CHAPTER 1

Chain Structures

P. R. Sundararajan

Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6

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, fullerence-based polymers, cyclics, rotaxanes, and dendrimers. The properties of polymers with other architectures and morphologies are discussed in various other chapters of this handbook.

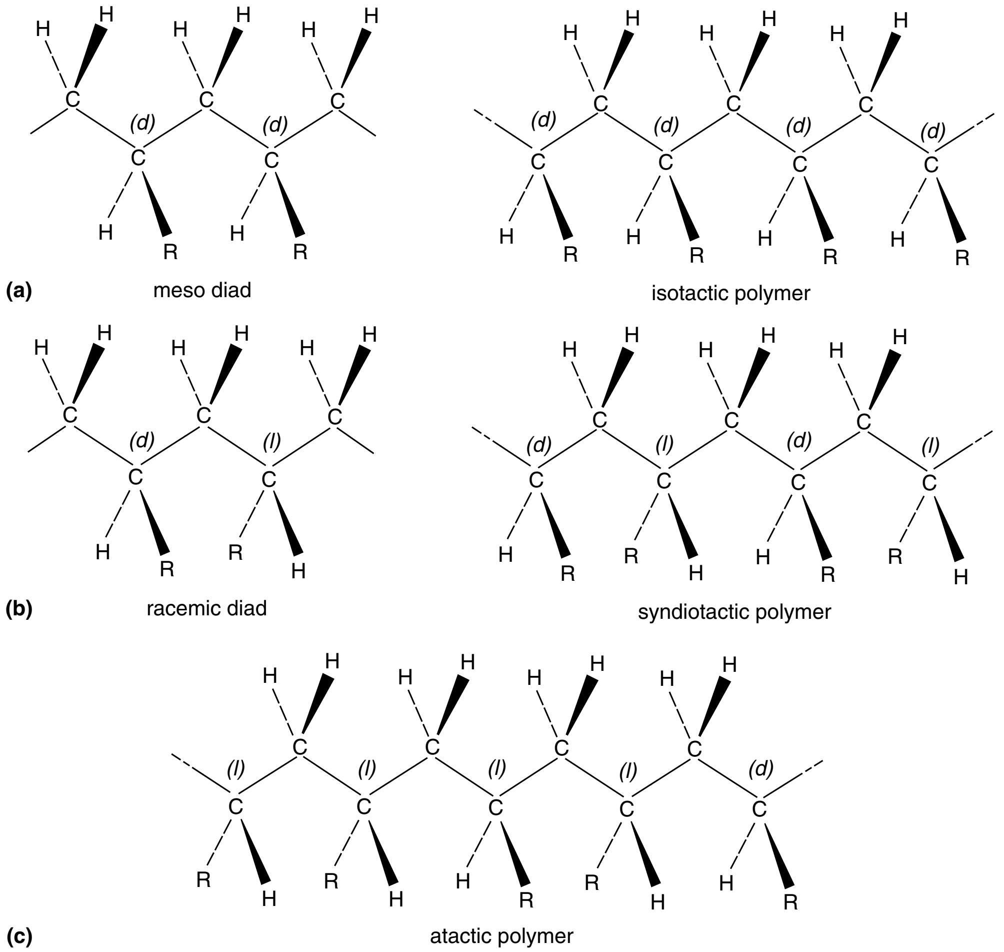
Please note that in this chapter, in the previous edition of this handbook, we had listed examples from published articles in Tables 1.1–1.8. Most of the topics discussed at that time were new and emerging. Since that time, publications in each of these topics have been numerous and cannot be accommodated 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 $[(CH_2)\text{—}(CHR)]_n$ 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


(a) meso diad

isotactic polymer

(b) racemic diad

syndiotactic polymer

(c) atactic polymer

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 (*rrrr*) 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 synthetic 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 anioinic 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(aklyl methacrylate)s	Ester group: -CH_2CH_3: $mr = 87.2\%$; $M_n = 7010$; $M_w/M_n = 1.08$ -$CH_2CH_2CH_2CH_3$: $mr = 87.1\%$; $M_n = 9300$; $M_w/M_n = 1.07$ -$CH_2CH(CH_3)_2$: $mr = 78.4\%$; $M_n = 6350$; $M_w/M_n = 1.07$ -$CH(CH_3)_2$: $mr = 69.2\%$; $M_n = 4730$; $M_w/M_n = 1.07$ 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: $mm = 95\%$; $M_v = 115,000$ 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_2H_5: 90% $CH(CH_3)_2$: 92% $(CH_2)_3CH_3$: 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: $rr = 88\%$, $mr = 9\%$; $M_v = 93,000$ 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-carbazolylethyl 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%; $M_w = 13.9.10^4$; $M_w/M_n = 1.3$; $T_g = 78\,°C$	[141]
Poly(cyclodecyl methacrylate)	*rr*: 67%, (*mr*+ *rm*): 30%; $M_w/M_n = 1.7$; $T_g = 58\,°C$	[141]
Poly(cyclododecyl methacrylate)	*rr*: 63%, (*mr*+ *rm*): 34%; $M_w = 9.8 \cdot 10^4$; $M_w/M_n = 1.4$; $T_g = 56\,°C$	[141]
Poly(cycloheptadecyl methacrylate)	$rr = 67\%$, (*mr*+ *rm*): 31%; $M_w/M_n = 1.6$; $T_g = 56\,°C$	[141]
Poly(cyclooctyl methacrylate)	*rr*: 63%, (*mr*+ *rm*): 34%; $M_w = 12.1 \cdot 10^4$, $M_w/M_n = 1.4$; $T_g = 73\,°C$	[141]
Poly(cyclopentyl methacrylate)	*rr*: 66%, (*mr*+ *rm*): 32%; $M_w = 11{:}0 \cdot 10^4$, $M_w/M_n = 1.2$; $T_g = 75\,°C$	[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)	$mr = 67.8\%$, $rr = 20.6\%$, $mm = 11.6\%$; $M_n = 11640$; $M_w/M_n = 1.09–1.14$; $T_g = 102.2\,°C$; Various *mr* and *rr* contents result depending on the synthetic conditions.	[32]
Isotactic poly(methyl methacrylate)	$mm > 98\%$; $M_w = 115\,000$; $M_w/M_n = 2.8$	[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%; $M_n = 33030$, $M_w/M_n = 1.25$ Stereocomplexation with syndiotactic methacrylates discussed.	[24]
Isotactic poly(methyl methacrylate)-*b*-poly (ethylmethacrylate)	*DP*: 59/59, 97/151, 64/182; *mm* = 95–97%; $M_w/M_n = 1.29{-}2.11$	[142,144]
Isotatic poly(methyl methacrylate)-*b*-poly (ethylmethacrylate)-*b*-poly (methyl methacrylate)-*b*- Poly(methylmethacrylate-*b*-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)-*co*-poly(ethylmethacrylate)	*mm* = 96–97%; MMA/EMA 78/22 to 26/74; $M_w/M_n = 1.53{-}3.57$	[142]
Poly(iso-MMA-*b*-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 *n*-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 $T_m = 186\,^\circ\mathrm{C}$.	[148] [for the crystal structure of the hydrogenated polymer, poly (4-methyl-1-pentene), see 149]
Isotactic poly(1-pentene)	*mmmm* (pentad) = 90%; $M_w = 17\,000$; $M_w/M_n = 2.3$; $T_m = 64\,^\circ\mathrm{C}$; x ray and NMR data.	[150]
Syndiotactic poly(1-pentene)	*rrrr* (pentad) = 85%; $M_w = 65000$; $M_w/M_n = 3.0$; $T_m = 42\,^\circ\mathrm{C}$; $T_g = -22.7\,^\circ\mathrm{C}$; 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	*rrrr* 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, mm = 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	*rr*>98%, *rrrrrr*>94%; NMR, IR and x ray diffraction results discussed; $T_m \approx 270$ °C.	[13,155]
Syndiotactic polystyrene	*rr*>98%	[14]
Syndiotactic polystyrene	*rrrr*>96%; T_m = 260−270 °C; IR and Raman spectroscopic studies of local chain conformation in glass and gels.	[156,157]
Isotatic polystyrene	*m*>95%; T_m = 230 °C; IR and Raman spectroscopic studies of local chain conformation in glass and gels.	[157]
Heterotactic poly(vinyl alcohol)	*mr* = 67%; *mm* = 18%; *rr* = 15%	[158]
Isotactic poly(2-vinyl pyridine)	*mm*>98% Cystallization and melt behavior discussed. M_v = 400000; maximum spherulite growth rate at T_c = 165 °C; $T_m{}^\circ$ = 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].

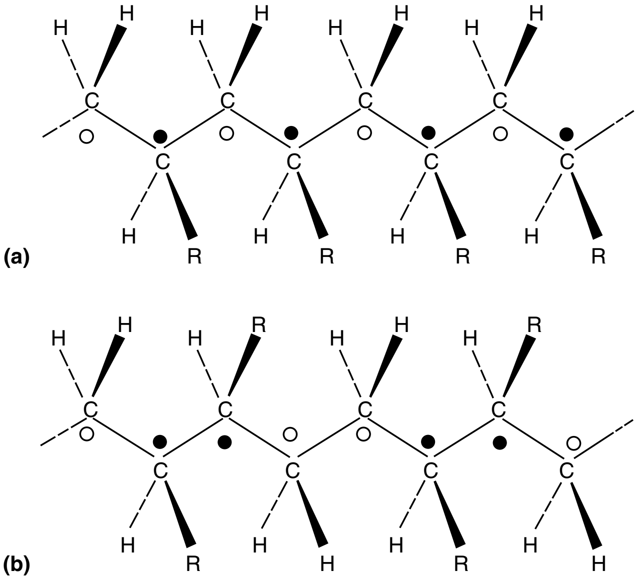


FIGURE 1.2. Schematic of the (a) head-to-tail and (b) head-to-head/tail-to-tail placements. Note the sequence of the "markers", ○●○●○● in (a) versus ●●○○●● in (b).

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}*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-dipyrromethene 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 solubility and processibility. 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.

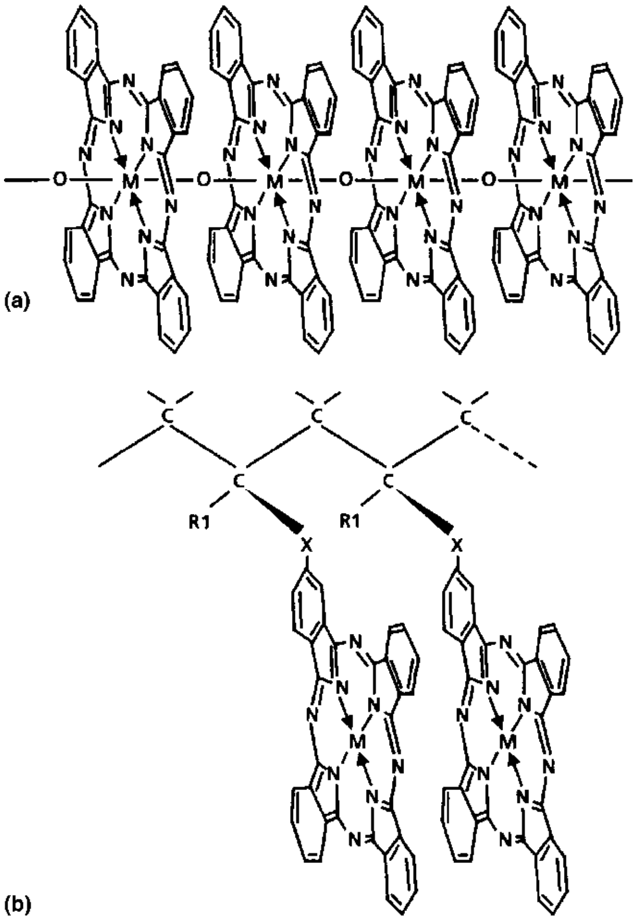


FIGURE 1.3. The main chain and side chain polymers incorporating metallophthalocyanines are shown schematically. (a) The main chain formed by linking the metallo-PC units, with an oxygen atom, leading to a cofacial arrangement of the macrocyclic rings. Flexible spacers can also be used instead of a single 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.

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) Poly(5-[4-(methacryloyloxy)phenyl]-10,15,20-triphenylporphyrin) Poly(methylmethacrylate-*co*-5-[4-(methacryloyloxy) phenyl]10,15,20-triphenylporphyrin)	Polyacrylate or methacrylate polymers with pendant porphyrin units; hypochromism and hyperchromism discussed.	[160]
Poly[porph-O-CH_2-](I) Poly[porph-O-$(CH_2)_6$-](II) Poly[porph-O-$(CH_2)_8$-](III) Poly[porph-O-$(CH_2)_8$-](IV)	Main chain porphyrin polymers; meso-tetraarylporphyrins used; I, II, III with CH_3 substituted Porph; IV with CH_2CH_3 substitution; III and IV also with Co, Mn, and Zn transition metals.	[161]
Poly[$(\text{O-porph-O-CH}_2)_x$-*co*-$(\text{O-bisph-O-CH}_2)_y$] Poly[$(\text{porph-O-CH}_2\text{-O})_x$-*co*-$(\text{bisph-O-CH}_2\text{-O})_y$]	Main chain porphyrin polymers; various copolymer compositions; M_w up to 125 000; Co and Cu transition metal inclusion with some copolymers.	[161a]
$(\text{Porph-Ph-porph})_3$ 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-$(\text{ZnPorph})_3$-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]	Co-facial packing of Pc rings; spectroscopy, electrical conductivity, electron microscopy, effect of doping discussed.	[165]
Poly[(SiPc)-O] Poly[(GePc)-O] Poly[(SnPc)-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 A for the two samples.	[170]
Poly(CH_2-CHCOOROPc)*R*: C_8H_{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-$(CH_2)_4$-$Si(C_6H_5)_2$-$(CH_2)_4$-O] Poly[(SiPc)-O-$(CH_2)_4$-$Si(CH_3)_2$-C_6H_4-$Si(CH_3)_2$-$(CH_2)_4$-O] Poly[(SiPc)-O-$(CH_2)_4$-$Si(CH_3)_2$-$(\text{O-Si(CH}_3)_2)_4$-$(CH_2)_4$-O] Poly[(SiPc)-$(\text{Si(CH}_3)(\text{C}_6\text{H}_5))_n$] ($n \approx 6.6$)	Main chain Pc polymers; symmetric and unsymmetric alkyl substituted Si phthalocyanines; absorption and emission spectroscopy, optical properties, cyclicvoltammetry 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-methoxy9,10,16,17,23,24, hexakis (dodecyloxy)phthalocyanine] (*polyundecyloxy methacrylate with side chain metal-free phthalocyanine*)	Langmuir-Blodgett monolayer formation studied with IR, ellipsometry, electron diffraction; effect of adding 1-arachidic acid discussed.	[177]
Poly(perylene imide): Poly(perylene-*R*) *subtituted perylenes*; *R*: *Linkage*: $(CH_2)_9$ or Ph-O-Ph or Ph-CH_2-Ph	Main chain perylene polyimide; M_w up to 64 100; soluble in various solvents; absorption, fluorescence spectra discussed.	[178]
Poly(4′-dialkylamino-4-nitrostilbene acrylate-*b*-methyl methacrylate) Poly(4′-dialkylamino-4-nitrostilbene methacrylate-*b*-methyl methacrylate) Poly(4′-dialkylamino-4-nitroazobenzene methacrylate-*b*-methyl methacrylate)	Polyacrylates with NLO active side chains; wide range of M_w up to 186 000; many soluble in methylene chloride or THF; two samples show liquid crystallinity; microscopy and thermal analysis discussed.	[179]
Poly[(R,R)-dibenzo-19-crown-6] Poly[(S,S)-dibenzo-19-crown-6]	Polymeric chiral crown ethers; hostguest complexation discussed.	[180]

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 C_{60} 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 C_{60} has also been reported [69]. A brief summary of polymer related fullerene work was given by Hirch [70]. Chemical derivitization of C_{60} has been described by Petrie *et al.* [71]. A summary of the initial work on polymers incorporating C_{60} 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 $C_{60}(C_6H_5\text{-}CH_3)_{12}$, respectively.	[181]
C_{60}-*p*-xylylene copolymer	Cross-linked; insoluble; xylylene/C_{60} rato: 3.4:1.0 Solid state NMR spectra discussed.	[182]
Poly(4,4′-diphenyl-C_{61} sebacate)	Side chain C_{60} polymer; 61% yield; soluble in nitrobenzene, benzonitrile; NMR, IR, cyclic voltammetry are discussed.	[183]
Poly(bisphenol *A* hexamethyleneurethane-C_{61})		[183]
Poly(ethylene imine-C_{60})	Side chain C_{60} polymer; molar mass 35 000 $\text{g}\,\text{mol}^{-1}$; 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 $\text{g}\,\text{mol}^{-1}$; 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% ($T_g = 112\,^\circ\text{C}$), 21% ($T_g = 142\,^\circ\text{C}$) and 29% ($T_g = 166\,^\circ\text{C}$) (w/w) of C_{60}; $M_w = 38500$; single T_g; soluble in methylenechloride, THF.	[187]
Poly(RbC_{60}) and poly(KC_{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; $T_g = 52\,^\circ\text{C}$ (13° higher thanstarting 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 oligmers 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 elatomeric 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-(4hydroxyphenyl)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].

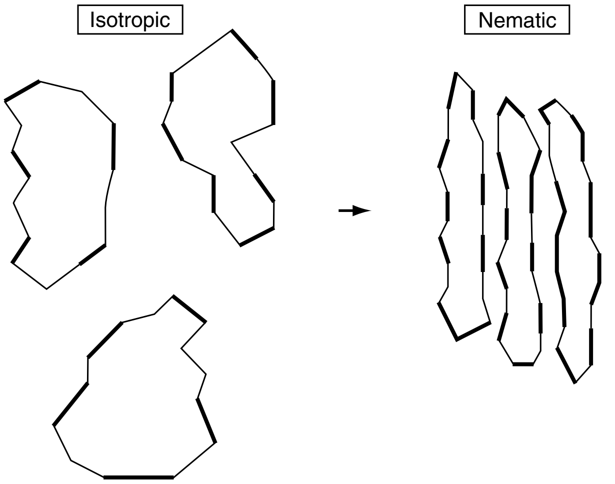


FIGURE 1.4. A model of the isotropic → nematic transition in cyclic oligomeric polyethers via intramolecular collapse of the cyclic.

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

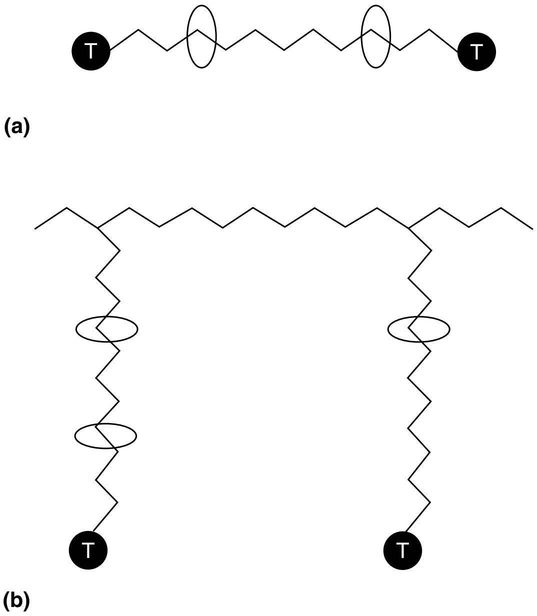


FIGURE 1.5. A schematic representation of the (a) main chain and (b) side chain rotaxanes. The *T* represents a large terminal group which may be used to prevent dethreading of the cyclic from the chain.

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(*n*-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. Calculations with RIS models.	[83]
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-b-styrene-*b*-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(n-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 cycllcs; 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, $T_m = 182\,^\circ\mathrm{C}$	[206]
Polyester [-$(CH_2)_{10}$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-*tri*oxacyclooctane	1–9	T_m for $x = 2$: $60\,^\circ\mathrm{C}$ $x = 4$: $35\,^\circ\mathrm{C}$ $x = 6$: $40\,^\circ\mathrm{C}$ K_x given.	[213]
(2R,5R,8R,11R)-2,5,8,11-tetra-tertbutyl-1,4,7,10- tetraoxa cyclododecane	4	$T_m = 168\,^\circ\mathrm{C}$ NMR, conformation discussed.	[214]
1,3,6,9,12,15-hexa oxacycloheptadecane	1–5		[213]
1,3,6,9,12-penta oxacyclotetradecane	1–7	T_m for $x = 2$: $44\,^\circ\mathrm{C}$ $x = 4$: $61\,^\circ\mathrm{C}$	[213]
1,3,6,9-tetra oxacycloundecane	2–8		[215]

TABLE 1.6. *Continued.*

Polymer	Number of monomers in cyclic	Remarks	Reference
1,3,6,9-tetra oxacycloundecane	1–8	T_m for $x = 2$: 88 °C $x = 4$: 54 °C $x = 6$: 39 °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 $[NaPO_3]_x$	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_w12 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*]-[*n*]-[*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 fragments 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

TABLE 1.7. *Poly(rotaxanes).*

Poly(rotaxane)	Remarks	Reference
Poly(amide)-*rotaxa*-β-cyclodextrin	Rotaxane becomes insoluble; no melting observed in DSC before decomposition.	[227]
Poly(ethylene glycol)-*rotaxa*-α-cyclodextrin	PEG M_w from 400 to 10 000 studied; complexation in aqueous solution at room temperature; maximum complexation with $M_w = 1000$; two ethylene glycol units/α-CD cavity; x ray study leads to an extended columnar structure.	[228]
Poly(ethylene glycol) bisamine-*rotaxa*-α-cyclodextrin	PEG end capped with 2,4-dinitrofluorobenzene after complexation in aqueous solution; 20–23 alpha-CD molecules entrapped on each chain; rotaxane is insoluble in water; hydrogen bonds between entrapped alpha-CD's suggest alternating face-to-face, back-to-back arrangement of the CD's.	[229,230]
Poly(iminoundecamethylene)-*rotaxa*-α-cyclodextrin Poly(iminoundecamethylene)-*rotaxa*-heptakis(2,6-di-O-methyl)-β-cyclodextrin Poly(iminotrimethylene-iminodecamethylene)-*rotaxa*-α-cyclodextrin Poly(iminotrimethylene-iminodecamethylene)-*rotaxa*-heptakis(2,6-di-O-methyl)-β-cyclodextrin	A nicotinoyl group was used for endcapping to prevent dethreading.	[231]
Poly(isobutylene)-*rotaxa*-β-cyclodextrin Poly(isobutylene)-*rotaxa*-γ-cyclodextrin	Complex formed in water although PIB is insoluble in it; complexation with β-and γ-CD's show opposite dependence on M_w of PIB. More than 90% yield with γ-CD and PIB M_w between 800 and 1350.	[232]
Poly(propylene glycol)-*rotaxa*-β cyclodextrin Poly(propylene glycol)-*rotaxa*-α cyclodextrin	96% yield with PPG $M_w = 1000$ and beta-CD and decreases with increasing M_w. Two PPG repeat units per β-CD. More than 70% yield with PPG M_w 400–1000 and γ-CD. Complexation in aqueous solution at room temperature.	[233]
Polyvinylidene chloride-*rotaxa*-β cyclodextrin	*In situ* polymerization; x ray diffraction of the inclusion compound discussed.	[234,235]
Poly(azomethine)-*rotaxa*-42-crown-14	*p*-tri(*p*-*t*-butylphenyl) derivatives used as blocking groups; liquid crystalline; T_m is 67 °C, and smectic between 67 and 73 °C. $T_i = 123$ °C. Parent polymer is insoluble; polyrotaxane is soluble in chloroform, acetone, etc.	[236]
Poly(butylene sebacate)-*rotaxa*-(30-crown-10) Poly(butylene sebacate)-*rotaxa*-(60-crown-20)	With and without a triarylmethyl derivative as blocking group; efficiency of threading depends on size of the macrocycle; blocking group is not always needed for stability.	[237]
Poly(decamethylene sebacate)-*rotaxa*-(30-crown-10)		[238]
Polystyrene-*rotaxa*-bisparaphenylene-34-crown-10	With a triphenyl blocking group; free-radical and anionic polymerizations.	[239]
Polystyrene-*rotaxa*-30-crown-10	Two T_g's observed.	
Poly(triethyleneoxy sebacate)-*rotaxa*-(30-crown-10) Poly(triethyleneoxy sebacate)-*rotaxa*-(60-crown-20)	With and without a triarylmethyl derivative as blocking group; efficiency of threading depends on size of the macrocycle; blocking groups is not always needed for stability.	[237]
Poly(urethane-*rotaxa*-bis(*p*-phenylene)-34-crown-10	Segmented polyurethane; host-guest complexation approach; 80% threading efficiency.	[240]
Poly(urethane)-*rotaxa*-(60-crown-20) Poly(urethane)-*rotaxa*-(36-crown-12)	Statistical threading approach; threading efficiency 57% with 60Cr20 and 16% with 36Cr12. T_g of rotaxanes (−28 °C for 60Cr20 and 19 °C for 36Cr12) lower than the parent polymer (51 °C).	[241]

m-crown-*n* refers to a crown ether containing *m* backbone atoms, with *n* oxygen atoms. α,β,γ- cyclodextrins: cyclics with 6, 7, and 8 α-1, 4′-*D*-glucose units, respectively.

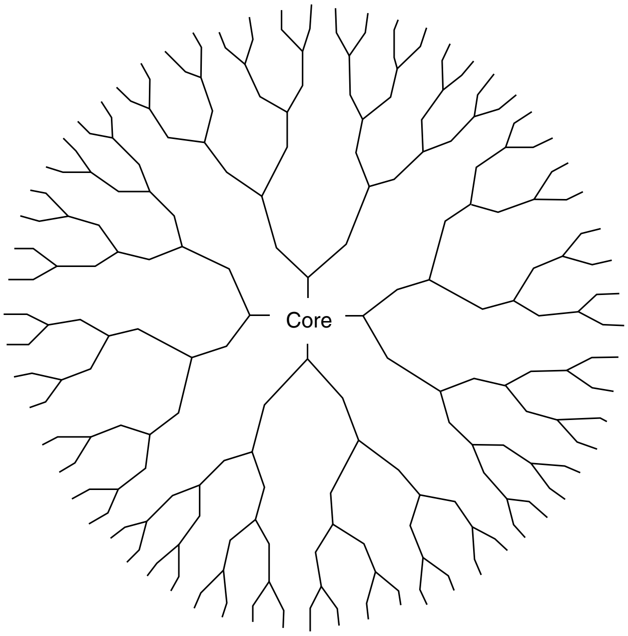


FIGURE 1.6. A schematic representation of a symmetric dendrimer.

dendrimer structures. Tomalia *et al*. [123] and Fréchet [128] also discuss the similarities and differences between starburst dendrimers and other starbranched or hyperbranched systems. While they are similar in terms of a core, radial branches, and perhaps telechelic functionality, the structure of hyperbranched polymers is neither regular nor highly symmetrical. The branch-segment densities decrease from the core in a concentric radial fashion in the case of starbranched systems. On the other hand, in the case of starburst dendrimers with symmetrical branch cells and topologies, the density increases with generations and it remains constant for the asymmetrically branched starburst dendrimers.

Other physical properties which contrasts them with linear polymers are [126] (1) the radius of gyration of a dendrimer is larger than that of a linear chain with the same M_w; (2) the T_g depends on the terminal groups as well as on the nature of the repeat unit blocks; (3) the high degree of branching prevents any interchain entanglements; and (4) the Mark-Houwink type relationship between M_w and intrinsic viscosity does not apply. The hydrodynamic radius increases more rapidly with generations than the radius of gyration.

Wooley *et al*. [138] made a systematic study of the glass transition temperatures of several types of dendrimers. They also derived an equation to relate the T_g of a dendrimer to $T_{g\infty}$ corresponding to infinite molecular weight:

$$T_g = T_{g\infty} - K'(n_e/M), \tag{1.1}$$

here n_e is the number of chain ends per molecule, M is the molecular weight, and K' includes several parameters such as the free volume per chain end, etc. It was found that the nature of the chain ends dramatically affects the T_g and that the latter increases with the polarity of the chain ends. The internal composition, as in the case of block copolymer dendrimers, also influences the T_g.

A summary of various published dendritic structures is given in Table 1.8.

TABLE 1.8. *Polymeric dendrimers.*

Dendrimer	Remarks	Reference
Acid-terminated dendrimers	*Z*- cascade:methane[4]:(3-oxo-6-oxa-2-azaheptylidyne):(3-oxo-2-azapentylidyne):propanoic acids. Five generations; pH dependence of hydrodynamic radii discussed.	[242]
Ammonium ion dendrimers		[243]
Aramid dendrimers	Fully aromatic amide dendrimers; 1,3,5-benzenetricarboxamide core; 3,5-dicarboxamidophenyl repeat units; phenyl or 3,5-dit-butyl isophthalate termini. Molecular modeling showed that the conformations of the isophthalate segment lead to the either open or conjested structure.	[244]
Aryl ester dendrimers	Based on symmetrically substituted benzenetricarboxylic acid esters; convergent synthesis; four generations.	[245]
Carbosilane dendrimers	Tetravinylsilane as the core; dichloromethylsilane as the propagating unit; four generations; M_w,[η] discussed.	[246]
"Comb burst" dendrimer	Backbone: styrene/divinylbenzene copolymer; teeth: triethanolamine; ion exchange material (anionic: core and branch points, cationic: termini).	[247]
Crown ether dendrimers	Based on *N*-benzyloxycarbonyl-1,4,10,13-tetraoxa-7,16 diazacyclooctadecane and with trichloroformyl mesitylene as core.	[248]
Dendrimer-*b*-polyethyleneglycol-*b*-dendrimer	Third and fourth generation polyether dendrimers used; DP of PEG from 24 to 447: M_w of copolymers 3600–20 300; $M_w/M_n \leq 1.1$; size and shape of the block copolymers discussed.	[249, see also 250 for further characterization]

TABLE 1.8. *Continued.*

Dendrimer	Remarks	Reference
Dendrimer-*b*-polyethyleneoxide-*b*-dendrimer Dendrimer-*b*-polyethyleneglycol-*b*-dendrimer	Polyether dendrimers from Hawker and Fréchet [132] used; reactivities in the melt and solution discussed.	[2, 49, 250]
Phosphonium dendrimers	Based on tris(*p*-methoxymethylphenyl)phosphine.	[250a, see also 250]
Phenylene dendrimers	1,3,5-phenylene based hydrocarbon dendrimers; $M_w/M_n = 1.08$; soluble in common organic solvents; spectroscopy, thermal analysis described.	[253]
Phenyl acetylene dendrimer	94 monomer units ($C_{1134}H_{1146}$); 3,5-di-*tert*-butylphenyl peripheral group; $M_w = 14776$; $M_w/M_n = 1.03$; soluble in pentane.	[254,255]
Propylene imine dendrimers	Method for large scale (several Kg) synthesis presented; diaminobutane as the core; NH_2 or CN end groups; five generations; T_g, viscosity discussed.	[256]
Quaternary ammonium ion dendrimer	36 terminal trimethylammonium groups, catalysis applications discussed.	[257]
Trimethylene imine dendrimers	Ammonia as the initiator core; nitrile or amine end groups; five generations.	[258]
Aromatic polyamide dendrimers	Lyotropic.	[136]
Polyamide dendrimers	Three polyamides with the same internal hierarchical architectures but with either acidic, neutral or basic terminal functionality; 5 generations, 972 terminal groups in 5th gen.; the polymers shrink or swell upon pH change (“smart behavior”).	[259]
Polyamido amine dendrimers	Ethylenediamine or ammonia core, *N*-(2-aminoethyl)acrylamide repeat units, seven generations; $M_w = 43\ 451$ with ammonia core, 57 972 with ethylenediamine core.	[260, 261]
	With CO_2Me or NH_2 head groups; hydrodynamic radii ($[\eta]$-M_w measurement), and surface area with generations discussed.	[262–264]
Polyarylamines	Based on 2,4-dinitrofluorobenzene and anilines. Complexation with iodine; T_m and cyclic voltammetry discussed.	[265]
Polyester dendrimers	Based on 3,5-bis(trimethylsiloxy) benzoyl chloride; M_w from 30 000 to 200 000; M_w and dispersity depend on temperature; 55 to 60% branching.	[266]
Polyester dendrimers	Hyperbranched aromatic polyesters based on 5-acetoxyisophthalic acid ($T_g = 239\,^\circ C$) and 5-(2-hydroxyethoxy)isophthalic acid ($T_g = 190\,^\circ C$); Carboxylic acid terminal groups; degree of branching: 50%; $[\eta]$, polyelectrolyte properties discussed.	[267]
Polyether dendrimer	3,5-dihydroxybenzyl alcohol monomer unit reacted with benzylic bromide; 1, 1, 1-tris(4′ hydroxyphenyl)ethane core; six generations; $M_w = 154\ 000$; $M_w/M_n = 1.02$.	[131, 132]
Polyether dendrimer	Size exclusion chromatography, $[\eta]$-M_w relationship; linear dependence of hydrodynamic radii on generation; a characteristic maximum in $[\eta]$ observed; samples from Hawker and Fréchet [131, 132] used.	[268]
Polyether dendrimer (thermotropic)	Dibromalkanes with 1-(4-hydroxy-4′-biphenylyl-2-(4-hydroxyphenyl); 6–10 methylene units as flexible spacers; those with 6, 8, and 10 CH_2 units or with benzyl chain end exhibit nematic mesophase.	[108]
Polyether dendrimers (thermotropic)	Monomers: 6-bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)hexane (TPH); 13-bromo-1-(4-hydroxyphenyl)-2- [4-(6-hydroxy-2-naphthalenylyl)-phenyl]tridecane (BPNT); 13- bromo-1-(4-hydroxyphenyl)-2-(4-hydro-4″-*p*- terphenylyl)tridecane (TPT); Chain ends: benzyl or allyl or alkyl. TPH and BPNT show narrow nematic meosphase; TPT nematic mesophase extends over 82 °C. Degree of branching for TPT with allyl end is 0.82.	[137]

TABLE 1.8. *Continued.*

Dendrimer	Remarks	Reference
Polyether-*b*-polyester dendrimer	3,5-dihydroxybenzyl alcohol as monomer for ether-linked fragments and 2,2,2-trichloroethyl 3,5-dihydroxybenzoate for ester linked fragments; radially alternating the dendritic segments produced segmented-block polymer and concentric alternation gave layer-block polymer; spectroscopy, thermal characterization described.	[269]
Polyether dendrimer-styrene copolymer	Copolymer of the type poly[(styrene)$_y$-co-(styrene-G-4)$_x$] where the fourth generation dendrimer is *p*-linked to styrene.	[270]
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]
Polyphenylene dendrimer	Carboxylate form is water soluble. complexation with *p*-toluidine reported.	[271]
Polyphenolic dendrimers	A double stage convergent synthesis is described; a ‘hypercore’ based on 4,4- bis(4′-hydroxyphenyl)pentanol.	[134]
Silane dendrimers	Tetraallylsilane as the zeroth generation; five generations synthesized ($C_{4368}H_{7764}Si_{485}$).	[272, 273]
Silicone dendrimers		[274]
Polysiloxysilane dendrimers		[275]
Polysiloxane dendrimers	Tris-[(phenyldimethylsiloxy) dimethylsiloxy]methylsilane core; bis[(phenylimethylsiloxy)methyl siloxy] dimethylsilanol as the building block; Three generations; $[\eta]$-M_w relationship/Mark-Houwink constants, NMR, molecular diameter discussed; $M_w/M_n \leq 1.1$.	[276]
Siloxane starburst dendrons and dendrimers	Allylbis[4-(hydroxydimethylsily)phenyl]-methylsilane as the building block; Four generations; $[\eta]$-M_w relationship and T_g reported.	[277]

1.9 SUPRAMOLECULAR POLYMERS

Using molecular recognition and self-assembly to construct macromolecules and to design devices using macromolecules is emerging as a fertile area of research. Both covalent and noncovalent bonding are used to this end. Along with interactions such as hydrogen bonding, charge transfer complex, ionic bonding, etc. the secondary and tertiary structures can be designed in a controlled and reversible manner [278–285]. Chain folding as a precursor to self-assembly has also been realized. Sequences of rigid hydrophobic chromophores, linked by flexible hydrophilic segments, fold and unfold [286]. While the intramolecular interaction between the chromophores leads to chain folding, intermolecular attractions favor self-assembly. Incorporating a specific "foldamer" [287] to cause, for example, a U turn in the polymer structure has been accomplished [288,289]. The possibilities for molecular architectures are thus endless.

ACKNOWLEDGMENTS

Financial support by the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

REFERENCES

1. D. H. Reneker, W. L. Mattice, and R. P. Quirk, Smart Mater. Struct. **1,** 84 (1992).
2. M. V. Gandhi and B. S. Thompson, *Smart materials and Structures* (Chapman & Hall, London, 1992).
3. B. C. Crandall and J. Lewis, Eds. *Nanotachnology: Research and Perspectives* (The MIT Press, Cambridge, MA, 1992).
4. “*New Macromolecular Architectures*,” Macromol. Symp., vol. 77, 1994.
5. *Abstracts of the 35th IUPAC International Symposium on Macromolecules*, Akron, Ohio, July 11–15, 1994.
6. P. J. Flory, *Statistical Mechanics of Chain Molecules* (John Wiley, NY, 1969), Chapter VI (republished by Hanser Publishers, 1988).
7. E. Lemieux, R. E. Prud’homme, R. Forte, *et al*., Macromolecules **21,** 2148 (1988).
8. G. Beaucage and R. S. Stein, Macromolecules **26,** 1609, 1617 (1993).
9. G. Beaucage, R. S. Stein, and R. Koningsveld, Macromolecules **26,** 1603 (1993).
10. B. Wunderlich, *Macromolecular Physics*, Volume 1 (Academic Press, New York, 1973).
11. H. Tadokoro, *Structure of Crystalline Polymers* (John Wiley & Sons, New York, 1979).
12. S.-N. Zhu, T. Asakura, and R. Chûjô, Polym. J. **16,** 895 (1984).
13. N. Ishihara, T. Seimiya, M. Kuramoto, *et al*., Macromolecules **19,** 2464 (1986).
14. C. Pellecchia, P. Longo, A. Grassi, *et al*., Makromol. Chem., Rapid Commun. **8,** 277 (1987).
15. P. Corradini, G. Natta, P. Ganis, *et al*., J. Polym. Sci., Part C **16,** 2477 (1967).
16. A. Immirzi, F. de Candia, P. Iannelli, *et al*., Makromol. Chem., Rapid Commun. **9,** 761 (1988).

16a. O. Greis, Y. Xu, T. Asano, *et al*., Polymer **30,** 590 (1989).

17. V. Vittoria, Makromol. Chem., Rapid Commun. **9,** 765 (1988).
17a. V. Vittoria, R. Russo, and F. de Candia, J. Macromol. Sci., Phys. **B28,** 419 (1989).
18. P. Corradini, R. Napolitano, and B. Pirozzi, Eur. Polym. J. **26,** 157 (1990).
18a. G. Guerra, V. M. Vitagliano, C. De Rosa, *et al*., Macromolecules **23,** 1539 (1990).
18b. Z. Sun and R. L. Miller, Polymer **34,** 1963 (1993).
19. M. A. Gomez and A. E. Tonelli, Macromolecules **23,** 3385 (1990).
20. A. J. Lovinger, B. Lotz, and D. D. Davis, Polymer **31,** 2253 (1990).
21. A. J. Lovinger, B. Lotz, D. D. Davis, *et al*., Macromolecules **26,** 3494 (1993).
22. C. De Rosa and P. Corradini, Macromolecules **26,** 5711 (1993).
23. A. M. Liquori, G. Anzuino, V. M. Coiro, *et al*., Nature (London) **206,** 358 (1965).
24. K. Hatada, T. Kitayama, K. Ute, *et al*., Macromol. Symp. **84,** 113 (1994).
25. R. Buter, Y. Y. Tan, and G. Challa, J. Polym. Sci., Part A-1 **10,** 1031 (1972).
26. R. Buter, Y. Y. Tan, and G. Challa, J. Polym. Sci., Polym. Chem. Ed **11,** 1003, 1013 (1973).
27. R. H. G. Brinkhuis and A. J. Schouten, Langmuir **8,** 2247 (1992).
27a. R. H. G. Brinkhuis and A. J. Schouten, Macromolecules **25,** 2717, 2725, 2732 (1992).
28. K. Hatada, S. Shimizu, Y. Terawaki, *et al*., Polym. J. **13,** 811 (1981).
29. K. Hatada, K. Ute, K. Tanaka, *et al*., Polym. J. **17,** 977 (1985).
30. K. Hatada, K. Ute, K. Tanaka, *et al*., Polym. J. **18,** 1037 (1986).
31. K. Ute, N. Miyatake, T. Asada, *et al*., Polym. Bull. **28,** 561 (1992).
32. T. Kitayama, Y. Zhang, and K. Hatada, Polym. Bull. **32,** 439 (1994).
33. T. Kitayama, Y. Zhang, and K. Hatada, Polym. J. **26,** 868 (1994).
34. Ph. Teyssié, R. Fayt, J. P. Hautekeer, *et al*., Makromol. Chem., Macromol. Symp. **32,** 61 (1990).
35. Ph. Teyssié, R. Fayt, C. Jacobs, *et al*., Polym. Preprints **32**(1), 299 (1991).
36. P. Bayard, R. Jérôme, Ph. Teyssié, *et al*., Polym. Bull. **32,** 381 (1994).
36a. D. Baskaran, Prog. Polym. Sci. **28**, 521 (2003).
37. J. S. Wang, R. Jérôme, and Ph. Teyssié, Macromolecules **27,** 4902 (1994).
38. T. Asanuma, Y. Nishimori, M. Ito, *et al*., Polym. Bull. **25,** 567 (1991).
39. M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, *et al*., TRIP **2,** 66 (1994).
40. M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, *et al*., Macromolecules **26,** 2987 (1993).
41. M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, *et al*., Macromolecules **27,** 7228 (1994).
42. R. P. N. Veregin, M. K. Georges, P. M. Kazmaier, *et al*., Macromolecules **26,** 5316 (1993).
43a. A. Szkurhan and M. K. Georges, Macromolecules **37**, 4776 (2004).
43b. K. Matyjaszewski, Chem. Eur. J. **5**, 3095 (1999).
43c. K. Matyjaszewski and J. Xia, Chem. Rev. **101**, 2921 (2001).
43d. V. Coessens, T. Pintauer, and K. Matyjaszewski, Prog. Polym. Sci. **26**, 337 (2001).
43e. K. Matyjaszewski and J. Spanswick, Materials Today (Elsevier) March 2005, pp. 26
43f. M. Kamigaito, T. Ando, and M. Sawamoto, Chem. Rev. **101**, 3689 (2001).
43g. M. Sawamoto and M. Kamigaito, New Methods Polym. Synth. (Blackie) 37 (1995)
43h. D. Grande, J.-L. Six, S. Breunig, V. Heroguez, M. Fontanille, and Y. Gnanou, Polym. Adv. Technol. **9**, 601 (1998).
44. P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY, 1953), Chapter VI.
45. O. Vogl and S. Grossman, in: *Encyclopedia of Polymer Science and Engineering* (John Wiley & Sons, New York, 1987), Vol. **7**, pp. 626.
46. E. Földes, G. Deak, F. Tüdös *et al*., Eur. Polym. J. **29,** 321 (1993).
47. O. Vogl, J. Macromol. Sci., Chem. **A21,** 1725 (1984).
48. S. Arichi, M. Y. Pedram, and J. M. G. Cowie, Eur. Polym. J. **15,** 107, 113 (1979).
49. C. Strazielle, H. Benoit, and O. Vogl, Eur. Polym. J. **14,** 331 (1978).
50. P. Hattam, S. Gauntlett, J. W. Mays, *et al*., Macromolecules **24,** 6199 (1991).
51. Y. Okamoto, K. Suzuki, K. Ohta, *et al*., J. Am. Chem. Soc. **101,** 4763 (1979).
52. Y. Okamoto, I. Okamoto, and H. Yuki, J. Polym. Sci., Polym. Lett. Ed. **19,** 451 (1981).
53. L. Cavallo, P. Corradini, and M. Vacatello, Polym. Commun. **30,** 236 (1989).
54. R. D. Miller and J. Michl, Chem. Rev., **89,** 1359 (1989).
55. F. C. Schilling, F. A. Bovey, A. J. Lovinger, *et al*., in *Silicon-Based Polymer Science*, J. M. Zeigler and F. W. Fearon, Eds., Am. Chem. Soc., Adv. Chem. Ser. **224,** pp. 341 (1990).
56. A. R. Wolff, I. Nozue, J. Maxka, *et al*., J. Polym. Sci., Polym. Chem. Ed. **26,** 701 (1988).
57. W.-K. Chan, Y. Chen, Z. Peng, *et al*., J. Am. Chem. Soc. **115,** 11735 (1993).
58. S. R. Marder and J. W. Perry, Science **263,** 1706 (1994).
59. A. V. Tkachev, V. A. Tverskoi, and V. P. Zubov, New Polymeric Mater. **3,** 187 (1992).
60. E. V. Anufrieva, O. V. Tcherkasskaya, M. G. Krakovyak, *et al*., Macromolecules **27,** 2623 (1994).
61. M. A. Winnik, in *Cyclic Polymers*, J. A. Semlyen, Ed. (Elsevier, London, 1986), Chapter 9.
62. M. Adam and K. Müllen, Adv. Mater. **6,** 439 (1994).
63. H. R. Allcock, Chem. Eng. News, March **18,** 22 (1985).
64. M. J. Crossley and P. L. Burn, J. Chem. Soc., Chem. Commun., 1569 (1991).
65. R. W. Wagner and J. S. Lindsey, J. Am. Chem. Soc. **116,** 9759 (1994).
66. E. Hädicke and F. Graser, Acta Crystallogr., Sect. C **42,** 189, 195 (1986).
66a. N. B. McKeown, J. Mater. Chem. **10**, 1979 (2000).
66b. D. T. McQuade, A. E. Pullen, and T. M. Swager, Chem. Rev. **100**, 2537 (2000).
67. G. Knothe, Makromol. Chem., Theory Simul. **2,** 503 (1993).
67a. H. Segawa, N. Nakayama, F. Wu, and T. Shimidzu, Synth. Met. **55**, 966 (1993).
67b. T. Shimidzu, Pure Appl. Chem. **67**, 2039 (1995); J. Jortner, M. Ratner, Eds. *Molecular Electronics*, (1997), pp. 381; *Photonic and Optoelectronic Polymers*, ACS Symposium Series, **672**, 460 (1997).
67c. B. Jiang, S. W. Yang, S. L. Bailey, L. G. Hermans, R. A. Niver, M. A. Bolcar, and W. E. Jones, Jr., Coord. Chem. Rev. **171**, 365 (1998).
67d. W. E. Jones, Jr., L. Hermans, and B. Jiang, Mole. Supramol. Photochem. **4**, 1 (1999).
67e. J. Roncali, Acc. Chem. Res. **33**, 147 (2000).
67f. J. M. Tour, in *Stimulating Concepts in Chemistry,* F. Voegtle, J. F. Stoddart, and M. Shibasaki, Eds. (Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2000)), pp. 237–253.
67g. J. M. Tour, Polym. News **25**, 329 (2000).
67h. A. Natansohn and P. Rochon, Chem. Rev. **102**, 4139 (2002).
67i. Z. Sekkat and W. Knoll, Eds. *Photoreactive Organic Thin Films* (Academic Press, San Diego, CA, 2002)
67j. T. Seki, S. Nagano, Y. Kawashima, and N. Zettsu, Mol. Cryst. Liq. Cryst. **430**, 107 (2005).
67k. G. K. Such, R. A. Evans, and T. P. Davis, Mol. Cryst. Liq. Cryst. **430**, 273 (2005).
68. R. M. Baum, Chem Eng. News **November 22, 8** (1993).
69. C. J. Hawker, K. L. Wooley, and J. M. J. Fréchet, J. Chem. Soc., Chem. Commun., 925 (1994).
70. A. Hirsch, Adv. Mater. **5,** 859 (1993).
71. S. Petrie, G. Javahery, and D. K. Bohme, J. Am. Chem. Soc. **115,** 1445 (1993).
71a. L. Dai, Polym. Adv. Technol. **10**, 357 (1999).
71b. P. C. Eklund and A. M. Rao, Eds. *Fullerene Polymers and Fullerene Polymer Composites*. Springer Ser. Mater. Sci. (Springer, Berlin, 2000).
71c. J.-F. Nierengarten, Top. Curr. Chem. **228**, 87 (2003); J.-F. Nierengarten, New J. Chem. **28**, 1177 (2004); J.-F. Nierengarten, M. Guttierez-Nava, S. Zhang, P. Masson, L. Oswald, C. Bourgogne, Y. Rio, G. Accorsi, N. Armaroli, and S. Setayesh, Carbon **42**, 1077 (2004).
71d. C. Wang, Z.-X. Guo, S. Fu, W. Wu, and D. Zhu, Prog. Polym. Sci. **29**, 1079 (2004).
71e. S. Iijima, Nature **354**, 56 (1991); S. Iijima and T. Ichihashi, Nature **363**, 603 (1993).
71f. D. S. Bethune, C. H. Klang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers, Nature **363**, 605 (1993).
71g. A. Hirsch, Angew. Chem. Int. Ed. **41**, 1853 (2002).
71h. A. Carrillo, J. A. Swartz, J. M. Gamba, R. S. Kane, N. Chakrapani, B. Wei, and P. M. Ajayan, Nano Lett. **3**, 1437 (2003).

71i. C. A. Dyke and J. M. Tour, J. Phys. Chem., Part A, **108**, 11151 (2004).

71j. P. M. Ajayan, L. S. Schadler, and P. V. Braun, *Nanocomposite Science and Technology*. (Wiley-VCH Verlag GmbH & Co., Germany, 2003).

71k. L. Dai, Smart Mater. Struct. **11**, 645 (2002).

71l. A. M. Fennimore, T. D. Yuzvinsky, W.-Q. Han, M. S. Fuhrer, J. Cuming, and A. Zettl, Nature **424**, 408 (2003).

71m. A. Star, J.-C. Gabriel, K. Bradley, and G. Grüner, Nano Lett. **3**, 459 (2003).

72. J. A. Semlyen, Adv. Polym. Sci. **21,** 41 (1976).

73. J. A. Semlyen, in: *Cyclic Polymers*, J. A. Semlyen, Ed. (Elsevier, London, 1986), pp 1.

74. J. A. Semlyen, in: *Siloxane Polymers*, S. J. Clarson and J. A. Semlyen, Eds. (PTR Prentice Hall, NJ, 1993), Chapter 3.

74a. J. A. Semlyen, in *Cyclic Polymers*, second edition, J. A. Semlyen, Ed. (Kluwer Academic Publ., Netherlands, 2000), pp. 1.

74b. C. W. Bielawski, D. Benitez, and R. H. Grubbs, Science **297,** 2041 (2002).

74c. N. Hadjichristidis, M. Pitsikalis, S. Pispas, and H. Iatrou, Chem. Rev. **101,** 3747 (2001).

75. H. Jacobson and W. H. Stockmayer, J. Chem. Phys. **18,** 1600 (1950).

75a. H. Jacobson, C. O. Beckman, and W. H. Stockmayer, J. Chem. Phys. **18,** 1607 (1950).

76. P. J. Flory and J. A. Semlyen, J. Am. Chem. Soc. **88,** 3209 (1966).

77. J. A. Semlyen, Trans. Faraday Soc. **63,** 2342 (1967).

78. P. J. Flory, *Statistical Mechanics of Chain Molecules* (John Wiley, New York, 1969; republished by Hanser Publishers, 1988), Appendix D.

79. M. A. Winnik, R. E. Trueman, G. Jackowski, *et al*., J. Am. Chem. Soc. **96,** 4843 (1974).

80. P. J. Flory, U. W. Suter, and M. Mutter, J. Am. Chem. Soc. **98,** 5733 (1976).

81. M. S. Beevers and J. A. Semlyen, Polymer **13,** 523 (1972).

82. J. F. Brown and G. M. J. Slusarczuk, J. Am. Chem. Soc. **87,** 931 (1965).

83. J. A. Semlyen and P. V. Wright, Polymer **10,** 543 (1969).

84. P. V. Wright, J. Polym. Sci., Polym. Phys. Ed. **11,** 51 (1973).

85. L. E. Scales and J. A. Semlyen, Polymer **17,** 601 (1976).

86. U. W. Suter, M. Mutter, and P. J. Flory, J. Am. Chem. Soc. **98,** 5740 (1976).

87. D. R. Cooper and J. A. Semlyen, Polymer **13,** 414 (1972).

88. J. M. Andrews, F. R. Jones, and J. A. Semlyen, Polymer **15,** 420 (1974).

89. U. W. Suter and M. Mutter, Makromol. Chem. **180,** 1761 (1979).

90. J. A. Semlyen, Polymer **12,** 383 and ref. therein (1971).

91. M. Morton and E. E. Bostick, J. Polym. Sci., Part A **2,** 523 (1964).

92. M. Morton, A. A. Rembaum, and E. E. Bostick, J. Appl. Polym. Sci. **8,** 2707 (1964).

93. J. C. Saam, D. J. Gordon, and S. Lindsey, Macromolecules **3,** 1 (1970).

94. D. J. Brunelle, E. P. Boden, and T. G. Shannon, J. Am. Chem. Soc. **112,** 2399 (1990).

95. D. J. Brunelle, T. L. Evans, T. L. Shannon, *et al*., Polym. Preprints **30,** (2), 569 (1989).

96. T. L. Evans, C. B. Berman, J. C. Carpenter, *et al*., Polym. Preprints **30**(2), 573 (1989).

97. D. J. Brunelle and E. P. Boden, Makromol. Chem., Macromol. Symp. **54/55,** 397 (1992).

98. T. L. Guggenheim, S. J. McCormick, J. J. Kelly, *et al*., Polym. Preprints **30**(2), 579 (1989).

99. J. A. Cella, J. J. Talley, and J. M. Fukuyama, Polym. Preprints **30**(2), 581 (1989).

100. L. Garrido, J. E. Mark, S. J. Clarson, *et al*., Polym. Commun. **25,** 218 (1984).

101. L. Garrido, J. E. Mark, S. J. Clarson, *et al*., Polym. Commun. **26,** 53 (1985).

102. S. J. Clarson, J. E. Mark, and J. A. Semlyen, Polym. Commun. **27,** 244 (1986).

103. S. J. Clarson, J. E. Mark, and J. A. Semlyen, Polym. Commun. **28,** 151 (1987).

104. T. J. Fyvie, H. L. Frich, J. A. Semlyen, *et al*., J. Polym. Sci., Polym. Chem. Ed. **25,** 2503 (1987).

105. W. Huang, H. L. Frisch, Y. Hua, *et al*., J. Polym. Sci., Polym. Chem. Ed. **28,** 1807 (1990).

106. B. R. Wood, S. J. Joyce, G. Scrivens, *et al*., Polymer **34,** 3052, 3059 (1993).

107. V. Percec and M. Kawasumi, Adv. Mater. **4,** 572 (1992).

108. V. Percec and M. Kawasumi, Macromolecules **25,** 3843 (1992).

109. V. Percec and M. Kawasumi, Macromolecules **26,** 3663, 3917 (1993).

110. V. Percec, M. Kawasumi, P. L. Rinaldi, *et al*., Macromolecules **25,** 3851 (1992).

111. B. A. Newman and H. F. Kay, J. Appl. Phys. **38,** 4105 (1967).

112. W. Heitz, H. Höcker, W. Kern, *et al*., Makromol. Chem. **150,** 73 (1971).

113. T. Trzebiatowski, M. Drager, and G. R. Strobl, Makromol. Chem. **183,** 731 (1982).

114. K. S. Lee and G. Wegner, Makromol. Chem., Rapid Commun. **6,** 203 (1985).

115. H. W. Gibson and H. Marand, Adv. Mater. **5,** 11 (1993).

115a. J. W. Lee and K. Kim, Top. Curr. Chem. **228,** 111 (2003).

116. S. Yu. Lipatov, T. E. Lipatova, *et al*., Adv. Polym. Sci. **88,** 49 (1989).

117. H. W. Gibson, C. Wu, Y. X. Shen, *et al*., Polym. Preprints **32**(3), 593 (1991).

118. H. W. Gibson, C. Wu, Y. X. Shen, *et al*., Polym. Preprints **32**(3), 637 (1991b).

119. H. Marand, A. Prasad, C. Wu, *et al*., Polym. Preprints **32**(3), 639 (1991).

120. P. L. Anelli, P. R. Ashton, R. Ballardini, *et al*., J. Am. Chem. Soc. **114,** 193 (1992).

121. S. J. Joyce, R. E. Hubbard, and J. A. Semlyen, Eur. Polym. J. **29,** 305 (1993).

122. G. Wenz, Angew. Chem. Int. Ed. Engl. **33,** 803 (1994).

122a. R. A. Bissell, E. Cordova, A. E. Kaifer, and J. F. Stoddart, Nature, London **369,** 133 (1994).

122b. M.-J. Blanco, J. M. Consuelo, J.-C. Chambron, V. Heitz, M. Linke, and J.-P. Sauvage, Chem. Soc. Rev. **28,** 293 (1999).

122c. M. Gomez-Lopez and J. F. Stoddart, in *Handbook of Nanostructured Materials and Nanotechnology*, H. S. Nalwa, Ed. (Academic Press, San Diego, CA, 2000), Vol. 5, pp. 225.

122d. J.-P. Collin, J.-M. Kern, L. Raehm, and J.-P. Sauvage, in *Molecular Switches*, B. L. Feringa, Ed. (Wiley-VCH, Germany, 2001), pp. 249.

122e. F. M. Raymo and J. F. Stoddart, in *Molecular Switches*, B. L. Feringa, Ed. (Wiley-VCH, Germany, 2001), pp. 219.

123. D. A. Tomalia, A. M. Naylor, and W. A. Goddard III, Angew. Chem. Int. Ed. Engl. **29,** 138 (1990).

124. P. G. de Gennes and H. J. Hervet, J. Phys. Lett. **44,** 351 (1983).

125. H. B. Mekelburger, W. Jaworek, and F. Vögtle, Angew, Chem., Int. Ed. Engl. **31,** 1571 (1992).

126. Y. H. Kim, Adv. Mater. **4,** 764 (1992).

127. D. A. Tomalia, Adv. Mater. **6,** 529 (1994).

127a. D. A. Tomalia and I. Majoros, in *Supramolecular Polymers*, A. Ciferri, Ed. (Marcel Dekker, Inc., NY, 2000), pp. 359.

127b. D. A. Tomalia, Aldrichim. Acta **37,** 39 (2004).

127c. D. A. Tomalia, Materials Today (Elsevier), March 2005, pp. 34.

128. J. M. J. Fréchet, *Science*, **263,** 1710 (1994).

128a. S. M. Grayson and J. M. J. Fréchet, Chem. Rev. **101,** 3819 (2001).

128b. D. C. Tully and J. M. J. Fréchet, Chem. Commun. 1229 (2001).

129. G. R. Newkome, G. R. Baker, M. J. Saunders, *et al*., J. Chem. Soc., Chem. Commun., 752 (1986).

130. G. R. Newkome, Z-q. Yao, G. R. Baker, *et al*., J. Am. Chem. Soc. **108,** 849 (1986).

131. C. J. Hawker and J. M. J. Fréchet, J. Chem. Soc., Chem. Commun., 1010 (1990).

132. C. J. Hawker and J. M. J. Fréchet, J. Am. Chem. Soc. **112,** 7638 (1990).

133. T. M. Miller and T. X. Neenan, Chem. Mater. **2,** 346 (1990).

134. K. L. Wooley, C. J. Hawker, and J. M. J. Fréchet, J. Am. Chem. Soc. **113,** 4252 (1991).

135. I. Gitsov, P. T. Ivanova, and J. M. J. Fréchet, Macromol. Rapid. Commun. **15,** 387 (1994).

136. Y. H. Kim, J. Am. Chem. Soc. **114,** 4947 (1992).

137. V. Percec, P. Chu, and M. Kawasumi, Macromolecules **27,** 4441 (1994).

138. K. L. Wooley, C. J. Hawker, J. M. Pochan, *et al*., Macromolecules **26,** 1514 (1993).

139. T. Kitayama, T. Shinozaki, T. Sakamoto, *et al*., Makromol. Chem., Supplement **15,** 167 (1989).
140. T. Uryu, H. Ohkawa, and R. Oshima, Macromolecules **20,** 712 (1987).
141. J. W. Mays, E. Siakali-Kioulafa, and N. Hadjichristidis, Macromolecules **23,** 3530 (1990).
142. T. Kitayama, K. Ute, M. Yamamoto, *et al*., Polym. J. **22,** 386 (1990).
143. J. M. O'Reilly, D. M. Teegarden, and R. A. Mosher, Macromolecules **14,** 602, 1693 (1981).
144. T. Kitayama, K. Ute, and K. Hatada, Brit. Polym. J. **23,** 5 (1990).
145. B. Sedláček, J. Spěváček, L. Mrkvičková, *et al*., Macromolecules **17,** 825 (1984).
146. J. Spěváček, B. Schneider, J. Dybal, *et al*., J. Polym. Sci., Polym. Phys. Ed. **22,** 617 (1984).
147. T. Kitayama, T. Shinozaki, E. Masuda, *et al*., Polym. Bull. **20,** 505 (1988).
148. A. Zambelli, P. Ammendola, and A. Proto, Macromolecules **22,** 2126 (1989).
149. C. De Rosa, V. Venditto, G. Guerra, *et al*., Macromolecules **25,** 6938 (1992).
150. M. Galimberti, G. Balbontin, I. Camurati, *et al*., Macromol. Rapid Commun. **15,** 633 (1994).
151. J. A. Ewen, R. L. Jones, A. Razavi, *et al*., J. Am. Chem. Soc. **110,** 6255 (1988).
152. Y. Chatani, H. Maruyama, K. Noguchi, *et al*., J. Polym. Sci., Polym. Lett. Ed. **28,** 393 (1990).
153. G. Balbontin, D. Dainelli, M. Galimberti, *et al*., Makromol. Chem. **193,** 693 (1992).
154. R. Paukkeri and A. Lehtinen, Polymer **34,** 4075 (1993).
155. N. Ishihara, M. Kuramoto, and M. Uoi, Macromolecules **21,** 3356 (1988).
156. M. Kobayashi, T. Nakaoki, and N. Ishihara, Macromolecules **22,** 4377 (1989).
157. M. Kobayashi, T. Nakaoki, and N. Ishihara, Macromolecules **23,** 78 (1990).
158. S. Nozakura, S. Ishihara, Y. Inaba, *et al*., J. Polym. Sci., Polym. Chem. Ed. **11,** 1053 (1973).
159. G. O. R. Alberda van Ekenstein, Y. Y. Tan, and G. Challa, Polymer **26,** 283 (1985).
160. M. Kamachi, X. S. Cheng, T. Kida, *et al*., Macromolecules **20,** 2665 (1987).
161. E. Scamporrino and D. Vitalini, Macromolecules **25,** 1625 (1992).
161a. D. Vitalini and E. Scamporrino, Macromolecules **25,** 6605 (1992).
162. D. Hammel, P. Erk, B. Schuler, *et al*., Adv. Mater. **4,** 737 (1992).
163. Z. Bao, Y. Chen, and L. Yu, Macromolecules **27,** 4629 (1994).
164. H. Kamogawa, S. Miyama, and S. Minoura, Macromolecules **22,** 2123 (1989).
165. P. M. Kuznesof, R. S. Nohr, K. J. Wynne, *et al*., J. Macromol. Sci., Chem. **A16,** 299 (1981).
166. C. W. Dirk, E. A. Mintz, K. F. Schoch, Jr., *et al*., J. Macromol. Sci., Chem. **A16,** 275 (1981).
167. C. W. Dirk, T. Inabe, K. F. Schoch, Jr., *et al*., J. Am. Chem. Soc. **105,** 1539 (1983).
168. B. N. Achar, G. M. Fohlen, J. A. Parker, and J. Keshavayya, J. Polym. Sci., Polym. Chem. Ed. **25,** 443 (1987).
169. J. R. Fryer and M. E. Kenney, *Macromolecules*, **21,** 259 (1988).
170. W. Caseri, T. Sauer, and G. Wegner, Makromol. Chem., Rapid Commun. **9,** 651 (1988).
171. J. F. van der Pol, E. Neeleman, R. J. Nolte *et al*., Makromol. Chem. **190,** 2727 (1989).
172. T. Sauer, W. Caseri, and G. Wegner, Mol. Cryst. Liq. Cryst. **183,** 387 (1990).
173. T. Sauer, T. Arndt, D. N. Batchelder *et al*., Thin Solid Films **187,** 357 (1990).
174. T. Sauer and G. Wegner, Macromolecules **24,** 2240 (1991).
175. H. Z. Chen, M. Wang, L. X. Feng, *et al*., J. Appl. Polym. Sci. **46,** 1033 (1992).
176. H. Z. Chen, M. Wang, L. X. Feng, and S. L. Yang, J. Appl. Polym. Sci. **49,** 679 (1993).
177. C. F. van Nostrum, R. J. M. Nolte, M. A. C. Devillers, *et al*., Macromolecules **26,** 3306 (1993).
178. D. Dotcheva, M. Klapper, and K. Müllen, Makromol. Chem. Phys. **195,** 1905 (1994).
179. D. R. Robello, J. Polym. Sci., Polym. Chem. Ed. **28,** 1 (1990).
180. H. Hashimoto, T. Kakuchi, O. Haba, *et al*., Macromolecules **25,** 1828 (1992).
181. G. A. Olah, I. Bucsi, C. Lambert, *et al*., J. Am. Chem. Soc. **113,** 9387 (1991).
181a. Z. Sun and R. L. Miller, Polymer **34,** 1963 (1993).
182. D. A. Loy and R. A. Assink, J. Am. Chem. Soc. **114,** 3978 (1992).
183. S. Shi, K. C. Khemani, Q. C. Li, *et al*., J. Am. Chem. Soc. **114,** 10656 (1992).
184. K. E. Geckeler and A. Hirsch, J. Am. Chem. Soc. **115,** 3850 (1993).
185. A. O. Patil, G. W. Schriver, B. Carstensen, *et al*., Polym. Bull. **30,** 187 (1993).
186. A. M. Rao, P. Zhou, K-A. Wang, *et al*., Science **259,** 955 (1993).
187. C. J. Hawker, Macromolecules **27,** 4836 (1994).
188. P. W. Stephens, G. Bortel, G. Faigel, *et al*., Nature (London) **370,** 636 (1994).
189. M. S. Beevers and J. A. Semlyen, Polymer **12,** 373 (1971).
190. K. Dodgson and J. A. Semlyen, Polymer **18,** 1265 (1977).
191. K. Dodgson, D. Sympson, and J. A. Semlyen, Polymer **19,** 1285 (1978).
192. J. S. Higgins, K. Dodgson, and J. A. Semlyen, Polymer **20,** 553 (1979).
193. F. R. Jones, Eur. Polym. J. **10,** 249 (1974).
194. P. V. Wright and J. A. Semlyen, Polymer **11,** 462 (1970).
195. W. A. Piccoli, G. G. Haberland, and R. L. Merker, J. Am. Chem. Soc. **82,** 1883 (1960).
196. E. D. Brown and J. B. Carmichael, J. Polym. Sci., Polym. Lett. Ed. **3,** 473 (1965).
197. T. R. Formoy and J. A. Semlyen, Polym. Commun. **30,** 86 (1989).
198. H. Höcker and K. Riebel. Makromol. Chem. **178,** 3101 (1977).
199. G. E. Hahn, P. Kusch, V. Rossbach, *et al*., Makromol. Chem. **186,** 297 (1985).
200. J. J. Kulig, W. J. Brittain, S. Gilmour, *et al*., Macromolecules **27,** 4838 (1994).
201. A. Horbach, H. Vernaleken, and K. Weirauch, Makromol. Chem. **181,** 111 (1980).
202. E. P. Boden, D. J. Brunelle, and T. G. Shannon, Polym. Preprints **30**(2), 571 (1989).
203. D. J. Brunelle and M. F. Garbauskas, Macromolecules **26,** 2724 (1993).
204. F. R. Jones, L. E. Scales, and J. A. Semlyen, Polymer **15,** 738 (1974).
205. J. M. Andrews and J. A. Semlyen, Polymer **13,** 142 (1972).
206. K. Hayashi, Macromolecules **3,** 5 (1970).
207. D. R. Cooper and J. A. Semlyen, Polymer **14,** 185 (1973).
208. E. Meraskentis and H. Zahn, J. Polym. Sci. **4,** 1890 (1966).
209. F. L. Hamb and L. C. Trent, J. Polym. Sci., Polym. Lett. Ed. **5,** 1057 (1967).
210. L. Reif and H. Höcker, Makromol. Chem., Rapid Commun. **2,** 183 (1981).
211. J. A. Semlyen and G. R. Walker, Polymer **10,** 597 (1969).
212. H. Höcker and R. Musch, Makromol. Chem. **175,** 1395 (1974).
212a. L. Reif and H. Höcker, Macromolecules **17,** 952 (1984).
213. Y. Yamashita, J. Mayumi, Y. Kawakami *et al*., Macromolecules **13,** 1075 (1980).
214. A. Sato, T. Hirano, M. Suga, *et al*., Polym. J. **9,** 209 (1977).
215. C. Rentsch and R. C. Schulz, Makromol. Chem. **178,** 2535 (1977).
216. J. Maxka, F. K. Mitter, D. R. Powell, *et al*., Organometallics **10,** 660 (1991).
217. G. P. Lorenzi, L. Tomasic, and U. W. Suter, Macromolecules **26,** 1183 (1993).
218. J. F. McCullough, J. R. van Wazer, and E. J. Griffith, J. Am. Chem. Soc. **78,** 4528 (1956).
219. G. Hild, A. Kohler, and P. Rempp, Eur. Polym. J. **16,** 525 (1980).
220. J. Roovers and P. M. Toporowski, Macromolecules **16,** 843 (1983).
221. M. Duval, P. Lutz, and C. Strazielle, Makromol. Chem., Rapid. Commun. **6,** 71 (1985).
222. M. Ragnetti, D. Geiser, H. Höcker, *et al*., Makromol. Chem. **186,** 1701 (1985).
223. G. Hadziioannou, P. M. Cotts, G. ten Brinke, *et al*., Macromolecules **20,** 493 (1987).
224. G. B. McKenna, G. Hadziioannou, P. Lutz, *et al*., Macromolecules **20,** 498 (1987).
225. G. B. McKenna, B. J. Hostetter, N. Hadjichristidis, *et al*., Macromolecules **22,** 1834 (1989).
226. J. M. McKenna, T. K. Wu, and G. Pruckmayr, Macromolecules **10,** 877 (1977).

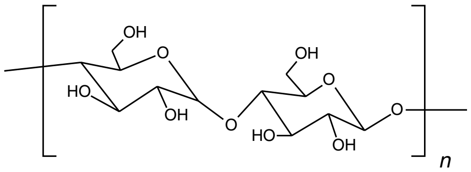
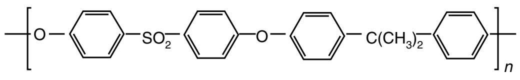
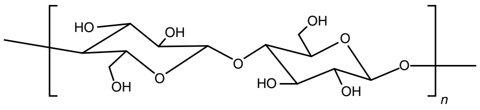
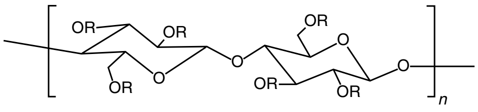
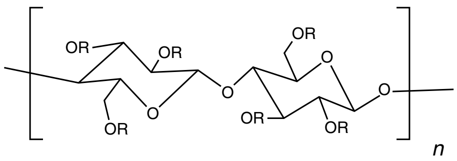
227. N. Ogata, K. Sanui, and J. Wada, J. Polym. Sci., Polym. Letters Ed. **14,** 459 (1976).
228. A. Harada and M. Kamachi, Macromolecules **23,** 2821 (1990).
229. A. Harada, J. Li, and M. Kamachi, Nature (London) **356,** 325 (1992).
230. A. Harada, J. Li, and M. Kamachi, Macromolecules **26,** 5698 (1993).
231. G. Wenz and B. Keller, Angew. Chem. Int. Ed. Engl. **31,** 197 (1992).
232. A. Harada, J. Li, S. Suzuki, *et al*., Macromolecules **26,** 5267 (1993).
233. A. Harada and M. Kamachi, J. Chem. Soc., Chem. Commun., 1322 (1990).
234. M. Maciejewski, J. Macromol. Sci., Chem. **A13,** 77, 1175 (1979).
235. M. Maciejewski, A. Gwizdowski, P. Peczak, *et al*., J. Macromol. Sci., Chem. **A13,** 87 (1979).
236. J. Y. Sze and H. W. Gibson, Polym. Preprints **33**(2), 331 (1992).
237. C. Wu, M. C. Bheda, C. Lim *et al*., Polym. Commun. **32,** 204 (1991).
238. H. W. Gibson, P. Engen, and P. LeCavalier, *Polym. Preprints*, **29**(1), 248 (1988); H. W. Gibson, M. C. Bheda, and P. T. Engen, "Rotaxanes, catenanes, polyrotaxanes, polycatenanes, and related materials," Prog. in Polym. Sci. **19,** 843 (1994).
239. P. T. Engen, P. R. LeCavalier, and H. W. Gibson, Polym. Preprints **31**(2), 703 (1990).
240. Y. X. Shen, C. Lim, and H. W. Gibson, Polym. Preprints **32**(1), 166 (1991).
241. Y. X. Shen and H. W. Gibson, Macromolecules **25,** 2058 (1992).
242. G. R. Newkome, J. K. Young, G. R. Baker, *et al*., Macromolecules **26,** 2394 (1993).
243. K. Rengan and R. Engel, J. Chem. Soc., Chem. Commun., 757 (1992).
244. S. C. E. Backson, P. M. Bayliff, W. J. Feast, *et al*., Polym. Preprints **34** (1), 50 (1993).
245. T. M. Miller, E. W. Kwock, and T. X. Neenan, Macromolecules **25,** 3143 (1992).
246. L-L. Zhou and J. Roovers, Macromolecules **26,** 963 (1993).
247. A. Cherestes and R. Engel, Polymer **35,** 3343 (1994).
248. T. Nagasaki, M. Ukon, S. Arimori, *et al*., J. Chem. Soc., Chem. Commun., 608 (1992).
249. I. Gitsov, K. L. Wooley, and J. M. J. Fréchet, *Angew. Chem. Int. Ed. Engl*., **31,** 1200 (1992).
250. I. Gitsov and J. M. J. Fréchet, Macromolecules **26,** 6536 (1993).
250a. I. Gitsov, K. L. Wooley, C. J. Hawker, *et al*., Macromolecules **26,** 5621 (1993).
251. K. Rengan and R. Engel, J. Chem. Soc., Chem. Commun., 1084 (1990).
252. K. Rengan and R. Engel, J. Chem. Soc., Perkin Trans. **I,** 987 (1991).
253. T. M. Miller, T. X. Neenan, R. Zayas, *et al*., J. Am. Chem. Soc. **114,** 1018 (1992).
254. J. S. Moore and Z. Xu, Macromolecules **24,** 5893 (1991).
255. Z. Xu and J. S. Moore, Angew. Chem. Int. Ed. Engl. **32,** 246 (1993).
256. E. M. M. de Brabander-van den Berg and E. W. Meijer, Angew. Chem. Int. Ed. Engl. **32,** 1308 (1993).
257. J-J. Lee, W. T. Ford, J. A. Moore, *et al*., Macromolecules **27,** 4632 (1994).
258. C. Wörner and R. Mülhaupt, Angew. Chem. Int. Ed. Engl. **32,** 1306 (1993).
259. J. K. Young, G. R. Baker, G. R. Newkome, *et al*., Macromolecules **27,** 3464 (1994).
260. D. A. Tomalia, H. Baker, J. Dewald, *et al*., Polym. J. **17,** 117 (1985).
261. D. A. Tomalia, H. Baker, J. Dewald, *et al*., Macromolecules **19,** 2466 (1986).
262. D. A. Tomalia, V. Berry, M. Hall, *et al*., Macromolecules **20,** 1164 (1987a).
263. D. A. Tomalia, M. Hall, and D. M. Hedstrand, J. Am. Chem. Soc. **109,** 1601 (1987b).
264. L. R. Wilson and D. A. Tomalia, Polym. Preprints **30**(1), 115 (1989).
265. H. K. Hall and D. W. Polis, Polym. Bull. **17,** 409 (1987).
266. C. J. Hawker, R. Lee, and J. M. G. Fréchet, J. Am. Chem. Soc. **113,** 4583 (1991).
267. S. R. Turner, F. Walter, B. I. Voit, *et al*., Macromolecules **27,** 1611 (1994).
268. T. H. Mourey, S. R. Turner, M. Rubinstein, *et al*., Macromolecules **25,** 2401 (1992).
269. C. J. Hawker and J. M. J. Fréchet, J. Am. Chem. Soc. **114,** 8405 (1992b).
270. C. J. Hawker and J. M. J. Fréchet, Polymer **33,** 1507 (1992a).
271. Y. H. Kim and O. W. Webster, J. Am. Chem. Soc. **112,** 4592 (1990).
272. A. W. van der Made and P. W. N. M. van Leeuwen, J. Chem. Soc., Chem Commun., 1400 (1992).
273. A. W. van der Made, P. W. N. M. van Leeuwen, J. C. de Wilde, *et al*., Adv. Mater. **5,** 466 (1993).
274. H. Uchida, Y. Kabe, K. Yoshino *et al*., J. Am. Chem. Soc. **112,** 7077 (1990).
275. L. J. Mathias and T. W. Carothers, J. Am. Chem. Soc. **113,** 4043 (1991).
276. A. Morikawa, M. Kakimoto, and Y. Imai, Macromolecules **24,** 3469 (1991).
277. A. Morikawa, M. Kakimoto, and Y. Imai, Macromolecules **25,** 3247 (1992).
278. J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives* (VCH Publishers, 1995).
279. S. I. Stupp, S. Son, L. S. Li, H. C. Lin, and M. Keser, J. Am. Chem. Soc. **117,** 5212 (1995); Science **276,** 384 (1997).
280. A. Ciferri, Ed. *Supramolecular Polymers*. (Marcel Dekker, NY, 2000).
281. O. Ikkala and G. ten Brinke, Science **295,** 2407 (2002).
282. Y. Guan, S.-H. Yu, M. Antonietti, C. Böttcher, and C. F. J. Faul, Chem. Eur. J. **11,** 1305 (2005).
283. K. V. Gothelf and R. S. Brown, Chem. Eur. J. **11,** 1062 (2005).
284. G. B. W. L. Ligthart, H. Ohkawa, R. P. Sijbesma, and E. W. Meijer, J. Am. Chem. Soc. **127,** 810 (2005).
285. S. Hecht, Materials Today (Elsevier) March 2005, pp. 48.
286. A. D. Q. Li, W. Wang, and L.-Q. Wang, Chem Eur. J. **9,** 4594 (2003).
287. S. H. Gellman, Acc. Chem. Res. **31,** 173 (1998).
288. P. D. Yarborough and D. Y. Sogah, Polym. Mater. Sci. Eng. **76,** 395 (1997); **77,** 601 (1997).
289. C. Kübel, M. J. Mio, J. S. Moore, and D. C. Martin, J. Am. Chem. Soc. **124,** 8605 (2002).

CHAPTER 2

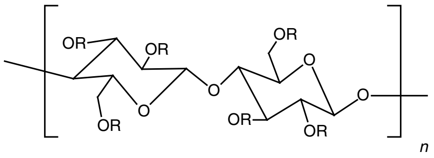
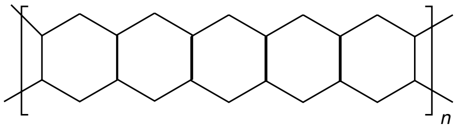
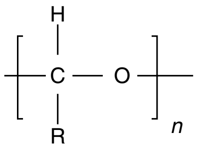
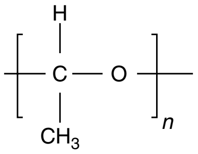
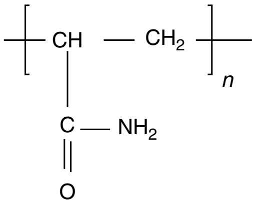
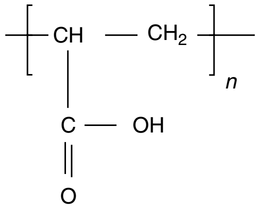
Names, Acronyms, Classes, and Structures of Some Important Polymers

Chandima Kumudinie Jayasuriya* and Jagath K. Premachandra†

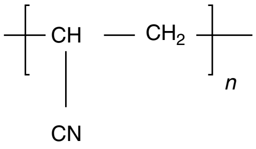
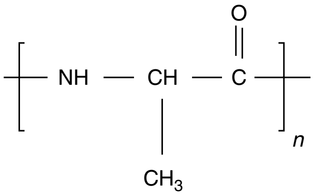
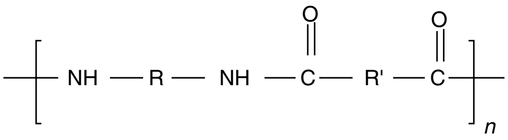
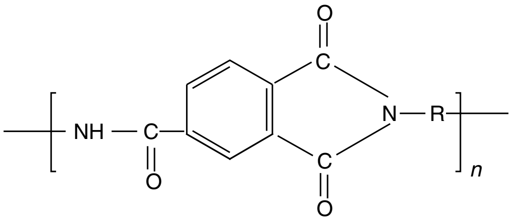
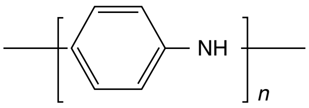
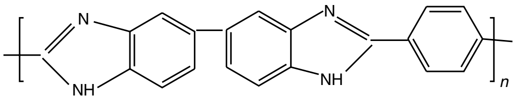
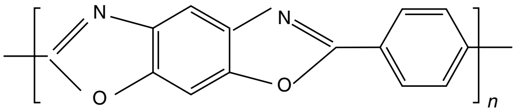
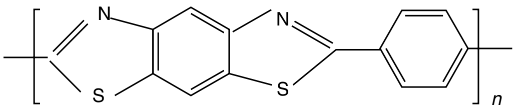
*Department of Chemistry, University of Kelaniya, Dalugama, Kelaniya, Sri Lanka; †Department of Chemical and Process Engineering, University of Moratuwa, Katubedda, Moratuwa, Sri Lanka

Common name	Acronym, alternate name	Class	Structure of repeat unit
Amylose		Polysaccharide	
Bisphenol A polysulfone		Polysulfone	
Cellulose	Rayon, cellophane, regenerated cellulose	Polysaccharide	
Cellulose acetate	CA	Cellulose ester	 R = –COCH$_3$
Cellulose nitrate	CN	Cellulose ester	 R = –NO$_2$

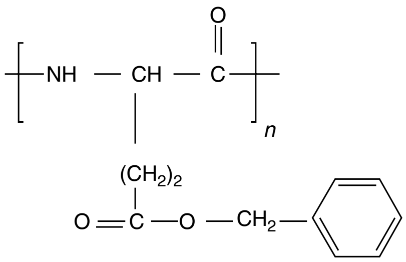
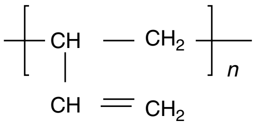
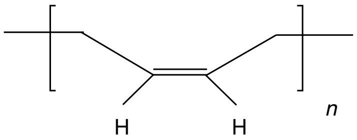
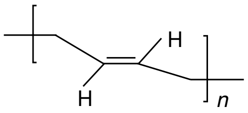
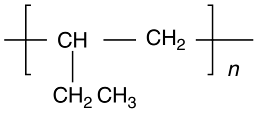
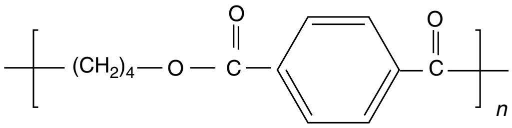
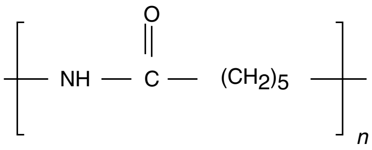
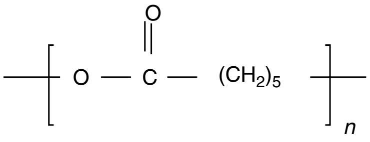
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Hydroxypropyl cellulose	HPC	Cellulose ester	 R = –$(CH_2)_3$–OH
Ladder polymer	Double-strand polymer		
Polyacetal		Polyether	 $\left[-\overset{H}{\underset{R}{C}}-O- \right]_n$
Polyacetaldehyde		Polyether	 $\left[-\overset{H}{\underset{CH_3}{C}}-O- \right]_n$
Polyacetylene		Polyalkyne	$\left[CH = CH \right]_n$
Polyacrylamide		Vinyl polymer, acrylic polymer	 $\left[\underset{C(=O)-NH_2}{CH}-CH_2 \right]_n$
Poly(acrylic acid)		Vinyl polymer, acrylic polymer	 $\left[\underset{C(=O)-OH}{CH}-CH_2 \right]_n$

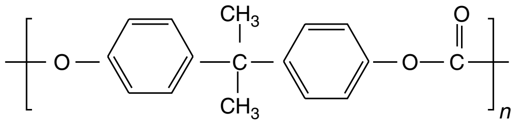
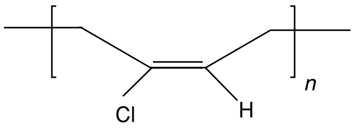
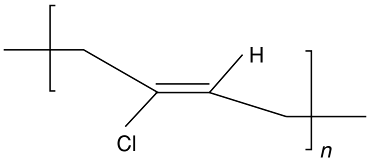
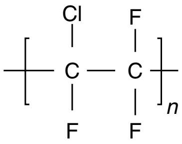
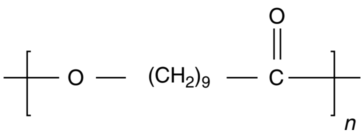
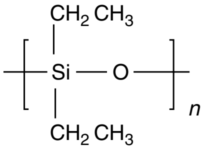
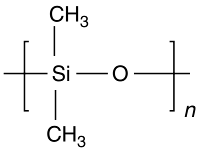
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Polyacrylonitrile	PAN	Vinyl polymer, acrylic polymer	 $\left[\underset{\underset{\mathrm{CN}}{\vert}}{\mathrm{CH}} - \mathrm{CH_2} \right]_n$
Poly(L-alanine)		Polypeptide	 $\left[\mathrm{NH} - \underset{\underset{\mathrm{CH_3}}{\vert}}{\mathrm{CH}} - \overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}} \right]_n$
Polyamide	Nylon	Polyamide	 $\left[\mathrm{NH} - \mathrm{R} - \mathrm{NH} - \overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}} - \mathrm{R'} - \overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}} \right]_n$
Polyamide imide	PAI		
Polyaniline		Polyamine	
Polybenzimidazole	PBI	Polyheteroaromatic	
Polybenzobisoxazole	PBO	Polyheteroaromatic	
Polybenzobisthiazole	PBT	Polyheteroaromatic	

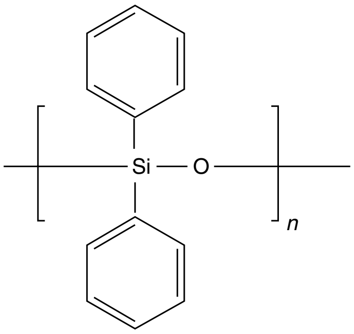
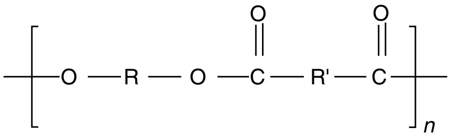
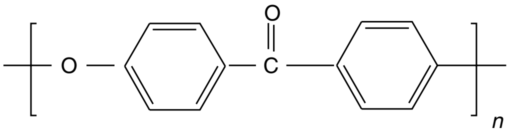
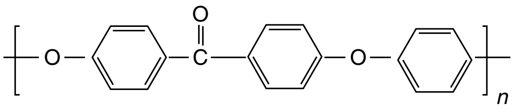
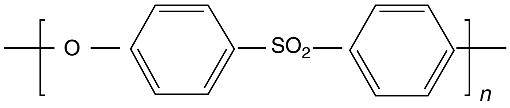
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Poly(γ-benzyl-L-glutamate)	PBLG	Polypeptide	
1,2-Polybutadiene	PBD	Diene polymer	 $\left[\mathrm{CH(CH{=}CH_2)-CH_2}\right]_n$
cis-1,4-Polybutadiene	PBD	Diene polymer	
trans-1,4-Polybutadiene	PBD	Diene polymer	
Poly(1-butene)	PB-1	Polyolefin	 $\left[\mathrm{CH(CH_2CH_3)-CH_2}\right]_n$
Polybutylene terephthalate	PBT	Polyester	
Poly(ε-caprolactam)	Nylon 6	Polyamide	 $\left[\mathrm{NH-C(=O)-(CH_2)_5}\right]_n$
Poly(ε-caprolactone)		Polyester	 $\left[\mathrm{O-C(=O)-(CH_2)_5}\right]_n$

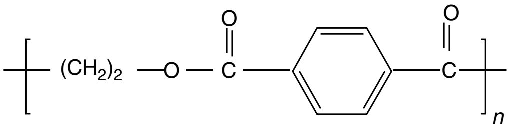
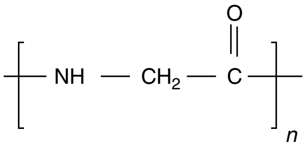
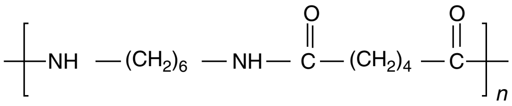
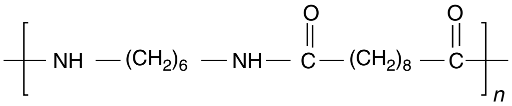
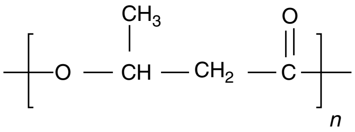
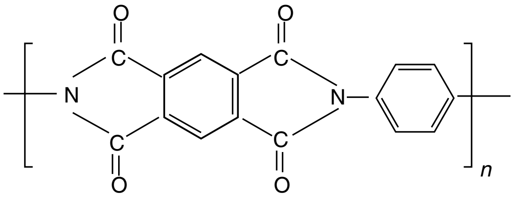
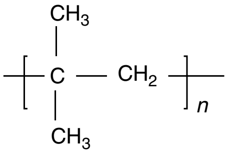
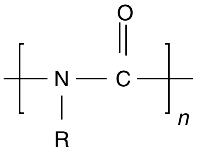
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Polycarbonate	PC	Polyester	
cis-1,4-Polychloroprene	Neoprene	Diene polymer	
trans-1,4-Polychloroprene	Neoprene	Diene polymer	
Polychlorotrifluoroethylene	PCTFE	Vinyl polymer, Fluoro polymer	 $\left[\underset{\mathrm{F}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{C}}}\right]_n$
Poly(10-decanoate)		Polyester	 $\left[\mathrm{O}-(\mathrm{CH_2})_9-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\right]_n$
Poly(diethyl siloxane)	PDES	Polysiloxane	 $\left[\underset{\mathrm{CH_2CH_3}}{\overset{\mathrm{CH_2CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_n$
Poly(dimethyl siloxane)	PDMS	Polysiloxane	 $\left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_n$

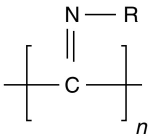
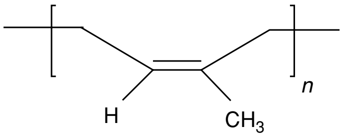
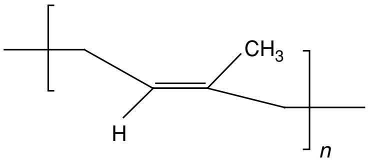
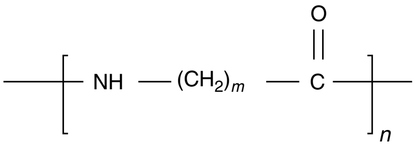
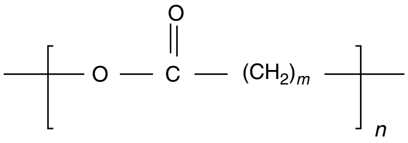
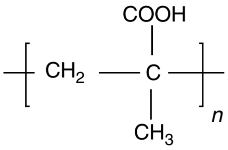
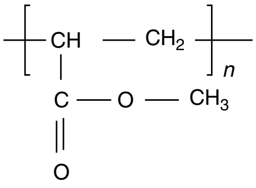
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Poly(diphenyl siloxane)	PDPS	Polysiloxane	
Polyester			 $\left[O - R - O - \overset{O}{\overset{\|}{C}} - R' - \overset{O}{\overset{\|}{C}} \right]_n$
Polyether ketone	PEK	Polyketone	
Polyether etherketone	PEEK	Polyketone	
Polyether sulfone	PES		
Polyethylene	PE	Polyolefin	$\left[CH_2 - CH_2 \right]_n$
Poly(ethylene imine)		Polyamine	$\left[CH_2 - CH_2 - NH \right]_n$
Poly(ethylene oxide) [Poly(ethylene glycol)]	PEO [PEG]	Polyether	$\left[CH_2 - CH_2 - O \right]_n$

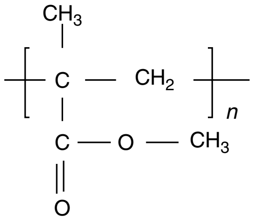
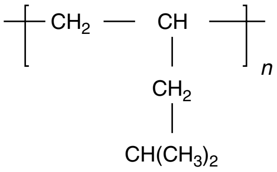
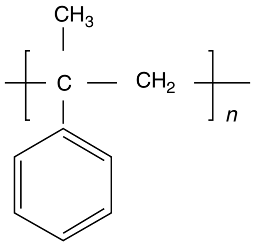
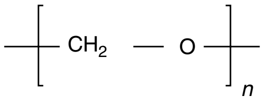
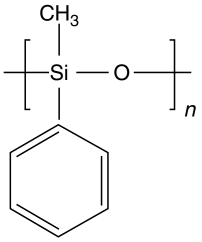
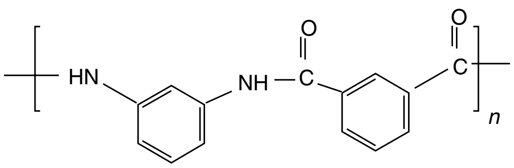
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Poly(ethylene terephthalate)	PET	Polyester	
Polyglycine		Polypeptide	 $\left[-NH-CH_2-\overset{\overset{O}{\|}}{C}- \right]_n$
Poly(hexamethylene adipamide)	Nylon 6,6	Polyamide	 $\left[-NH-(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}- \right]_n$
Poly(hexamethylene sebacamide)	Nylon 6,10	Polyamide	 $\left[-NH-(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}- \right]_n$
Polyhydroxybutyrate	PHB	Polyester	 $\left[-O-\overset{\overset{CH_3}{\|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}- \right]_n$
Polyimide	PI	Polyimide	
Polyisobutylene	Butyl rubber	Vinylidine polymer	 $\left[-\underset{\underset{CH_3}{\|}}{\overset{\overset{CH_3}{\|}}{C}}-CH_2- \right]_n$
Polyisocyanate	PIC	Polyamide	 $\left[-\underset{\underset{R}{\|}}{N}-\overset{\overset{O}{\|}}{C}- \right]_n$

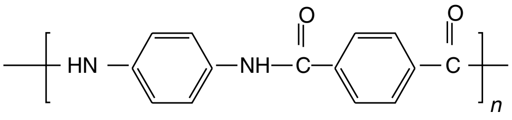
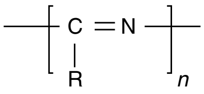
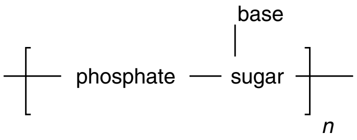
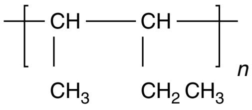
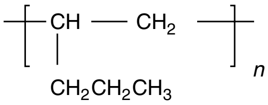
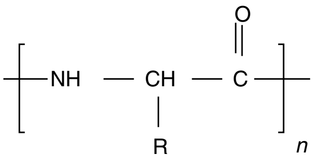
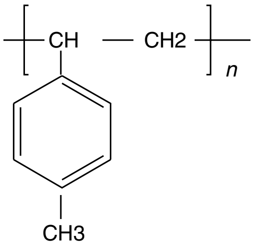
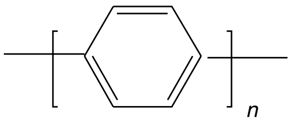
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Polyisocyanide		Polyisocyanide	 $-\!\!\left[\overset{N-R}{\overset{\|\|}{C}}\right]_n\!\!-$
cis-1,4-Polyisoprene	*cis*-PIP, natural rubber	Diene polymer	
trans-1,4-Polyisoprene	*trans*-PIP Gutta percha	Diene polymer	
Polylactam		Polyamide	 $-\!\!\left[NH-(CH_2)_m-\overset{O}{\overset{\|\|}{C}}\right]_n\!\!-$
Polylactone		Polyester	 $-\!\!\left[O-\overset{O}{\overset{\|\|}{C}}-(CH_2)_m\right]_n\!\!-$
Poly(methacrylic acid)		Vinyl polymer, acrylic polymer	 $-\!\!\left[CH_2-\underset{CH_3}{\overset{COOH}{C}}\right]_n\!\!-$
Poly(methyl acrylate)	PMA	Vinyl polymer, acrylic polymer	 $-\!\!\left[\underset{C(=O)-O-CH_3}{CH}-CH_2\right]_n\!\!-$

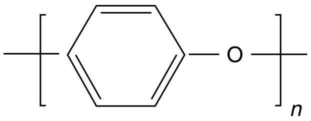
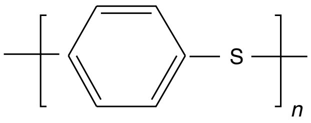
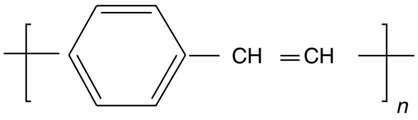
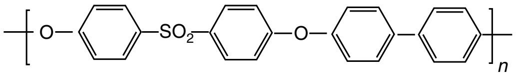
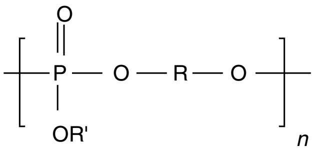
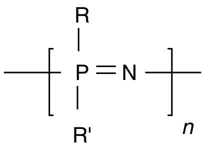
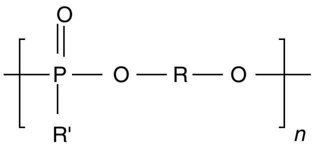
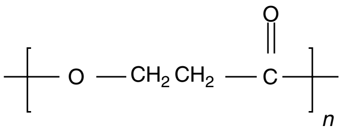
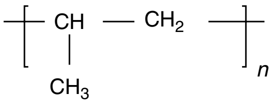
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Poly(methyl methacrylate)	PMMA	Vinylidene polymer, acrylic polymer	
Poly(4-methyl pentene)		Polyolefin	
Poly(α-methyl stryrene)		Vinylidene polymer	
Poly(methylene oxide)	PMO Polyformaldehyde	Polyether	
Poly(methyl phenyl siloxane)	PMPS	Polysiloxane	
Poly(*m*-phenylene terephthalamide)	Nomex	Polyaramid	

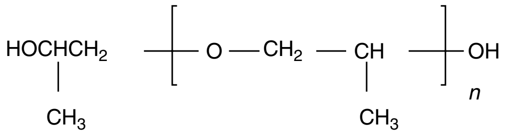
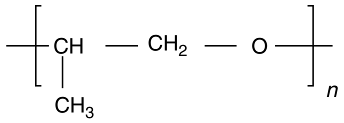
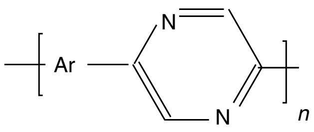
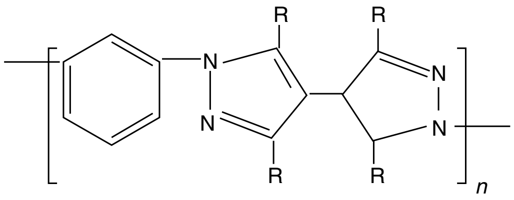
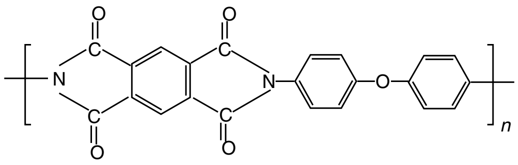
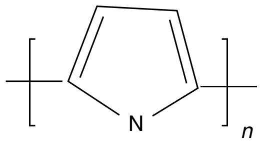
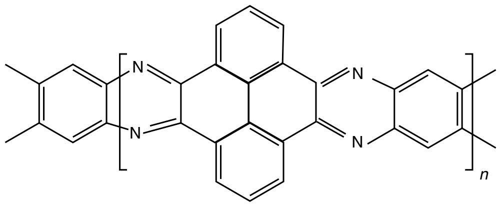
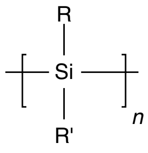
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Poly(*p*-phenylene terephthalamide)	Kevlar	Polyaramid	
Polynitrile		Polyimine	
Polynucleotide		Polynucleotide	
Poly(*n*-pentene-2)		Poly(α-olefin)	
Poly(*n*-pentene-1)	Poly (1-pentene)	Poly(α-olefin)	
Polypeptides [Poly(α-amino acid)]		Polypeptide	
Poly(*p*-methyl styrene)		Vinyl polymer	
Poly(*p*-phenylene)	PP	Polyaromatic	

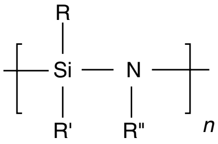
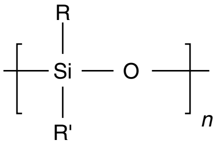
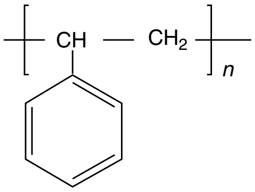
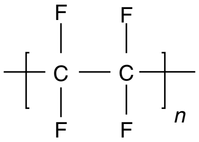
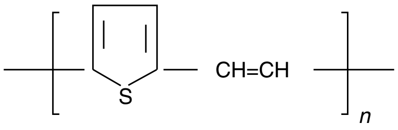
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Poly(*p*-phenylene oxide)	PPO	Polyether	
Poly(*p*-phenylene sulfide)	PPS	Polysulfide	
Poly(*p*-phenylene vinylene)		Polyaromatic	
Polyphenylsulfone		Polysulfone	
Polyphosphate		Inorganic polymer	 $-\!\left[\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle OR'}{\underset{\|}{P}}}}-O-R-O\right]_n\!-$
Polyphosphazene		Inorganic polymer	 $-\!\left[\overset{\displaystyle R}{\overset{\|}{\underset{\displaystyle R'}{\underset{\|}{P}}}}=N\right]_n\!-$
Polyphosphonate		Inorganic polymer	 $-\!\left[\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle R'}{\underset{\|}{P}}}}-O-R-O\right]_n\!-$
Poly(3-propionate)	Poly(β-propiolactone)	Polyester	 $-\!\left[O-CH_2CH_2-\overset{\displaystyle O}{\overset{\|}{C}}\right]_n\!-$
Polypropylene	PP	Poly(α-olefin)	 $-\!\left[\underset{\displaystyle CH_3}{\underset{\|}{CH}}-CH_2\right]_n\!-$

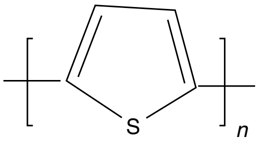
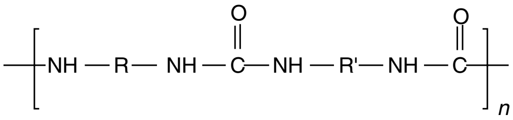
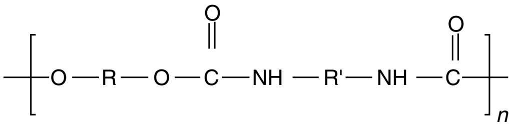
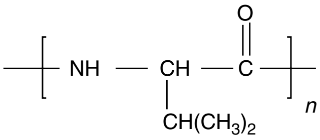
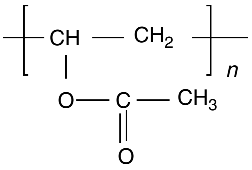
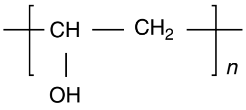
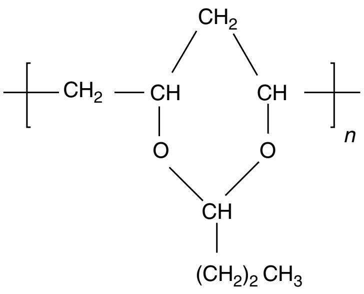
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Poly(propylene glycol)	PPG	Polyether	 $\mathrm{HOCH(CH_3)CH_2}\left[\mathrm{O-CH_2-CH(CH_3)}\right]_n\mathrm{OH}$
Poly(propylene oxide)	PPO	Polyether	 $\left[\mathrm{CH(CH_3)-CH_2-O}\right]_n$
Polypyrazine		Heterocyclic polymer	
Polypyrazole		Heterocyclic polymer	
Poly(pyromellitimide-1,4-diphenyl ether)	Kapton	Polyimide	
Polypyrrole		Heterocyclic polymer	
Polyquinoxaline		Heterocyclic polymer	
Polysilane		Inorganic polymer	 $\left[\mathrm{SiRR'}\right]_n$

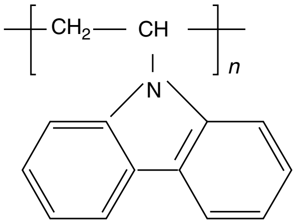
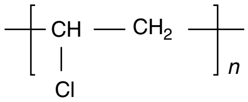
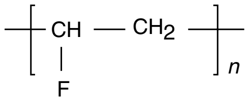
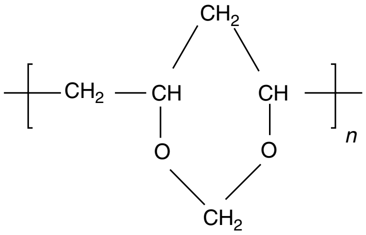
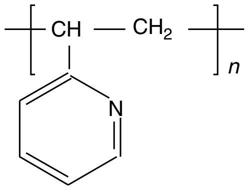
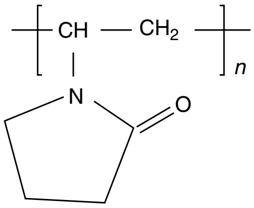
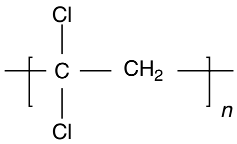
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Polysilazane		Inorganic polymer	 $-\!\!\left[\underset{R'}{\overset{R}{\mathrm{Si}}}-\underset{R''}{\mathrm{N}}\right]_n\!\!-$
Polysiloxane	Silicone	Inorganic polymer	 $-\!\!\left[\underset{R'}{\overset{R}{\mathrm{Si}}}-\mathrm{O}\right]_n\!\!-$
Polystyrene	PS, styrofoam	Vinyl polymer	
Polysulfide	Thiokol	Polysulfide	$-\!\!\left[\mathrm{R}-\mathrm{S}_m\right]_n\!\!-$
Polysulfur		Polysulfur	$-\!\!\left[\mathrm{S}\right]_n\!\!-$
Polytetrafluoroethylene	PTFE, Teflon	Poly(α-olefin)	 $-\!\!\left[\underset{F}{\overset{F}{\mathrm{C}}}-\underset{F}{\overset{F}{\mathrm{C}}}\right]_n\!\!-$
Poly(tetramethylene oxide)	PTMO	Polyether	$-\!\!\left[\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}\right]_n\!\!-$
Polythiazyl			$-\!\!\left[\mathrm{S}=\mathrm{N}\right]_n\!\!-$
Polythienyl vinylene			

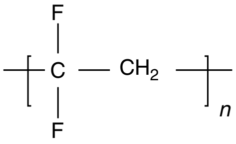
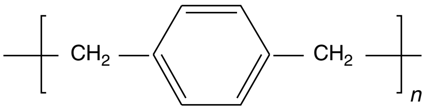
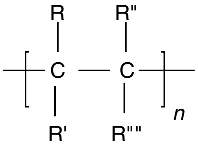
Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Polythiopene		Polyheterocyclic	
Poly(trimethylene ethylene urethane)			$\left[O-CH_2CH_2CH_2-OCONH-CH_2CH_2-NHCO\right]_n$
Polyurea		Polyurea	 $\left[NH-R-NH-\overset{O}{\overset{\|}{C}}-NH-R'-NH-\overset{O}{\overset{\|}{C}}\right]_n$
Polyurethane	Adiprene	Polyurethane	 $\left[O-R-O-\overset{O}{\overset{\|}{C}}-NH-R'-NH-\overset{O}{\overset{\|}{C}}\right]_n$
Poly(L-valine)		Polypeptide	 $\left[NH-\underset{CH(CH_3)_2}{\underset{\|}{CH}}-\overset{O}{\overset{\|}{C}}\right]_n$
Poly(vinyl acetate)	PVAc	Vinyl polymer	 $\left[\underset{O-\underset{O}{\underset{\|}{C}}-CH_3}{\underset{\|}{CH}}-CH_2\right]_n$
Poly(vinyl alcohol)	PVA	Vinyl polymer	 $\left[\underset{OH}{\underset{\|}{CH}}-CH_2\right]_n$
Poly(vinyl butyral)	PVB	Vinyl polymer	

Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Poly(vinyl carbazole)			
Poly(vinyl chloride)	PVC	Vinyl polymer	 $\left[\underset{\mathrm{Cl}}{\underset{\mid}{\mathrm{CH}}} - \mathrm{CH_2} \right]_n$
Poly(vinyl fluoride)	PVF	Vinyl polymer, fluoro polymer	 $\left[\underset{\mathrm{F}}{\underset{\mid}{\mathrm{CH}}} - \mathrm{CH_2} \right]_n$
Poly(vinyl formal)		Vinyl polymer	
Poly(2-vinyl pyridine)	PVP	Vinyl polymer	
Poly(*N*-vinyl pyrrolidone)		Vinyl polymer	
Poly(vinylidene chloride)	PVDC	Vinylidene polymer	 $\left[\overset{\mathrm{Cl}}{\overset{\mid}{\underset{\mathrm{Cl}}{\underset{\mid}{\mathrm{C}}}}} - \mathrm{CH_2} \right]_n$

Continued.

Common name	Acronym, alternate name	Class	Structure of repeat unit
Poly(vinylidene fluoride)	PVDF	Vinylidene polymer	
Poly(*p*-xylylene)			
Vinyl polymer		Vinyl polymer	

ACKNOWLEDGEMENT

The authors wish to acknowledge the contribution of W. Zhao, formerly of SRI International, to this chapter.