

Physical Properties of Polymers Handbook

Second Edition

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Second Edition

Edited by

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Library of Congress Control Number: 2005938500

ISBN-13: 978-0-387-31235-4 eISBN-13: 978-0-387-69002-5
ISBN-10: 0-387-31235-8 eISBN-10: 0-387-69002-6

Printed on acid-free paper.

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Preface to the Second Edition

As before, the goal of this handbook is to provide concise information on the properties of polymeric materials, particularly those most relevant to the areas of physical chemistry and chemical physics. The hope is that it will simplify some of the problems of finding useful information on polymer properties.

All of the chapters of the first edition were updated and 11 entirely new chapters added. Four of them focus on novel polymeric structures, specifically dendrimers, polyrotaxanes, foldamers, and supramolecular polymers in general. Another group of chapters covers reinforcing phases in polymers, including carbon black, silica, clays, polyhedral oligomeric silsesquioxanes (POSS), carbon nanotubes, and relevant theories. The final new chapter describes experiments on single polymer chains.

It is a pleasure to acknowledge with gratitude the encouragement, support, and technical assistance provided by Springer, particularly David Packer, Lee Lubarsky, Felix Portnoy, and, earlier, Hans Koelsch. The editor also wishes to thank his wife Helen for the type of understanding and support that helps get one through book projects of this complexity.

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December 2006

Preface to the First Edition

This handbook offers concise information on the properties of polymeric materials, particularly those most relevant to the areas of physical chemistry and chemical physics. It thus emphasizes those properties of greatest utility to polymer chemists, physicists, and engineers interested in characterizing such materials. With this emphasis, the more synthetic-organic topics such as the polymerization process and the chemical modification of polymers were considered beyond its scope.

The contributors to this handbook have endeavored to be highly selective, choosing and documenting those results considered to have the highest relevance and reliability. There was thus no attempt to be exhaustive and comprehensive. The careful selection of the results included, however, suggests it should nonetheless provide the great majority of topics and data on polymer properties likely to be sought by members of the polymer community. Extensive indexing should facilitate locating the desired information, and it is hoped that the modest size of the handbook will give it considerable portability and wide availability.

Every attempt has been made to include modern topics not covered in a convenient handbook format elsewhere, such as scaling and fractal dimensions, computational parameters, rotational isomeric state models, liquid-crystalline polymers, medical applications, biodegradability, surface and interfacial properties, microlithography, supercritical fluids, pyrolyzability, electrical conductivity, nonlinear optical properties, and electroluminescence.

All contributions to this volume were extensively reviewed by a minimum of two referees, to insure articles of the highest quality and relevance. Many of the reviewers were chosen from the Editorial Board of the *AIP Series in Polymers and Complex Materials*, of which this handbook is a part. Their important contributions are gratefully acknowledged, as are those of the Editors-in-Chief of the Series, Ronald Larson and Philip A. Pincus. One Editorial Board member, Robert E. Cohen, deserves special acknowledgment and sincere thanks. He not only originated the idea of doing a handbook of this type, but also contributed tremendously to its realization. Charles H. Doering and Maria Taylor (and earlier, Zvi Ruder) also provided unflinching support and encouragement in this project. It has been a distinct pleasure working with them and other members of the AIP Press: K. Okun, K. S. Kleinstiver, M. Star, and C. Blaut. The editor also wishes to thank his wife Helen for the type of understanding and support that is not always easy to put into words.

Both the editor and contributors to this volume would feel well rewarded if this handbook helps relieve some of the problems of finding useful information on polymer properties in the ever-growing scientific literature.

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November 1995

PART I

Structure

CHAPTER 1

Chain Structures

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1.1 INTRODUCTION

It is known that the physical properties of a polymer depend not only on the type of monomer(s) comprising it, but also on the secondary and tertiary structures, i.e., the stereochemistry of the linkage, the chain length and its distribution, its ability to crystallize or remain amorphous under various conditions, and the shape or distribution of the shapes of the chain in the crystalline and amorphous states. Through advances in polymer chemistry, in most cases polymers can be designed with specific properties. Control of the microstructure, e.g., the tacticity and molecular weight distribution of vinyl polymers, has been the focus of a number of papers in the last two decades.

In most applications, a polymer, once designed as a product, has to be stable and maintain its structure and morphology under various temperatures and other environmental conditions during the lifetime of the product. However, the recent interest is also in changing the shape or morphology of the molecule instantaneously and reversibly, without any memory or hysteresis effects, with electrical, optical or mechanical stimulus. These "smart" materials are aimed towards such applications as information processing, storage, and retrieval, and molecular recognition similar to the biological systems. Synthetic efforts on *in situ* devices such as the photonic molecular wire, electronic molecular wire,

and molecular shuttle have been the focus of several research groups (see below). The intent is to acquire the ability to control the material at the atomic/molecular level, i.e., on the nano scale [1–5].

This chapter gives an overview of the literature on microstructures, "photonic" polymers, fullerene-based polymers, cyclics, rotaxanes, and dendrimers. The properties of polymers with other architectures and morphologies are discussed in various other chapters of this handbook.

Please note that in this chapter, in the previous edition of this handbook, we had listed examples from published articles in Tables 1.1–1.8. Most of the topics discussed at that time were new and emerging. Since that time, publications in each of these topics have been numerous and cannot be accommodated within the scope and size of this chapter. The original tables are kept, however, since these include the initial work in these areas.

1.2 MICROSTRUCTURE

Since the stereospecific polymerization of polyolefins pioneered by Natta, an extensive literature has developed in the synthesis, characterization, and utilization of polymers of defined microstructure. Although x ray diffraction could confirm the existence or absence of regular

microstructure, and infrared spectroscopy could be used to estimate the isotactic or syndiotactic content of a polymer, it was not until the development of NMR spectroscopy for microstructure analysis that the isotactic, syndiotactic, or atactic perpetuation extending to pentads and hexads could be determined quantitatively and accurately. This is dealt with in detail in the chapter by Tonelli in this handbook.

A schematic for defining the tacticity of vinyl polymers of the type $[(CH_2)-(CHR)]_n$ is shown in Fig. 1.1. If, as shown in Fig. 1.1(a), the skeletal bonds are in the *trans* conformation and lie in the plane of the paper, the *R* groups on successive asymmetric carbons projecting on the same side (up in this figure) defines a meso diad and perpetuation of this configuration leads to an isotactic polymer. Assignment of a configuration *d* to the asymmetric carbons in this figure is arbitrary. If, by a 180° rotation of the chain, all the *R* groups are rendered to lie below the plane of the paper, the carbon centers are assigned an *l* configuration. The stereochemistry of the chain would not differ, however, if the chain ends are indistinguishable. Thus, an “all *d*” or “all *l*” chain is isotactic in character. If one of the asymmetric carbons of the diad is in the *d* configuration and the other is in *l*, the

diad is racemic (Fig. 1.1b) and regular alternation of the *d* and *l* centers along the chain defines a syndiotactic polymer. Random occurrence of *d* and *l* centers along the chain leads to an atactic polymer, as shown schematically in Fig. 1.1c. The convenience of defining the tacticity of a vinyl polymer in this manner and its application to developing the matrix methods for calculating the configurational average properties of these chains have been discussed by Flory [6].

The effect of tacticity on the properties of polymers has long been recognized, with such basic differences as in the glass transition temperature. Lemieux *et al.* [7] studied the effect of the tacticity of poly(methyl methacrylate) (PMMA) on its miscibility with poly(vinyl chloride) (PVC), chlorinated PVC and Saran. In a series of papers, Beaucage and Stein [8] and Beaucage *et al.* [9] examined the effect of the tacticity of poly(vinyl methyl ether) on its blend characteristics with polystyrene. Many of the “regular” or isotactic polymers have been studied in terms of the crystalline structure, crystal growth, and morphology [10,11]. These studies also prompted development of theories on chain folding, nucleation, and growth, etc., to model the experimental observations, as well as to predict the properties of these

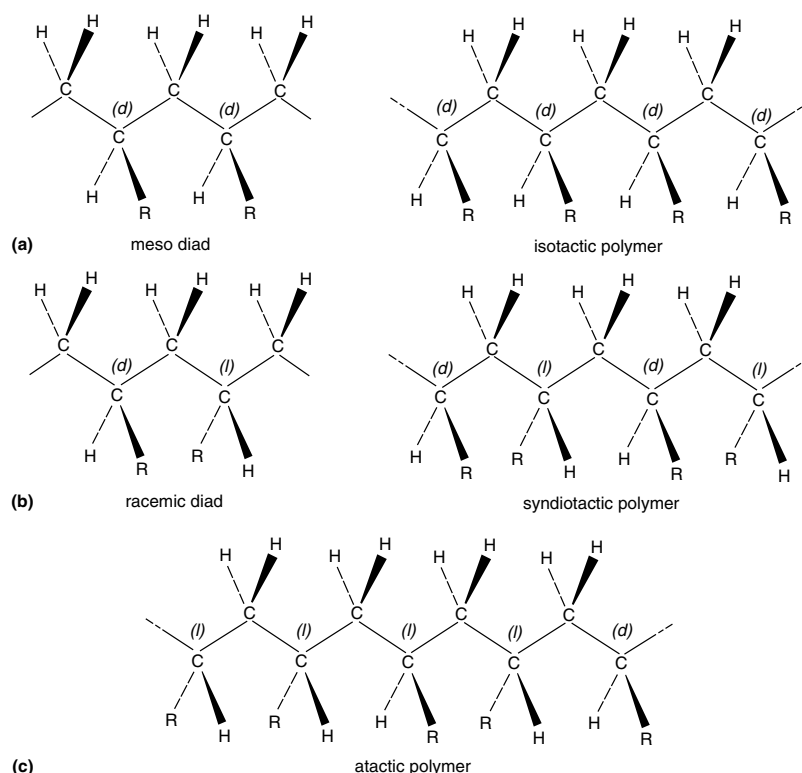


FIGURE 1.1. Schematic of the definition of tacticity of an asymmetric chain of the type $[(CH_2)(CHR)]_n$.

polymers. Solution properties of these isotactic chains could in most cases be interpreted in terms of the local conformation of the chain segments using the rotational isomeric state schemes. However, the rationalization of these properties for stereoirregular or syndiotactic chains was impeded to some extent by the lack of experimental results on polymer samples with precisely tailored microstructure. In a highly isotactic chain, the stereo defects can be not only an isolated *r* diad, but a short perpetuation of it. Zhu *et al.* [12], from ^{13}C NMR analysis of highly isotactic polypropylene, concluded that isolated racemic units can occur up to a pentad (*rrrrr*) sequence.

Whereas most of the early work on crystallization, etc., were concerned with predominantly isotactic chains, the recent developments in synthetic methodologies have enabled the preparation of highly syndiotactic polymers [13,14]. Since the high stereoregularity of these syndiotactic polymers facilitates their crystallization, several papers have been published on the x-ray crystal structure and polymorphism of syndiotactic polystyrene [15–18]. The chain conformation in the crystalline state has also been analyzed using NMR [19]. Similarly, the crystal structure of syndiotactic polypropylene has also been studied by a number of authors [20–22].

Liquori *et al.* [23] first discovered that isotactic and syndiotactic PMMA chains form a crystalline stereocomplex. A number of authors have since studied this phenomenon [24]. Buter *et al.* [25,26] reported the formation of an “*in situ*” complex during stereospecific replica polymerization of methyl methacrylate in the presence of preformed isotactic or syndiotactic PMMA. Hatada *et al.* [24] reported a detailed study of the complex formation, using highly stereoregular PMMA polymers with narrow molecular weight distribution. The effect of tacticity on the characteristics of Langmuir-Blodgett films of PMMA and the stereocomplex between isotactic and syndiotactic PMMA in such monolayers at the air-water interface have been reported in a series of papers by Brinkhuis and Schouten [27,27a]. Similar to this system, Hatada *et al.* [28] reported stereocomplex formation in solution and in the bulk between isotactic polymers of *R*-(+)- and *S*-(-)- α -methylbenzyl methacrylates.

1.3 ARCHITECTURE

In addition to the tacticity, the molecular weight and its distribution are also major factors which influence the ultimate properties of these chains. Whereas a wide molecular weight distribution can even be a merit for some commodity resin applications, consistent control of the distribution is obviously a requirement for commercial applications. With a wide molecular weight distribution, factors of concern are the internal plasticization of the high molecular weight component by the low molecular weight fraction and the resultant effects on properties such as the T_g . Recent syn-

thetic efforts focus on controlling not only the tacticity but the molecular weight distribution as well.

Anionic living polymerization was used by Hatada *et al.* [29,30] to prepare narrow molecular weight, highly stereoregular poly(methyl methacrylate). These authors also discussed isolation of stereoregular oligomers of PMMA using a preparative supercritical fluid chromatography method [31]. Preparation of heterotactic-rich poly(methyl methacrylate) and other alkyl methacrylates has also been described [32,33]. The living anionic polymerization of methacrylic esters and block copolymers with low dispersity has been discussed by Teyssié *et al.* [34,35], Bayard *et al.* [36], and Baskaran [36a]. Diblock copolymers of styrene and *t*-Bu acrylate with $M_w/M_n = 1.05$ have been obtained. Wang *et al.* [37] presented an extensive set of results on the effect of various types of ligands and different solvents and solvent mixtures on the stereochemistry of anionically polymerized poly(methyl methacrylate). Predominantly isotactic or syndiotactic polymers, with narrow polydispersity or bimodal or multimodal distribution of molecular weights were obtained depending on the synthetic conditions. Using different types of catalysts, Asanuma *et al.* [38] prepared iso- and syndiotactic poly(1-butene), poly(1-pentene), poly(1-hexene), and poly(1-octene) with narrow molecular weight distribution.

Whereas the authors cited above employed anionic polymerization to control the molecular weight distribution, Georges *et al.* [39–42] developed a living, stable-free radical polymerization process that can be performed in solution, bulk, or suspension. This was also extended to emulsion polymerization of block copolymers [43a]. Since then, there has been a burst of activity on several polymerization methods such as atom transfer radical polymerization (ATRP) [43b–e], living metal catalyzed radical polymerization [43f], and living cationic polymerization [43g]. Designing novel polymer topologies using living ROMP methods has also been developed [43h].

Table 1.1 summarizes some of the work on the control of tacticity and molecular weight distribution with common polymers such as the PMMA and polystyrene.

In addition to the occurrence of defects in a stereoregular vinyl polymer in terms of a diad of alternate tacticity, the head-to-head/tail-to-tail (H-H/T-T) defect is also of interest [44]. This type of defect is shown schematically in Fig. 1.2. Different types of polymerization conditions which would introduce these defects have been summarized by Vogl and Grossman [45]. The H-H content has been known to vary from about ~4% in PVC to ~30% in polychlorotrifluoroethylene. Such a linkage would no doubt affect the properties of the chain to different extents. Indirect synthetic methods (e.g., hydrogenation of polydienes) have been developed to specifically prepare H-H polymers and compare their properties with regular head-to-tail (HT) counterparts. For example, Földes *et al.* [46] have developed a synthetic route to prepare H-H polystyrene, with molecular weights ranging from 240 000 to 1 200 000, and close to

TABLE 1.1. Microstructure.

Polymer	Tacticity (%) and remarks	Reference
Atactic poly(alkyl methacrylate)s	Methyl methacrylate: $rr = 64\%$, $mr = 31\%$, $mm = 5\%$; $M_n = 33,000$; $M_w/M_n = 1.14$ Ethyl methacrylate: $rr = 66\%$, $mr = 28\%$, $mm = 6\%$ Isobutyl methacrylate: $rr = 66\%$, $mr = 28\%$, $mm = 6\%$; $M_n = 30,000$; $M_w/M_n = 1.31$ Langmuir Blodgett monolayer behavior with tacticity discussed.	[27]
Heterotactic poly(alkyl methacrylate)s	Ester group: -CH ₂ CH ₃ : $mr = 87.2\%$; $M_n = 7010$; $M_w/M_n = 1.08$ -CH ₂ CH ₂ CH ₂ CH ₃ : $mr = 87.1\%$; $M_n = 9300$; $M_w/M_n = 1.07$ -CH ₂ CH(CH ₃) ₂ : $mr = 78.4\%$; $M_n = 6350$; $M_w/M_n = 1.07$ -CH(CH ₃) ₂ : $mr = 69.2\%$; $M_n = 4730$; $M_w/M_n = 1.07$ Tacticity variation of poly(ethyl methacrylate) with synthetic conditions discussed in detail.	[33]
Isotactic poly(alkyl methacrylate)s	Methyl methacrylate: $mm > 97\%$; $M_n = 36,000$; $M_w/M_n = 1.17$ Ethyl methacrylate: $mm = 95\%$; $M_n = 115,000$ Isobutyl methacrylate: $mm = 95\%$; $M_n = 3200$; $M_w/M_n = 4.8$ Langmuir Blodgett monolayer behavior with tacticity discussed.	[27a]
Syndiotactic poly(alkyl methacrylate)s	rr content with side group: C ₂ H ₅ : 90% CH(CH ₃) ₂ : 92% (CH ₂) ₃ CH ₃ : 92% CH ₂ -CH(CH ₃) ₂ : 93% C(CH ₃) ₃ : $rr = 57\%$, $mr = 33\%$ M_n : 6000–8690; M_w/M_n : 1.06–1.64	[139]
Syndiotactic poly(alkyl methacrylate)s	Various types of side chain ester groups. rr : 82–92% DP 31–421; $M_w/M_n = 1.07$ –1.43 Stereocomplex with iso-PMMA discussed.	[24]
Syndiotactic poly(alkyl methacrylate)s	Methyl methacrylate: $rr = 85\%$, $mr = 14\%$; $M_n = 46,000$; $M_w/M_n = 1.2$ Ethyl methacrylate: $rr = 88\%$, $mr = 9\%$; $M_n = 93,000$ Isobutyl methacrylate: $rr = 97\%$, $mr = 3\%$; $M_n = 16,000$; $M_w/M_n = 1.09$ Langmuir Blodgett monolayer behavior with tacticity discussed.	[27a]
Isotactic poly(2-N-carbazolethyl acrylate)	$m = 87$ –97%; $M_n = 0.56 \cdot 10^4$ to 5.10^4 ; $M_w/M_n = 4.0$ –4.8 Hole mobility is discussed.	[140]
Poly(cyclobutyl methacrylate)	rr : 65%, ($mr + rm$): 32%; $M_w = 13.9 \cdot 10^4$; $M_w/M_n = 1.3$; $T_g = 78^\circ\text{C}$	[141]
Poly(cyclodecyl methacrylate)	rr : 67%, ($mr + rm$): 30%; $M_w/M_n = 1.7$; $T_g = 58^\circ\text{C}$	[141]
Poly(cyclododecyl methacrylate)	rr : 63%, ($mr + rm$): 34%; $M_w = 9.8 \cdot 10^4$; $M_w/M_n = 1.4$; $T_g = 56^\circ\text{C}$	[141]
Poly(cycloheptadecyl methacrylate)	$rr = 67\%$, ($mr + rm$): 31%; $M_w/M_n = 1.6$; $T_g = 56^\circ\text{C}$	[141]
Poly(cyclooctyl methacrylate)	rr : 63%, ($mr + rm$): 34%; $M_w = 12.1 \cdot 10^4$; $M_w/M_n = 1.4$; $T_g = 73^\circ\text{C}$	[141]
Poly(cyclopentyl methacrylate)	rr : 66%, ($mr + rm$): 32%; $M_w = 11.0 \cdot 10^4$; $M_w/M_n = 1.2$; $T_g = 75^\circ\text{C}$	[141]
Isotactic poly(ethyl methacrylate)	$mm = 97\%$	[142]
Isotactic oligo(methyl methacrylate)	$mm:mr:rr = 96.1:3.9:0$ 19–29-mer isolated by preparative supercritical fluid chromatography; $\overline{DP} = 28.6$; $M_w/M_n = 1.15$; T_g of 28mer = 34.5°C ; Stereocomplex with syndiotactic oligo(methyl methacrylate) discussed.	[31]
Syndiotactic oligo(methyl methacrylate)	$mm:mr:rr = 0.3:7.6:92.1$ isolated by preparative supercritical fluid chromatography; $\overline{DP} = 26.8$; $M_w/M_n = 1.09$; stereocomplex with isotactic oligo(methyl methacrylate) discussed.	[31]
Atactic poly(methyl methacrylate)	$mm = 6\%$, $mr = 36\%$, $rr = 58\%$; $M_w = 124,000$; $M_w/M_n = 2.8$;	[143]
Atactic poly(methyl methacrylate)- d_2	FTIR spectroscopic analysis of the conformational energy differences between rotational isomeric states is presented.	[32]
Heterotactic poly(methyl methacrylate)	$mr = 67.8\%$, $rr = 20.6\%$, $mm = 11.6\%$; $M_n = 11640$; $M_w/M_n = 1.09$ –1.14; $T_g = 102.2^\circ\text{C}$;	[32]
Isotactic poly(methyl methacrylate)	Various mr and rr contents result depending on the synthetic conditions. $mm > 98\%$; $M_w = 115,000$; $M_w/M_n = 2.8$	[143]

TABLE 1.1. *Continued.*

Polymer	Tacticity (%) and remarks	Reference
Isotactic poly(methyl methacrylate)- d_2	FTIR spectroscopic analysis of the conformational energy differences between rotational isomeric states is presented.	
Isotactic poly(methyl methacrylate)	$mm = 96\%$; $M_w/M_n = 1.1$	[30]
Isotactic poly(methyl methacrylate)	$mm = 97\%$, $mr = 2\%$; $rr = 1\%$; $M_n = 33030$, $M_w/M_n = 1.25$	[24]
Isotactic poly(methyl methacrylate)- <i>b</i> -poly(ethylmethacrylate)	Stereocomplexation with syndiotactic methacrylates discussed. DP : 59/59, 97/151, 64/182; $mm = 95$ – 97% ; $M_w/M_n = 1.29$ – 2.11	[142,144]
Isotactic poly(methyl methacrylate)- <i>b</i> -poly(ethylmethacrylate)- <i>b</i> -poly(methyl methacrylate)- <i>b</i> -Poly(methylmethacrylate)- <i>b</i> -ethylmethacrylate)	DP : 35/50/200, 25/28/25; mm 95–97%; $M_w/M_n = 1.17$, 1.42 rr : 89–91% ($mm = 0$, $mr = 9$ –11%); M_n 8900–12,300; $M_w/M_n = 1.07$ – 1.25	[142,144] [139]
Isotactic poly(methyl methacrylate)- <i>co</i> -poly(ethylmethacrylate)	$mm = 96$ – 97% ; MMA/EMA 78/22 to 26/74; $M_w/M_n = 1.53$ – 3.57	[142]
Poly(iso-MMA- <i>b</i> -syndio-MMA)	Stereoblock polymer with isotactic and syndiotactic blocks. $M_w/M_n = 1.27$; Isotactic block: $mm = 97\%$, $mr = 2\%$, $rr = 1\%$ Syndiotactic block: $mm = 7\%$, $mr = 17\%$, $rr = 76\%$ Stereocomplex between the block polymer and iso or syndiotactic PMMA discussed.	[24]
Syndiotactic poly(methyl methacrylate)	$rr = 76\%$, $mr = 22\%$, $mm = 2\%$; $M_w = 152,000$; $M_w/M_n = 2.0$; FTIR	[143]
Syndiotactic poly(methyl methacrylate)- d_2	Spectroscopic analysis of the conformational energy differences between rotational isomeric states is presented.	
Syndiotactic poly(methyl methacrylate)	Two samples with rr : 89.5 and 91.5%. $M_w = 2.6 \cdot 10^5$ to $5.5 \cdot 10^5$; $M_w/M_n = 1.3$ – 1.4 Aggregation process in <i>n</i> -butyl acetate discussed.	[145]
Syndiotactic poly(methyl methacrylate)	Two samples (i) $mm = 2\%$, $mr = 8.5\%$, $rr = 89.5\%$ (ii) $mm = 3\%$, $mr = 31\%$, $rr = 66\%$ (i) $M_n = 145,000$; $M_w/M_n = 1.6$ (ii) $M_n = 45,000$ NMR, IR studies of aggregation in solution; IR and x-ray studies of crystallinity. Sample (i) crystallinity 27–32%, crystallite size 46–57 Å rr up to 96%.	[146]
Syndiotactic poly(methyl methacrylate)	Anionic living polymerization; $M_n = 2000$ – 14500 ; $M_w/M_n = 1.13$ – 5.5 ; effect of synthetic variables on tacticity, molecular weight and distribution and yield discussed.	[139,147]
Syndiotactic poly-1,2-(4-methyl-1,3-pentadiene)	More than 88% 1,2 content; amorphous; hydrogenation produced crystalline syndiotactic poly(4-methyl-1-pentene) with $T_m = 186^\circ\text{C}$.	[148] [for the crystal structure of the hydrogenated polymer, poly(4-methyl-1-pentene), see 149]
Isotactic poly(1-pentene)	$mmmm$ (pentad) = 90%; $M_w = 17\,000$; $M_w/M_n = 2.3$; $T_m = 64^\circ\text{C}$; x ray and NMR data.	[150]
Syndiotactic poly(1-pentene)	$rrrr$ (pentad) = 85%; $M_w = 65000$; $M_w/M_n = 3.0$; $T_m = 42^\circ\text{C}$; $T_g = -22.7^\circ\text{C}$; crystallinity 30%; x ray and NMR data.	[150]
Syndiotactic polypropylene	$rrrr$ 74–86%; $M_w = 52 \cdot 10^3$ to $777 \cdot 10^3$, $M_w/M_n = 1.8$ – 2.4	[151]
Syndiotactic polypropylene	$rrrr = 91.5\%$; $M_w = 1.5 \cdot 10^5$; $M_w/M_n = 1.9$; crystalline structure of the zig-zag form is reported.	[152]

TABLE 1.1. Continued.

Polymer	Tacticity (%) and remarks	Reference
Syndiotactic polypropylene	<i>rrrr</i> pentads 81.4–94.5% $M_w = 9.6 \cdot 10^4 - 17.3 \cdot 10^4$; T_m : 135–186 °C; thermal behavior discussed.	[153] [for the crystal structure using one of these samples, see 22]
Polypropylene	Five samples, <i>mm</i> = 92.2–94.9% (NMR); M_w = 22 000–947 000; fractionation according to stereoregularity; crystallization and melting behavior with IR tacticity studied.	[154]
Syndiotactic polystyrene	<i>rr</i> > 98%, <i>rrrrr</i> > 94%; NMR, IR and x ray diffraction results discussed; $T_m \approx 270$ °C.	[13,155]
Syndiotactic polystyrene	<i>rr</i> > 98%	[14]
Syndiotactic polystyrene	<i>rrrr</i> > 96%; T_m = 260–270 °C; IR and Raman spectroscopic studies of local chain conformation in glass and gels.	[156,157]
Isotactic polystyrene	<i>m</i> > 95%; T_m = 230 °C; IR and Raman spectroscopic studies of local chain conformation in glass and gels.	[157]
Heterotactic poly(vinyl alcohol)	<i>mr</i> = 67%; <i>mm</i> = 18%; <i>rr</i> = 15%	[158]
Isotactic poly(2-vinyl pyridine)	<i>mm</i> > 98% Crystallization and melt behavior discussed. M_v = 400000; maximum spherulite growth rate at T_c = 165 °C; T_m° = 212.5 °C.	[159]

100% conversion. The synthesis and properties of H-H polymers have been reviewed by Vogl [47] and Vogl and Grossman [45]. The chain flexibility of a H-H polymer either increases or decreases as compared to the H-T chain, depending on the nature of the side group. A comparison [45,47] of the glass transition temperatures of some of the polymers is given in Table 1.2. Arichi *et al.* [48] found

that the theta temperature of H-H polypropylene in isoamylacetate was about 9° higher than that of atactic H-T polypropylene (34°C). On the other hand, a study of dilute solution properties of H-H polystyrene by Strazielle *et al.* [49] showed that the theta temperature in cyclohexane was 19°C, which is lower by 16° than the theta temperature of H-T polystyrene in the same solvent. Hattam *et al.* [50] studied the solution properties of H-H polypropylene (see chapter on “Theta Temperatures”).

Another type of specificity that can occur is the chirality. Isotactic poly(triphenylmethyl methacrylate) is the first known case in which the helicity of the polymer leads to chirality and optical activity [51,52]. A conformational analysis of this polymer has been reported by Cavallo *et al.* [53].

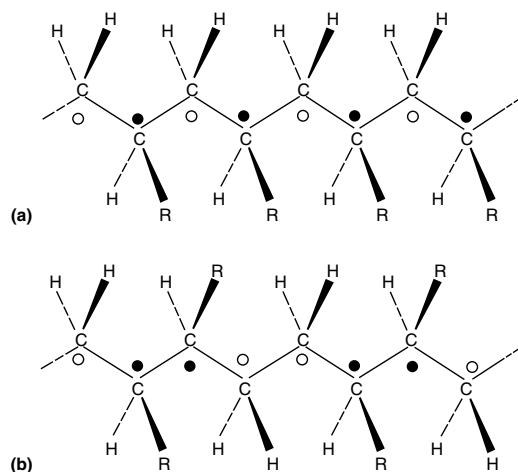


FIGURE 1.2. Schematic of the (a) head-to-tail and (b) head-to-head/tail-to-tail placements. Note the sequence of the “markers”, $\circ \bullet \circ \bullet \circ \bullet \circ \bullet$ in (a) versus $\bullet \bullet \circ \circ \bullet \bullet \circ \circ$ in (b).

TABLE 1.2. Glass transition temperatures of some head-to-head and head-to-tail polymers.

Polymer	Head-to-Head (°C)	Head-to-Tail (°C)
Poly(isobutylene)	87	–61
Poly(methyl acrylate)	40	12
Poly(methyl crotonate)	107	80
Poly(methyl cinnamate)	210	190
Poly(methyl methacrylate)	160–170	100
Poly(propylene)	–39	–17
Poly(styrene)	97	98
Poly(vinyl cyclohexane)	88	138
Poly(vinyl chloride)	91	83

Taken in part from Ref. 45.

Apart from the carbon chain polymers discussed above, the silicon chain polymers have also been investigated extensively in terms of microstructure. The stereochemistry of polysilanes has been studied using $^{29}\text{Si-NMR}$ spectroscopy [54,55]. Wolff *et al.* [56] concluded that for a poly(phenylmethyl silane), the ratio of mm:rr:mr(rm) to be 3:3:4 and that the spectra of poly(1,2,2-trimethyl-1-phenyldisilane) are consistent with approximately equal amounts of head-to-head and head-to-tail sequences and an atactic configuration.

1.4 POLYMERS WITH MACROCYCLIC AND OTHER PHOTOACTIVE GROUPS

Synthetic efforts in designing polymers with functional moieties in the main chain or the side chain to impart photoconductivity, eletro-optic, nonlinear optical properties, etc., has been an active area in recent years [57,58]. Covalent tagging of chromophores to polymers in order to study the conformational dynamics and to study charge transfer complexes has been reported by a number of authors [59–61]. A summary of the work on π and σ conjugated oligomeric tetrathiafulvalenes for increasing the dimensionality of electrical conduction was presented by Adam and Müllen [62]. In searching for polymers with photorefractivity, photoconductivity and optical nonlinearity, metalloporphyrins, and metallophthalocyanines have been candidate materials for inclusion in the main chain or the side chain. A brief overview of this area was discussed by Allcock [63]. For example, initial designs on the *molecular electronic* wires, with backbone-linked porphyrins have been reported by Crossley and Burn [64]. Following this analogy, a *molecular photonic* wire was announced by Wagner and Lindsey [65]. In the latter, a boron-dipyromethene dye provides an optical input at one end of the chain, a linear array of three zinc porphyrins serves as a signal transmission element and a free base porphyrin provides an optical output at the other end of the chain.

In the case of main chain porphyrin or phthalocyanine polymers, (1) the central metal atoms are covalently linked by a single atom such as O such that the porphyrin (porph) or phthalocyanine (Pc) macrocyclic rings are cofacial, as shown in Fig. 1.3a or (2) the central metal atoms are linked by a flexible or rigid spacer. In the case of side chain polymers, polymerization is performed via side chains attached to the macrocyclic using an acrylic or methacrylic polymer as the backbone. This is illustrated in Fig. 1.3b. (The designs of Crossley and Burn [64], and Wagner and Linsey [65] are different from these general classes.) Intra- or inter-molecular π overlap of these macrocyclics dictate the ultimate properties. It is known from the work on small molecule analogues that the extent of π overlap of these macrocyclics influence the photoconductivity, absorption wavelength, etc. [66]. The flexible spacers as well as the side groups attached to these macrocyclics improve their

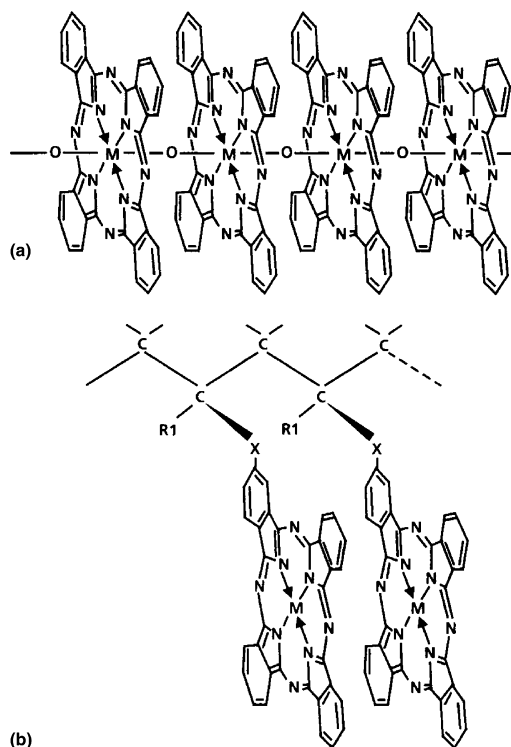


FIGURE 1.3. The main chain and side chain polymers incorporating metallophthalocyanines are shown schematically. (a) The main chain formed by linking the metallo-PC units, with an oxygen atom, leading to a cofacial arrangement of the macrocyclic rings. Flexible spacers can also be used instead of a single oxygen atom. (b) The metallo-Pc is attached to a side group of a chain such as PMMA. Although two adjacent Pc's are shown here in the cofacial arrangement, such an intramolecular overlap would depend on the tacticity and the conformation of the chain. The metal *M* can be Cu, Al, Si, Ge, etc.

solubility and processability. It is well known that phthalocyanines, without any flexible side groups, are notoriously insoluble in any convenient solvent. A summary of some of these activities are presented in Table 1.3. Phthalocyanine-containing polymers [66a] and conjugated polymer-based chemical sensors [66b] have been discussed.

The asymmetrically substituted porphyrins or phthalocyanines exhibit isomerism. A theoretical treatment of this aspect was published by Knothe [67].

With the emergence of photonics for telecommunication applications, there have been extensive activities related to the development of polymeric materials to this end. Several reviews are available on the synthesis and fabrication of polymer-based molecular wires and switches [67a–g]. In addition, a number of studies on azobenzene-containing

TABLE 1.3. *Polymers with macrocyclic photoactive groups.*

Polymer	Remarks	Reference
Poly(5-[4-(acryloyloxy)phenyl]-10,15,20-triphenylporphyrin)	Polyacrylate or methacrylate polymers with pendant porphyrin units; hypochromism and hyperchromism discussed.	[160]
Poly(5-[4-(methacryloyloxy)phenyl]-10,15,20-triphenylporphyrin)		
Poly(methylmethacrylate-co-5-[4-(methacryloyloxy)phenyl]10,15,20-triphenylporphyrin)		
Poly[porph-O-CH ₂ -(I)]	Main chain porphyrin polymers; meso-tetraarylporphyrins used; I, II, III with CH ₃ substituted Porph; IV with CH ₂ CH ₃ substitution; III and IV also with Co, Mn, and Zn transition metals.	[161]
Poly[porph-O-(CH ₂) ₆ -(II)]		
Poly[porph-O-(CH ₂) ₈ -(III)]		
Poly[porph-O-(CH ₂) ₈ -(IV)]		
Poly[(O-porph-O-CH ₂) _x -co-(O-bisph-O-CH ₂) _y]	Main chain porphyrin polymers; various copolymer compositions; M_w up to 125 000; Co and Cu transition metal inclusion with some copolymers.	[161a]
Poly[(porph-O-CH ₂ -O) _x -co-(bisph-O-CH ₂ -O) _y]		
(Porph-Ph-porph) ₃ 1,4-phenylene bridged porphyrins	Metal free and Zn; several types of substitutions on the porphyrin.	[162]
Poly(porph-phenylenevinylene)	Main chain porphyrin polymers; 68% yield; metallized with Zn, Cu, or Ni; NMR, FTIR and cyclic voltammetric results.	[163]
Tetrakisporphyrin and oligomeric porphyrin	An approach to molecular electronic wire; Tetrakisporphyrin (C ₃₂₂ H ₃₇₀ N ₂₈) is about 65 Å long. The tert-butyl groups along the backbone provide an insulating sheath around the conjugated core and enables solubility.	[64]
Boron-dipyrromethene dye-(ZnPorph) ₃ -Porph	An approach to photonic molecular wire. Absorption and emission spectra discussed.	[65]
Poly(N-vinyl-2-pyrrolidone-Porph)	Poly(N-vinyl-2-pyrrolidone) with metal free or Mg porphyrin side group; spectroscopic behavior discussed.	[164]
Poly[(AlPc)-F] Poly[(GaPc)-F] Poly[(CrPc)-F] Poly[(SiPc)-O] Poly[(GePc)-O] Poly[(SnPc)-O] Poly[(iSiPc)-O] Poly[(GePc)-O] Poly[(SnPc)-O]	Co-facial packing of Pc rings; spectroscopy, electrical conductivity, electron microscopy, effect of doping discussed.	[165]
Poly[(SiPc)-O]	DP = 120 with SiPc (density $\rho = 1.432$), 70 with GePc ($\rho = 1.512$) and 100 with SnPc ($\rho = 1.719$). Cofacial structure of Pc rings. Crystal structure discussed based on powder x ray diffraction data and modeling.	[166,167]
Poly(CuPc) Poly(CoPc) Poly(NiPc)	Sheet polymers of metal phthalocyanines; insoluble; electronic spectra, magnetic susceptibility, electrical conductivity, x ray diffraction discussed.	[168]
Poly(AlPc-F) Poly(SiPc-O)	Main chain metallized phthalocyanine (Pc) polymers; electron microscopy and electron diffraction; both AlPc and SiPc are cofacial.	[169]
Poly[octakis(decyloxy)SiPc-O]	Substituted SiPc main chain, soluble polymer; $M_w = 118\ 000$ and $250\ 000$ by SAXS of heptane solutions; rod length 219 and 472 Å for the two samples.	[170]
Poly(CH ₂ -CHCOOROPc) <i>R</i> : C ₈ H ₁₇ or C ₁₂ H ₂₅	Side chain phthalocyanine polymers; Pc substituted with various groups; metal free, Cu and Ni Pc's; M_w up to 47 000; liquid crystalline; absorption and fluorescence spectroscopy.	[171]
Poly[(SiPc)-O] Poly[(SiPc)-O-(CH ₂) ₄ -Si(C ₆ H ₅) ₂ -(CH ₂) ₄ -O] Poly[(SiPc)-O-(CH ₂) ₄ -Si(CH ₃) ₂ -C ₆ H ₄ -Si(CH ₃) ₂ -(CH ₂) ₄ -O] Poly[(SiPc)-O-(CH ₂) ₄ -Si(CH ₃) ₂ -(O-Si(CH ₃) ₂) ₄ -(CH ₂) ₄ -O] Poly[(SiPc)-(Si(CH ₃)(C ₆ H ₅)) _n] ($n \approx 6.6$)	Main chain Pc polymers; symmetric and unsymmetric alkyl substituted Si phthalocyanines; absorption and emission spectroscopy, optical properties, cyclic voltammetry are discussed in terms of packing and interactions of phthalocyanines.	[172]

TABLE 1.3. *Continued.*

Polymer	Remarks	Reference
Tetra(methoxy)-tetra(octyloxy)-phthalocyaninato-polysiloxane	Langmuir-Blodgett film properties studied.	[173]
Poly[(SiPc)-O]	SAXS from dilute solutions.	[174]
Poly[acrylamide-CuPc(NO) ₂]	Side chain phthalocyanine polymer; water soluble; also doped with iodine; photoconductivity discussed.	[175]
Poly[vinylcarbazole-CuPc(NO) ₂]	Copolymer with vinyl carbazole and dinitro CuPc covalently attached to the carbazole moiety. 21 mol % CuPc(NO) ₂ bonded to PVK. The polymer shows better photoconductivity than monomeric CuPc or CuPc(NO ₂) ₄ .	[176]
Poly[2-[[11-(methacryloyloxy)undecyl]oxy]-3-methoxy-9,10,16,17,23,24, hexakis (dodecyloxy)phthalocyanine] (<i>polyundecyloxy methacrylate with side chain metal-free phthalocyanine</i>)	Langmuir-Blodgett monolayer formation studied with IR, ellipsometry, electron diffraction; effect of adding 1-arachidic acid discussed.	[177]
Poly(perylene imide): Poly(perylene- <i>R</i>) substituted perylenes; <i>R</i> : Linkage: (CH ₂) ₉ or Ph-O-Ph or Ph-CH ₂ -Ph	Main chain perylene polyimide; <i>M_w</i> up to 64 100; soluble in various solvents; absorption, fluorescence spectra discussed.	[178]
Poly(4'-dialkylamino-4-nitrostilbene acrylate- <i>b</i> -methyl methacrylate)	Polyacrylates with NLO active side chains; wide range of <i>M_w</i> up to 186 000; many soluble in methylene chloride or THF; two samples show liquid crystallinity; microscopy and thermal analysis discussed.	[179]
Poly(4'-dialkylamino-4-nitrostilbene methacrylate- <i>b</i> -methyl methacrylate)		
Poly(4'-dialkylamino-4-nitroazobenzene methacrylate- <i>b</i> -methyl methacrylate)		
Poly[(R,R)-dibenzo-19-crown-6]	Polymeric chiral crown ethers; hostguest complexation discussed.	[180]
Poly[(S,S)-dibenzo-19-crown-6]		

polymers have been reported [67h,i], including the fabrication of light driven organized layered materials [67j]. Advances in polymerization methods have played a key role in recent efforts to design materials with specific properties. As an example, the ATRP technique mentioned in Sect. 1.3 has recently been used to tailor the photochromic performance of polymer-dye conjugates [67k].

1.5 POLYMERS WITH FULLERENE AND CARBON NANOTUBE

Summarizing the research activities on fullerenes, Baum [68] wrote "...the question most commonly asked of fullerene researchers has been very simple: What is it good for? The answer to that question has generally gone something like this: We don't yet know what applications will be discovered for C₆₀ and the other fullerenes. However, the remarkable properties of these new forms of carbon will inevitably lead to many new products that will range from new types of polymers..." Fullerenes have been incorporated into polymeric backbones as "pearl necklace" or as side chains ("charm bracelet"). The synthesis of dendrimers with C₆₀ has also been reported [69]. A brief summary of polymer related fullerene work was given by Hirsch [70]. Chemical derivitization of C₆₀ has been described by Petrie

et al. [71]. A summary of the initial work on polymers incorporating C₆₀ is given in Table 1.4.

Various forms of polymeric fullerenes have been prepared in the past decade: side chain polymers, main chain polymers, dendritic fullerenes, star-shaped polymers, fullerene endcapped polymers, etc. [71a-d]. With the invention of the carbon nanotubes [71e,f] and the development of methods to functionalize them [71g-i], their applications in the area of polymers range from opto-electronic devices to biosensors [71j-m].

1.6 CYCLIC POLYMERS

The cyclic polymers or oligomers are distinct in their physical properties from the corresponding linear chains. There has been considerable interest in the synthesis, isolation, characterization, and utilization of polymeric cyclics, although in a number of cases, they are at best oligomeric. A collection of reviews on various aspects of cyclic polymers has been published and an introduction to this area has been given [72-74a-c].

Chromatographic methods are normally used experimentally to determine the population of the cyclics which may coexist with the corresponding linear chains. Three methods have been reviewed by Semlyen [73] to

TABLE 1.4. *Polymers with fullerenes.*

Polymer	Remarks	Reference
Polyarenefullerenes	Reaction with benzene and toluene led to $C_{60}-(C_6H_6)_{12}$ and $C_{60}(C_6H_5-CH_3)_{12}$, respectively.	[181]
C_{60} - <i>p</i> -xylene copolymer	Cross-linked; insoluble; xylene/ C_{60} ratio: 3.4:1.0	[182]
Poly(4,4'-diphenyl- C_{61} sebacate)	Solid state NMR spectra discussed.	[183]
Poly(bisphenol A hexamethyleneurethane- C_{61})	Side chain C_{60} polymer; 61% yield; soluble in nitrobenzene, benzonitrile; NMR, IR, cyclic voltammetry are discussed.	[183]
Poly(ethylene imine- C_{60})	Side chain C_{60} polymer; molar mass 35 000 $gmol^{-1}$; molar ratio polymer/ C_{60} : 18/1.	[184]
Poly(ethylene propylene)terpolymer- C_{60} (amine functionalized)	Side chain C_{60} polymer.	[185]
Poly[4-[(2-aminoethyl)imino]methyl]styrene- C_{60}]	Side chain C_{60} polymer; molar mass 20 000 $gmol^{-1}$; molar ratio polymer/ C_{60} : 19/1; soluble in toluene, carbon disulfide.	[184]
$C_{60}(=C=C=C_{58})_n$	Solid state photopolymerization; soluble in boiling isodurene.	[186]
Poly[(styrene)-co-(styrene/ C_{60})]	Side chain C_{60} polymer; polymers made with 5.5% ($T_g = 112^\circ C$), 21% ($T_g = 142^\circ C$) and 29% ($T_g = 166^\circ C$) (w/w) of C_{60} ; $M_w = 38500$; single T_g ; soluble in methylenechloride, THF.	[187]
Poly(Rb C_{60}) and poly(KC C_{60})	Lattice parameters and x ray data.	[188]
Polyether dendrimer- C_{60}	A deuteriated fourth generation azide dendrimer ¹³⁸ with C_{60} as the core; 68% yield; extremely soluble; $T_g = 52^\circ C$ (13° higher than starting dendrimer).	[69]

theoretically calculate the population of the cyclics in cyclic-chain equilibrium [75–80]. The molar cyclization equilibrium constants have been determined both experimentally and by calculations for a number of cases such as dihydrogen siloxanes [81], dimethyl siloxanes [76,81–86], and sodium metaphosphates [87], cyclic nylon 6 [88], poly(ethylene terephthalate) [89], and liquid sulphur [90].

Cyclics offer a wide range of opportunities for polymer synthesis, processing, and modification. Ring opening polymerization of cyclics leads to high molecular weight polymers. This was demonstrated using octamethylcyclotetrasiloxane to synthesize long chain polysiloxanes [91]. This process of involving the cyclics has also been used to control the block length of polysiloxane in the preparation of siloxane-styrene-siloxane or siloxane-isoprene-siloxane triblock copolymers [92] and styrene-dimethylsiloxane diblock copolymers [93]. The cyclics offer the advantage of the ease of processing due to their low viscosity at the product fabrication temperature. Hence, in applications such as injection molding, the cyclics can be used for postpolymerization to achieve high molecular weight polymer end products [94]. Macrocyclic oligomers of bisphenol A polycarbonate have been used to prepare polycarbonates of very high molecular weight ($M_w = 200\,000$ – $400\,000$), by ring-opening polymerization which avoids the creation of byproducts. Cyclics with 2–21 monomer units have been prepared and the cyclics yield can be varied from 0% to over 85% by manipulating the synthetic conditions [95–97]. Synthesis and polymerization of cyclic oligomeric arylates [98] and cyclic ether

ketones, ether sulfones, and ether imides have also been reported [99].

Mark and Semlyen, in a series of papers, have studied the mechanism and the effect of trapping cyclics in end-linked elastomeric networks [100–103]. Sharp fractions of cyclics of poly(dimethylsiloxane) (PDMS), varying in size from 31 to 517 skeletal atoms, were mixed with linear chains for different periods of time and the linear chains were then end-linked using a tetrafunctional silane. The untrapped cyclics were extracted to determine the amount trapped. It was found that while cyclics with less than 38 skeletal atoms were not at all trapped, for $n > 38$, the percentage of cyclics trapped increased with size, with 94% trapped in the case of the cyclic with 517 skeletal atoms. In effect, the system of trapped cyclics in the end linked PDMS network is a polymeric catenane. It is thus possible to control the elastomeric properties of the network by incorporating the appropriate sized cyclics. This study has been extended to cyclic PDMS in poly(2,6-dimethyl-1,4-phenylene oxide) [104,105] and cyclic polyesters in PDMS [106].

Percec and coworkers [107–110] have synthesized liquid crystalline cyclic oligomeric polyethers based on 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane with dibromoalkanes. Rings varying from 2 to 5 monomer units were prepared and show isotropic-nematic transition. The nematic order is modeled to arise from the collapse of the rings in the form of a "folded chain" structure, as shown schematically in Fig. 1.4. This is similar to the case of chain folded crystallization of cyclic alkanes (with 34–288 CH_2 groups) and cyclic urethanes [111–114].

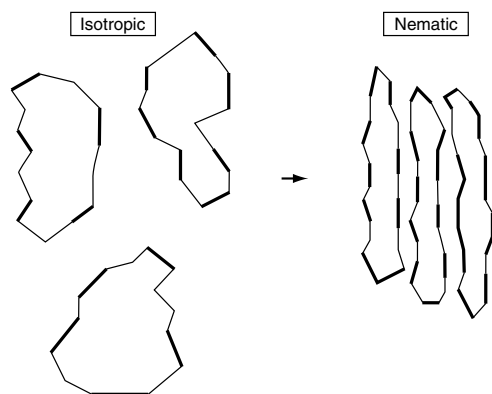


FIGURE 1.4. A model of the isotropic \rightarrow nematic transition in cyclic oligomeric polyethers via intramolecular collapse of the cyclic.

Table 1.5 summarizes the studies on cyclics of poly(dimethyl siloxane) and derivatives, and Table 1.6, those of other polymers. In these tables, K_x refers to the molar cyclization equilibrium constant and RIS, to the rotational isomeric state scheme to analyze chain conformations.

1.7 ROTAXANES

Polyrotaxanes (the name derived from Latin words for wheel and axle) are essentially *in situ* molecular composites consisting of a linear chain threaded through a cyclic molecule. The interior diameter of the cyclic must be large enough to accommodate the linear chain. Large end groups might be necessary to prevent the unthreading of the chain from the cyclic.

Two principal approaches have been used in the synthesis of polyrotaxanes. In the statistical method, no specific interaction exists between the linear and the cyclic species. The equilibrium for threading is driven by entropic factors. This hence provides a wide choice of pairs of cyclics and linear chains. However, the resulting yield is often low. In the template or directed method, specific attractive interaction (such as metal chelation, charge transfer interactions, etc.) between the cyclic and the linear species is taken advantage of.

The polyrotaxanes can be of the “main chain” or the “side chain” type [115], as illustrated schematically in Fig. 1.5, along with a bulky terminal group to prevent dethreading. In the former, the cyclic is threaded through a linear chain and is free to glide along the chain as the steric interactions would permit. In the case of side chain rotaxanes, the cyclic is threaded through a long side chain of a polymer. Thus, a wide range of options and architectures are possible.

Rotaxanes have also been part of dendrimers, i.e., dendritic molecules containing rotaxane-like bonds to link

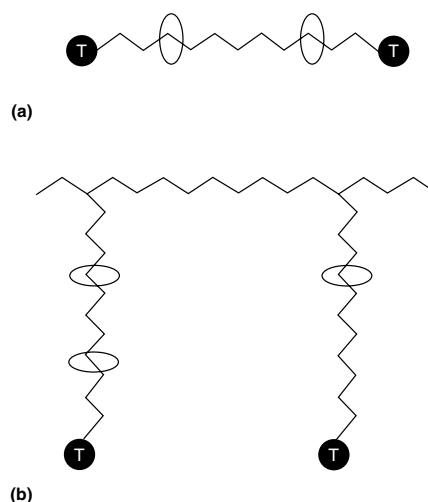


FIGURE 1.5. A schematic representation of the (a) main chain and (b) side chain rotaxanes. The *T* represents a large terminal group which may be used to prevent dethreading of the cyclic from the chain.

their components, either at the core, termini, or branches [115a].

Comprehensive reviews of the history, chemistry, and physical chemistry of rotaxanes and the related architecture, the catenanes, have been published [115–120]. Joyce *et al.* [121] reported a molecular modeling study of cyclics of poly(dimethylsiloxane) to understand the energetics of the threading process of linear chains with particular reference to rotaxanes. Of relevance is also the exhaustive review by Wenz [122] on the role of cyclodextrins in the building of supramolecular structures. Cyclodextrins are cyclics of D-glucose, with α -1,4' linkages. The common ones are α , β , γ -cyclodextrins, with 6, 7, and 8 D-glucose units, respectively.

The rotaxanes offer a plethora of possibilities in terms of supramolecular architecture [115, 116, 122a]. Applications toward molecular machines, motors, and switches have been extensively explored [122b–e].

Table 1.7 lists the examples of different types of rotaxanes reported in the literature. Some of the early work on the chemistry is omitted but can be found in the reviews cited above. In naming the rotaxanes in this table, we follow the nomenclature of Gibson and Marand [115]: polymer-*rotaxa*-cyclic.

1.8 DENDRIMERS

Dendrimers (Greek) or arborols (arbor: tree+alcohol=arborol) are tree-like macromolecular structures topologically controlled during the synthesis. Starting from

TABLE 1.5. *Cyclics of poly(dimethyl siloxane) and its derivatives.*

Polymer	Number of monomers in cyclics	Remarks	Reference
Poly(<i>n</i> -butyl methylsiloxane)		K_4 : 0.37; K_5 : 0.19	[189]
Poly(dimethyl siloxane)	4–200	K_x determined.	[82]
Poly(dimethyl siloxane)	4–40	K_x determined with bulk and solution equilibrates; characteristic ratio measured.	[83]
Poly(dimethyl siloxane)		Calculations with RIS models.	
Poly(dimethyl siloxane)		K_4 : 0.19; K_5 : 0.09	[189]
Poly(dimethyl siloxane)	4–200	K_x measured; dilute solution behavior and RIS treatment discussed.	[84]
Poly(dimethyl siloxane)	3–6	$[\eta]$ - M_w relationships.	[190]
Poly(dimethyl siloxane)	up to approx. 650 (number average number of skeletal bonds 1300)	Construction of a preparative GPC for isolating sharp fractions of cyclics; $M_w/M_n = 1.05$; viscosity of fractions measured.	[191]
Poly(dimethyl siloxane)	65–275	Neutron scattering measurements of chain dimensions.	[192]
Poly(dimethyl siloxane)	16–259	Used in trapping experiments with linear chains; effect of ring size on trapping and elastic properties of the network studied.	[100–103, 106]
Poly(dimethyl siloxane)	92	Cyclics trapped to form catenanes with poly(2,6-dimethyl-1,4-phenylene oxide). 26% w/w cyclics permanently captured in network. 1μ phase domains seen after extraction; mechanical and thermal properties discussed.	[104]
Poly(dimethyl siloxane)	33–122	Trapped to form catenanes with poly(2,6-dimethyl-1,4-phenylene oxide); weight fraction of cyclics trapped increases with their DP. Two T_g 's observed; phase separated domains form.	[105]
Poly(dimethyl siloxane- <i>b</i> -styrene- <i>b</i> -dimethylsiloxane)	4–8	Solution equilibrates; short styrene and DMS blocks, M_w approx 1.1×10^4 .	[193]
Poly(ethyl methyl siloxane)	4–20	Equilibrated in bulk and in toluene; 25.8% w/w cyclics; K_x measured	[194]
Poly(ethyl methyl siloxane)		K_4 : 0.25; K_5 : 0.16.	[189]
Poly(hydrogen methyl siloxane) [-H(CH ₃)SiO-]	4–15	Equilibrated in bulk and in toluene; 12.5% w/w cyclics; K_x measured.	[194]
Imide-disiloxane			[98]
Paraffin-siloxanes			[195]
Paraffin siloxane [-(CH ₃) ₂ Si-(CH ₂) ₄ -(CH ₃) ₂ Si-O-]	2–10	K_x measured for $x = 1$ –6.	[81]
Poly(phenyl methylsiloxane)	3–50	30% w/w undiluted, 90% with toluene; $K_4 = 0.25$; K_5 : 0.16; populations of configurational isomers for $x = 3$ –5.	[189]
Poly(<i>n</i> -propylmethyl siloxane)	4–8	Equilibrated in bulk and in toluene; 31% w/w cyclics; K_x measured.	[194]
3,3,3-trifluoropropyl methyl siloxane	3–13	>80% (w/w) population.	[196]
Poly(3,3,3-trifluoropropylmethyl siloxane)	4–20	Equilibrated in bulk and in cyclohexanone; 82.7% w/w cyclics; K_x measured.	[194]
Poly(vinylmethyl siloxane)	4–23	K_x , dilute solution viscosity, melt viscosity, T_g measured.	[197]

a single branch cell, repeat units or branch cells are iteratively added, to produce “star-burst” structures, one generation after another (STARBURST is a registered

trademark of Dow Chemical Company) [123]. During such multiplicative growth, the polymer adopts a spherical shape, free of chain entanglements, as shown schematically

TABLE 1.6. *Cyclics of other polymers.*

Polymer	Number of monomers in cyclic	Remarks	Reference
Cycloalkane	34	X ray crystal structure.	[111]
Cycloalkane	12–84	Thermal behavior studied; entropy of fusion/unit increases with chain length; melting temperatures discussed.	[198]
Cycloalkane	36	X ray crystal structure	[113]
Cycloalkane	24–288	T_m , LAM frequencies. Discussion of chain folding.	[114]
Cyclic amides		Prepared with dodecanedioyl dichloride and pure isomers of 4,4'-methylenedicyclohexylamine; NMR, IR, x ray diffraction discussed.	[199]
Amide-imides			[98]
Bisphenol-A-co-4,5-bis(p-hydroxyphenyl)-2-(p-nitrophenyl)-oxazole		Macrocycles for NLO copolycarbonates; T_g increases with 2nd component.	[200]
Polycarbonate		Up to 95% yield of cyclics; large cyclics with M_w more than 100,000.	[201]
Polycarbonate	2–21	Cyclics content (0–85%) depends on catalyst.	[95, 97]
Polycarbonate		Dimer 5%; trimer 18%; tetramer 16%; pentamer 12%; hexamer 9%; higher oligomers 25%.	[202]
Polycarbonate	2,4	X ray crystal structure.	[203]
Poly(decamethylene adipate)			[75a]
Poly(decamethylene adipate)	1–5	K_x measured and compared with theory; RIS treatment discussed.	[204]
Poly(1,3-dioxolane)	2–9	K_x measured; RIS treatment discussed.	[205]
2,2'-dithiobis(2-methyl propionaldehyde)	ester tetramer	95% yield, $T_m = 182^\circ\text{C}$	[206]
Polyester $[-(\text{CH}_2)_{10}\text{COO}-]$	5–15	Trapping experiments with linear PDMS chains; molecular modeling of the phenomenon.	[106]
Polyethers with 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl) butane and dibromoalkanes	2–5	Exhibit nematic mesophase; chiral cyclics display cholesteric phase.	[107,109,110]
Ether imides		25–75% yield.	[99]
Ether ketones		40–52% yield.	[99]
Ether sulphones		40–52% yield.	[99]
Ethylene terephthalate	3–9	Extracted from PET; K_x given.	[207]
Tris(ethylene terephthalate)	3	Synthesized.	[208]
Tris(ethylene terephthalate)	3	Synthesized; 46% yield.	[209]
2-Norbornene	2–7		[210]
Nylon-6	1–6	2% w/w cyclics; melt equilibrates; K_x measured.	[88,211]
Oligo(cyclooctene)s	2–10		[212,212a]
1,3,6-trioxacyclooctane	1–9	T_m for $x = 2: 60^\circ\text{C}$ $x = 4: 35^\circ\text{C}$ $x = 6: 40^\circ\text{C}$ K_x given.	[213]
(2R,5R,8R,11R)-2,5,8,11-tetra-tertbutyl-1,4,7,10-tetraoxa cyclododecane	4	$T_m = 168^\circ\text{C}$ NMR, conformation discussed.	[214]
1,3,6,9,12,15-hexaoxacycloheptadecane	1–5		[213]
1,3,6,9,12-pentaoxacyclotetradecane	1–7	T_m for $x = 2: 44^\circ\text{C}$ $x = 4: 61^\circ\text{C}$	[213]
1,3,6,9-tetraoxacycloundecane	2–8		[215]

TABLE 1.6. *Continued.*

Polymer	Number of monomers in cyclic	Remarks	Reference
1,3,6,9-tetraoxacycloundecane	1–8	T_m for $x = 2: 88^\circ\text{C}$ $x = 4: 54^\circ\text{C}$ $x = 6: 39^\circ\text{C}$ K_x given.	[213]
Poly(phenyl methyl silane)	6	Two isomers characterized by NMR; crystal structure determined for one.	[216]
N-methylated oligo(p-phenyleneterephthal amide)	3–6		[217]
Polyphosphate $[\text{NaPO}_3]_x$	3–7	10 w/w cyclics	[218]
Polystyrene	$M_w: 4$ 500–20 000	Yields from 10 to 45%	[219]
Polystyrene		Synthesis and fractionation described; M_w of rings 5×10^3 to 4.5×10^5 ; yield decreases with M_w from 55% to 18%	[220]
Polystyrene		M_w 11 100 to 181 500, $M_w/M_n < 1.2$; quasi elastic light scattering experiments to determine translational diffusion coefficients and compare with linear chains.	[221]
Polystyrene		M_w 12 000–22 000 SANS experiments to determine mean square radii of gyration and second virial coefficient for cyclic and linear chains.	[222]
Polystyrene		Macrocyclic fractions with $11,500 \leq M_w \leq 181\,000$; thermodynamic and hydrodynamic properties in dilute solution and melt viscosity studied and compared with corresponding linear fractions.	[223, 224]
Polystyrene		Macrocyclic fractions with $1.9 \times 10^4 \leq M_w \leq 3.9 \times 10^5$ viscoelastic properties measured and compared with theory.	[225]
Poly(trimethylene succinate)	1–7	K_x measured, compared with theory; RIS treatment discussed.	[204]
Poly(sulphur)	>8		[90]
Poly(sulphur)	6 to 26		[73]
Cyclo(oligourethane)s	1–7	Melting temperatures, long periods, x ray diffraction and structure discussed.	[112]
Poly(tetra hydrofuran)	4–6		[226]

in Fig. 1.6. However, theory predicts [124] a limit of 10 generations beyond which the reaction rates decrease significantly and defects begin to predominate. Extensive reviews of advances in this field have been published [123,125–128].

The synthesis of “cascade molecules” or arborols as spherical micelles has been described by Newkome *et al.* [129,130] who also proposed a nomenclature for such structures. A designation $[m]\text{--}[n]\text{--}[p]$ would refer to a case in which m and p represent the number of surface groups and n denotes the bridge size.

The conventional synthesis of dendrimers involves the “divergent” method, in which branch cells are constructed *in situ* around the initiator core or preformed branch cells are attached to the core. Successive generations are then built. On the other hand, in the “convergent” method [131–133] the dendritic fragments are prepared by starting from frag-

ments which would ultimately comprise the periphery and progressing inward. The resulting dendritic wedges, after several generations of growth, are coupled to a polyfunctional core. A double-stage convergent growth approach has also been described by Wooley *et al.* [134], which enables synthesis of a dendrimer with a “hypercore” made of flexible segments and a rigid outer layer or vice versa. Dendrimers have also been used as macroinitiators for forming hybrid linear-globular AB block copolymers [135]. A summary of all known synthetic strategies to dendrimers has been given by Tomalia [127]. Self-aggregation of certain dendrimers into lyotropic and thermotropic mesophases has been reported [108, 136, 137].

In particular, the review by Tomalia *et al.* [124] traces the similarities and scope of the dendrimer designs to biological systems tailored by Mother Nature and the prospects and applications of supramolecular mimetics via man-made