Available online at www.sciencedirect.com
ScienceDirect
Prog. Polym. Sci. 33 (2008) 346–364
PROGRESS IN POLYMER SCIENCE
www.elsevier.com/locate/ppolysci

Cyclophane-containing polymers

Y. Morisaki, Y. Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Received 22 May 2007; received in revised form 8 November 2007; accepted 8 November 2007
Available online 19 November 2007

Abstract

In spite of the remarkable progress of cyclophane chemistry, syntheses of polymers containing cyclophane units in the main chain and side chain by utilizing the transannular π–π interaction are considerably limited. In this review, syntheses, properties, and applications of [m,n]cyclophanes-containing ($m \leqslant 3$ and $n \leqslant 3$) polymers prepared to date are presented. The main body of the review is classified into broadly four categories: introduction of (i) main-chain-type cyclophane-containing polymers, (ii) side-chain-type cyclophane-containing polymers, (iii) rigid-rod conjugated polymers containing pendent aromatic rings, and finally (iv) aromatic-ring-layered polymers comprising [2.2]paracyclophane.

Keywords: Cyclophane; Through-space interaction; Pendent aromatic rings; Aromatic-ring-layered polymers

Contents

1. Introduction

In the field of organic chemistry, cyclophane compounds, particularly those comprising intramolecular face-to-face-oriented π-conjugated systems,

*Corresponding author. Tel.: +81 75 383 2604; fax: +81 75 383 2605.
E-mail address: chujo@chujo.synchem.kyoto-u.ac.jp (Y. Chujo).

0079-6700/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.progpolymsci.2007.11.003

have been extensively studied [1–3]. Among these, [m,n]paracyclophanes and [m,n]metacyclophanes possess structures in which there are electronic interactions between rings (Fig. 1). For example, the benzene rings of [2.2]paracyclophane are rigidly held with two ethylene chains at the *para* positions, and the distance between the bridging carbon atoms and the centers of the two benzene rings is approximately 2.8 and 3.1 Å (Fig. 1A). This class of cyclophanes has been central to the study of cyclophane chemistry since the first synthesis of [2.2]paracyclophane [4]. A number of cyclophane compounds have been prepared to date, and their unique structural, optical, and electronic properties resulting from characteristic π–π interactions between the two co-facial π-electron systems have been investigated in detail [1–7].

Cyclophanes have optically, electrically, and topologically intriguing features [1–3]. The addition of cyclophane compounds in polymer main chains as well as polymer side chains as pendent groups can lead to potential applications of the resulting polymers. However, there have been few studies on [m,n]cyclophane-containing (particularly $m \leqslant 3$ and $n \leqslant 3$) polymers in spite of the remarkable progress made in the field of cyclophane chemistry.

This review presents a summary of the syntheses, properties, and applications of cyclophane-containing polymers, which include not only main-chain-type cyclophane-containing polymers but also polymers possessing cyclophane units in the side chains. The review is limited to polymers possessing small [m,n]cyclophanes ($m \leqslant 3$ and $n \leqslant 3$). The first half of the review focuses on main-chain-type [m,n]cyclophane-containing polymers. This is followed by a description of the syntheses and applications of side-chain-type cyclophane-containing polymers and rigid-rod conjugated polymers containing pendent aromatic rings. Finally, aromatic-ring-layered polymers comprising [2.2]paracyclophane and xanthene moieties are also briefly introduced.

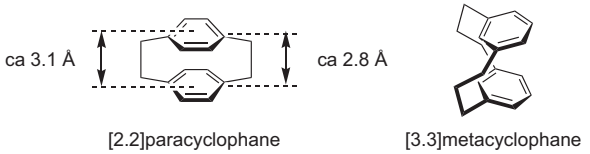

Fig. 1. Representative cyclophane compounds.

2. Main-chain-type cyclophane-containing polymers

2.1. [2.2]*Metacyclophane-containing conjugated polymers*

The first examples of cyclophane-containing conjugated polymers were reported by Mizogami and Yoshimura [8,9]. The oxidative coupling reaction of 8,16-dihydroxy[2.2]metacyclophane **1** yielded polymer **2**, which had repeating diphenoquinone moieties, as shown in Scheme 1 [8]. In addition, Scheme 1 also shows the polycondensation reaction of oxidative dimer **3** that yields poly[2.2]metacyclophane **4** [9]. These polymers were characterized by using IR spectra and elemental analysis, and they exhibited an enhancement in conductivity when they were chemically doped. For example, the electrical conductivity of poly[2.2]metacyclophane **4** increased from 10^{-9} to $10^{-1}\,S\,cm^{-1}$ when doped with H_2SO_4 vapor [9].

However, in the recent past, considerably less attention has been paid to the syntheses of conjugated polymers containing [m,n]cyclophanes ($m \leqslant 3$ and $n \leqslant 3$) in the main chain, in spite of the considerable importance of the π–π interaction in conjugated polymer backbones.

2.2. [2.2]*Paracyclophane-containing conjugated polymers*

Polymers with extended conjugation containing [2.2]paracyclophane were reported in the 2000s. The electrochemical polymerization of oligothienyl-substituted [2.2]paracyclophanes was performed independently by two research groups [10–13]. Guyard and Audebert synthesized the first [2.2]paracyclophane-containing conjugated polymer **6** by electrochemical polymerization of dithiophene-substituted [2.2]paracyclophane **5**, as shown in Scheme 2 [10]. Thiophene rings were oxidized electrochemically by cyclic voltammetry, and the film of the corresponding polymer **6** was formed on the electrode surface. Polymers **7**–**10** (Fig. 2) were obtained by this method [10–13]. Polymer **10** could be obtained by chemical oxidation polymerization by using $FeCl_3$ in $CHCl_3$ as well as electrochemical oxidation polymerization [13]. This polymer was soluble in organic solvents such as hexane and $CHCl_3$, and the weight-average molecular weight (M_w) of the $CHCl_3$-soluble part of **10** could be estimated as 50,000 by gel permeation chromatography (GPC).