was not found. A complex two-dimensional network of hydrogen bonds was formed instead. Fortuitously, even in the absence of the expected hydrogen bond network, neighboring 2-substituted butadienes were at a distance, (4.764(2)Å,) amenable to the 1-4 polymerization (Fig 2). The closest contact between C1 and C4 centers of neighboring monomers was 3.84Å.



1

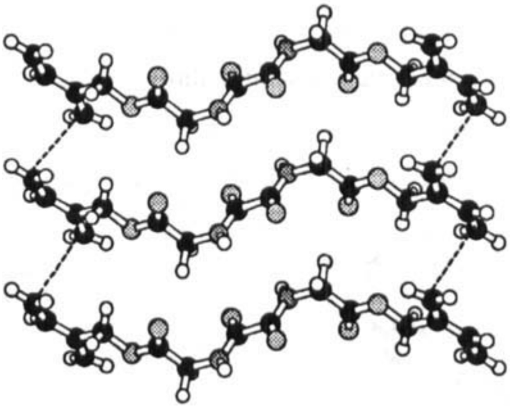


FIGURE 2 Xray crystal structure of 1. The C1 and C4 atoms connected by dotted lines are 3.84 Å apart.

Polymerization was induced by irradiating the crystals with a broad band µV lamp and followed by IR spectroscopy. The polymerization of the 2-substituted butadiene functionality is indicated by the appearance of a characteristic IR band at 840-790 cm^{-1} corresponding to a trisubstituted C=C wagging mode. A sample irradiated for 17.5 hours produced crystals with a strong peak at 803 cm^{-1}: the IR signature expected for the polymerized product (Fig 3). These crystals exhibit polarization when viewed on a light microscope and showed no apparent morphological differences from the non-irradiated crystals. Single crystal X-ray analysis was unsuccessful indicating that disruption of the crystal lattice had occurred. Prior to irradiation the compound is highly soluble in common organic solvents. After irradiation the crystals lost this solubility and did not dissolve even in hot DMSO, instead the crystals deformed and took on a 'wavy' appearance. Interestingly, the sample that underwent this hot DMSO treatment still exhibited polarization when viewed with a light microscope. It appears, from this initial study, that a topochemical polymerization of compound 1 has taken place.

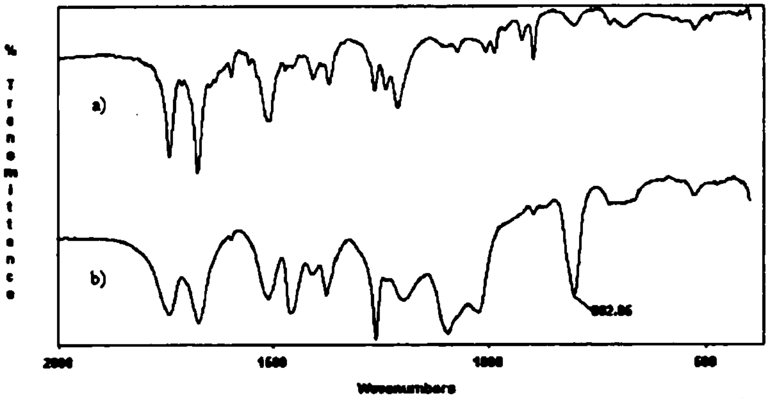


FIGURE 3 a) Infrared spectrum of a non-irradiated sample. b) similar sample after 17.5 hours of UV irradiation.

Conclusion

Our initial studies of oxalamide butadiene derivatives have been successful. Preliminary results indicate that a topochemical polymerization reaction has occurred. The spacing and orientation of 2-substituted butadienes in the solid state is a viable strategy for inducing a 1-4 topochemical polymerization. Synthesis of additional members of the series and further study in this area is currently under way.

Acknowledgements

This research is supported by the National Science Foundation under Grant No. CHE-9630042.

References

1. M. Lahav , G. M. J. Schmidt, J. Chem. Soc. B, 312 (1967); B. S. Green, M. Lahav, G. M. J. Schmidt, J. Chem. Soc. B, 11552 (1971).
2. B. Tieke, J. Polym. Sci. Polym. Chem. Ed., **22**, 2895 (1984).
3. B. Tieke, Adv.Polym.Sci., **71**, 79 (1985).
4. M. Farina, G. D. Silvestro, P. Sozzani, ACS. Symp. Ser., **337**, 79 (1987).
5. S. Coe, J. Kane, T. L. Nyguen, L. M. Toledo, E. Winiger, F. W. Fowler, J. W. Lauher, J. Am. Chem. Soc., **119**, 86 (1997).
6. R. G. Riley, R. M. Silverstein, J. Org. Chem, **39**, 1957 (1974).
7. General procedure: 1.0 eqv. of the oxalamide dicarboxylic acid, 0.3 eqv. DMAP, and 3.0 eqv. Of 1-(3-dimethylaminopropyl) 3-ethyl carbodimide hydrochloride were stirred in dry DMF under nitrogen for 15 minutes. 3.0 eqv of 2-(hydroxymethyl) 1,3-butadiene are syringed into the reaction mixture. After stirring at ambient temperature overnight water was added and the product extracted into ethylacetate. The crystalline product never melts, but decomposes above 170 °C.
8. Crystal data for 1: a = 12.777(7)Å, b = 4.764(2)Å, c = 15.66(1)Å, β = 111.25(4)°, monoclinic, $P2_1/a$, Z = 4, R = .078, R_w = .084 for 249 independent reflections. Data refinement was carried out using an isotropic model for all nonhydrogen atoms.