Review

Extended Chain Lamellae Self-Assembled in Liquid Crystal Phase of Soluble Polydiacetylenes through Chain Segregation

Wei Wang

Institute of Materials Research and Engineering, 3 Research Link, National University of Singapore, Singapore 117602

Dedicated to Professor Dr. Gerhard Wegner, Max-Planck-Institute for Polymer Research, Germany, together with my wishes on the occasion of his 60th birthday.

Received January 10, 2000; revised January 31, 2000; accepted March 4, 2000

Abstract: This review article highlights our efforts in the past years toward a fundamental understanding of the supramolecular structures of a soluble but rigid polydiacetylene. In our earlier works we presented evidence to indicate that this polymer formed a lyotropic phase in solutions. TEM, AFM and SEM observations on solidified thin films showed an extended chain lamellar structure which is surmised to be self-assembled in the lyotropic phase through chain segregation. Our results revealed that the supramolecular structures formed are closely associated with the structures formed in the lyotropic state. Due to three attributes of rigid macromolecules at the molecular level—high molecular weight, broad molecular weight distribution, and worm-like chain conformation, the supramolecular structures observed are also greatly different from those of conventional nematics or smectics.

Keywords: Soluble Polydiacetylene, Lyotropic liquid crystals, Extended chain lamellae, Chain segregation, Defect core structure, Frank elastic constant anisotropy.

Introduction

Rigid or semi-rigid macromolecules usually include a conjugated π-backbone that endows the molecules with some very interesting properties, such as electrical conductivity, optical non-linearity and electroluminescence. These properties have been systematically reviewed in ref. [1]. Over the past two decades many rigid macromolecules, particularly those that are soluble in conventional organic solvents, have been successfully synthesized and their properties have been intensively investigated [1]. The success in improving the solubility of rigid macromolecules has led to a revolution in fabricating products from solutions. Therefore, it is important to have a fundamental understanding of these structures, especially those at a length scale larger than a molecular length which are self-assembled from solutions, to establish a correlation between process, structure, and properties. In this review article we highlight our efforts on the supramolecular structures visualized from the thin films of some soluble but rigid polydiacetylenes solidified from their lyotropic phase. We will present evidence gained by using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) to demonstrate the formation of extended chain (EC) lamellae by these rigid macromolecules and further discuss the formation of EC lamellae in terms of chain segregation. Chain segregation refers to a selective arrangement of the rigid macromolecules with respect to chain length. The results obtained in solidified samples and presented in this article provide us with a chance to have a fundamental understanding of the formation and development of structures and morpholo-

*To whom all correspondence should be addressed.
Tel: 65-874-8346; Fax: 65-872-0785
E-mail: wei-wang@imre.org.sg

J. Polym. Res. is covered in ISI (CD, D, MS, Q, RC, S). CA, EL, and Polymer Contents.
Chemical structures and liquid crystal behavior

Polydiacetylenes are synthesized by solid-state or topochemical polymerization from diacetylene monomer single crystals [2], giving rise to macromolecules with a conjugated π-backbone consisting of a sequence of double, single and triple bonds, as illustrated in Scheme 1. Extensive delocalization of the π-electrons along the backbone results in a rigid backbone and also provides interesting optical properties [3]. Normally, most polydiacetylenes are insoluble, but the poly{5,7-dodecadiyne-1,12-diol bis[(4-butoxy carbonyl)methyl]urethane} (P-4BCMU) used in our studies forms good solutions in some conventional organic solvents, such as chloroform and tetrahydrofuran [4], owing to its long side substituents as shown in Scheme 1.

Soluble polydiacetylenes usually exhibit a worm-like chain conformation in solution [5]. When the polymer concentration gradually rises to a critical concentration, rigid polydiacetylene molecules will self-assemble into an ordered state, namely, a lyotropic liquid crystal (LC) phase. This phenomenon has been systematically studied [6] and clear-cut evidence obtained by polarized light microscopy (PLM) from a concentrated solution of P-4BCMU in chloroform is demonstrated in Figure 1. At first glance the image shows a typical Schlieren texture of nematics [7]. When the sample solidifies slowly by strictly controlling the evaporation of the solvent, the liquid crystal texture can be "frozen" and then preserved in the solidified samples, as evidenced by Figure 2. The structures formed in the lyotropic state can further be investigated by studying the solidified samples.

Extended chain lamellae

The LC feature of such macromolecules naturally enables us to expect that structures of rigid macromolecules in a solid state will be highly dependent on the structures well developed in the LC phase. During the early stage of studying the LC behavior of rigid macromolecules, Flory assumed that the LC phase formed should possess a nematic feature simply due to a consideration of the most important feature of polymers- molecular length distribution [8]. In liquid crystal physics, the term of nematics describes an LC state of rigid molecules that has no long-range order but contains some orientational order: all molecules tend to be parallel to some common axis microscopically and they will smoothly change their directors macroscopically [7,9]. Therefore, the nematic feature seems to further imply that there is no special supramolecular structure which can form in the LC phase of rigid macromolecule solutions.

However, our TEM [6,10-15], AFM [16] and SEM [16] observations have shown a lamellar struc-