

POLYMER ANALYSIS

Barbara H. Stuart

University of Technology, Sydney, Australia



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POLYMER ANALYSIS

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Series Preface

There has been a rapid expansion in the provision of further education in recent years, which has brought with it the need to provide more flexible methods of teaching in order to satisfy the requirements of an increasingly more diverse type of student. In this respect, the *open learning* approach has proved to be a valuable and effective teaching method, in particular for those students who for a variety of reasons cannot pursue full-time traditional courses. As a result, John Wiley & Sons, Ltd first published the Analytical Chemistry by Open Learning (ACOL) series of textbooks in the late 1980s. This series, which covers all of the major analytical techniques, rapidly established itself as a valuable teaching resource, providing a convenient and flexible means of studying for those people who, on account of their individual circumstances, were not able to take advantage of more conventional methods of education in this particular subject area.

Following upon the success of the ACOL series, which by its very name is predominately concerned with Analytical *Chemistry*, the *Analytical Techniques in the Sciences* (AnTS) series of open learning texts has now been introduced with the aim of providing a broader coverage of the many areas of science in which analytical techniques and methods are now increasingly applied. With this in mind, the AnTS series of texts seeks to provide a range of books which will cover not only the actual techniques themselves, but *also* those scientific disciplines which have a necessary requirement for analytical characterization methods.

Analytical instrumentation continues to increase in sophistication, and as a consequence, the range of materials that can now be almost routinely analysed has increased accordingly. Books in this series which are concerned with the *techniques* themselves will reflect such advances in analytical instrumentation, while at the same time providing full and detailed discussions of the fundamental concepts and theories of the particular analytical method being considered. Such books will cover a variety of techniques, including general instrumental analysis,

spectroscopy, chromatography, electrophoresis, tandem techniques, electroanalytical methods, X-ray analysis and other significant topics. In addition, books in the series will include the *application* of analytical techniques in areas such as environmental science, the life sciences, clinical analysis, food science, forensic analysis, pharmaceutical science, conservation and archaeology, polymer science and general solid-state materials science.

Written by experts in their own particular fields, the books are presented in an easy-to-read, user-friendly style, with each chapter including both learning objectives and summaries of the subject matter being covered. The progress of the reader can be assessed by the use of frequent self-assessment questions (SAQs) and discussion questions (DQs), along with their corresponding reinforcing or remedial responses, which appear regularly throughout the texts. The books are thus eminently suitable both for self-study applications and for forming the basis of industrial company in-house training schemes. Each text also contains a large amount of supplementary material, including bibliographies, lists of acronyms and abbreviations, and tables of SI Units and important physical constants, plus where appropriate, glossaries and references to original literature sources.

It is therefore hoped that this present series of text books will prove to be a useful and valuable source of teaching material, both for individual students and for teachers of science courses.

Dave Ando
Dartford, UK

Preface

Polymers are of major economic and social importance and thus it is necessary to understand the appropriate methods for characterizing such materials. Although there are a number of polymer science texts currently on the market, there are few which are directed at the true beginner to the field. Therefore, one of the aims of this present book is to explain the fundamentals of the subject in a straightforward, clear and concise manner. There are also several books available which cover the specific techniques used to analyse and characterize polymers. This text further aims to introduce the most commonly used techniques for polymer analysis in one book – again, at a level suitable for the beginner.

This text is not intended to be comprehensive – polymer science is a very extensive field! However, it is hoped that the information provided here can be used as a starting point for more detailed investigations. The book is laid out with chapters covering the main aspects of polymer science and technology, namely identification, polymerization, molecular weight, structure, surface properties, degradation, and mechanical properties. The background to each analytical technique is introduced and explained, and how these techniques may be applied to the study of polymers is then covered in the various chapters. Suitable questions and problems (in the form of self-assessment and discussion questions (SAQs and DQs)) are included in each chapter to assist the reader in understanding the specific techniques/analytical methods being discussed.

I should like to thank Kin Hong Friolo and Kristen Nissen for providing data, and, in particular, Paul Thomas for his contributions and his support during the period that this book was being prepared.

Finally, I very much hope that those learning about and researching polymers will find this text both a useful and valuable introduction to the area of ‘Polymer Analysis’.

*Barbara Stuart
University of Technology, Sydney, Australia*

Acronyms, Abbreviations and Symbols

ABS	acrylonitrile–butadiene–styrene
AFM	atomic force microscopy
AIBN	azobisisobutyronitrile
ATR	attenuated total reflectance
DGEBA	diglycidyl ether of bisphenol A
DMA	dynamic mechanical analysis
DMTA	dynamic mechanical thermal analysis
DOP	dioctyl phthalate
DP	degree of polymerization
DRIFT	diffuse reflectance
DSC	differential scanning calorimetry
DTA	differential thermal analysis
EPR	electron paramagnetic resonance
ESCA	electron spectroscopy for chemical analysis
ESEM	environmental scanning electron microscopy
ESR	electron spin resonance
FIB	fast-ion bombardment
FID	free-induction decay
FT	Fourier transform
FTIR	Fourier-transform infrared (spectroscopy)
GC	gas chromatography
GPC	gel permeation chromatography
HDPE	high-density polyethylene
HMA	hexyl methacrylate
HPLC	high performance liquid chromatography
HPP	high-performance polymer

ICP	intrinsically conducting polymer
IGC	inverse gas chromatography
IPN	interpenetrating polymer network
I	initiator concentration
K–K	Kramers–Kronig
KRS-5	thallium iodide
LCD	liquid crystal display
LCP	liquid crystalline polymer
LCST	lower critical solution temperature
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
LOI	limiting oxygen index
MALDI	matrix-assisted laser desorption ionization
M–F	melamine–formaldehyde
MMA	methyl methacrylate
MS	mass spectrometry
M•	radical species concentration
NBR	acrylonitrile–butadiene rubber
NMR	nuclear magnetic resonance
OM	optical microscopy
PA	polyacetylene
PAN	polyacrylonitrile
PAS	photoacoustic spectroscopy
PBT	poly(butylene terephthalate)
PC	polycarbonate
PCL	polycaprolactone
PCTFE	polychlorotrifluoroethylene
PDI	polydispersity index
PDMS	polydimethylsiloxane
PE	polyethylene
PEEK	poly(ether ether ketone)
PEES	poly(ether ether sulfone)
PEI	poly(ether imide)
PEO	poly(ethylene oxide)
PES	poly(ether sulfone)
PET	poly(ethylene terephthalate)
PGC	pyrolysis gas chromatography
PHEMA	poly(hydroxyethyl methacrylate)
PIP	piperidine
PMMA	poly(methyl methacrylate)
PP	polypropylene
PPO	poly(phenylene oxide)
PPP	poly(<i>p</i> -phenylene)

PPS	poly(phenylene sulfide)
PPY	polypyrrole
PS	polystyrene
PTFE	polytetrafluoroethylene
PU	polyurethane
PVA	poly(vinyl acetate)
PVAI	poly(vinyl alcohol)
PVC	poly(vinyl chloride)
R•	free radical
SALS	small-angle light scattering
SAN	styrene–acrylonitrile
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
SBR	styrene–butadiene rubber
SDS	sodium dodecyl sulfate
SEC	size-exclusion chromatography
SEM	scanning electron microscopy
SIMS	secondary-ion mass spectrometry
TCE	tetrachloroethane
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TLC	thin layer chromatography
TMA	thermal mechanical analysis
TMS	tetramethylsilane
TOF	time-of-flight
TPE	thermoplastic elastomer
UCST	upper critical solution temperature
U–F	urea–formaldehyde
UHMWPE	ultra-high-molecular-weight polyethylene
UTS	ultimate tensile strength
UV–Vis	ultraviolet–visible
WAXS	wide-angle X-ray scattering
WLF	Williams–Landel–Ferry
XPS	X-ray photoelectron spectroscopy

a	Mark–Houwink–Sakurada constant; capillary constant
a_T	shift factor
A	absorbance; area
B	field strength; osmotic virial coefficient
c	concentration
C_p	heat capacity (at constant pressure)
d	distance
d_p	depth of penetration

D	diffusion coefficient
E	Young's modulus
E'	storage modulus
E''	loss modulus
E^*	complex modulus
E_A	activation energy
E_B	binding energy
E_c	Young's modulus of composite
E_D	activation energy for transport of polymer chains
E_f	Young's modulus of fibre
E_K	kinetic energy
E_m	Young's modulus of matrix
f	initiator frequency; mole fraction in monomer feed
F	degree of orientation; flow rate; force; mole fraction of monomer
g	g -value
h	height; Planck constant
H	optical constant
H_0	external magnetic field strength
I	spin number; intensity
I_f	fluorescence intensity
I_p	phosphorescence intensity
I_0	incident intensity
J	coupling constant; gas compressibility factor
$J(t)$	creep compliance
k	rate constant; molar absorption coefficient
K	calibration factor; Mark–Houwink–Sakurada constant; proportionality constant
l	pathlength; bond length; length
m	mass
M	molecular weight
$\overline{M}_n$	number-average molecular weight
$\overline{M}_w$	weight-average molecular weight
m/z	mass-to-charge (ratio)
n	refractive index; Avrami exponent; melt flow index
$\bar{n}_n$	number-average degree of polymerization
N	number of molecules; number of bonds; cycles to failure
p	extent of reaction
P	pressure
$P(x)$	probability
q	heating rate; quantum yield
Q	rate of extrusion
r	radius; reactivity ratio

R	universal constant; X-ray distance; reaction rate
R_c	contour length
R_g	radius of gyration
R_{rms}	root-mean-square end-to-end distance
R_∞	absolute reflectance
$R(\theta)$	Rayleigh ratio
s	speed
S	sedimentation constant
S_0	ground singlet state
S_1	excited singlet state
t	time (general); elution time
T	transmittance; temperature
T_c	crystallization temperature
T_d	degradation temperature
T_g	glass transition temperature
T_m	melting temperature
T_l	excited triplet state
v	volume fraction; velocity
v_s	specific volume
V	volume
V_f	fibre volume
V_g	specific retention volume
V_m	matrix volume
V_R	retention volume
w	weight
w_i	weight fraction
x	X-ray line spacing
x_c	mass fraction of crystals
x_i	number fraction
x_n	number-average chain length
x_w	weight-average chain length
Z_c	critical chain length
Z_w	weight-average chain length
α	coefficient of thermal expansion
β	Bohr magneton
γ	magnetogyric ratio; shear rate
γ_c	critical surface tension
γ_L	surface tension
δ	chemical shift; phase angle; solubility parameter
ΔC_p	heat capacity change
ΔE	energy change
ΔG_m	Gibbs free energy change on mixing

ΔH	enthalpy change
ΔH_a	enthalpy change of amorphous standard
ΔH_c	enthalpy change of crystalline standard
ΔH_m	enthalpy change on mixing
Δn	birefringence
ΔS_m	entropy change on mixing
ΔT	temperature change
ε	molar absorptivity; strain
η	viscosity
$[\eta]$	intrinsic viscosity
θ	angle of incidence; contact angle; Flory temperature
θ_d	dynamic contact angle
θ_s	static contact angle
λ	wavelength; extension ratio
μ	friction coefficient
ν	frequency; linear spherulite growth rate
ν_0	universal constant for crystalline polymers
π	osmotic pressure
ρ	density
ρ_a	density of amorphous polymer
ρ_c	composite density; density of crystalline polymer
ρ_f	fibre density
ρ_m	matrix density
ρ_s	density of polymer sample
σ	stress
σ_c	tensile strength of composite
σ_f	tensile strength of fibre
σ_m	tensile strength of matrix
σ_Y	yield strength
τ	shear stress; relaxation time
ϕ	angle of refraction
Φ	work function
ω	angular velocity

About the Author

Barbara Stuart, B.Sc., M.Sc. (Hons), Ph.D., DIC, MRACI, CChem MRSC

After graduating with a B.Sc. degree from the University of Sydney in Australia, Barbara Stuart then worked as a tutor at this university. She also carried out research in the field of biophysical chemistry in the Department of Physical Chemistry and graduated with an M.Sc. degree in 1990. The author then moved to the UK to carry out doctoral studies in polymer engineering within the Department of Chemical Engineering and Chemical Technology at Imperial College (University of London). After obtaining her Ph.D. in 1993, she took up a position as a Lecturer in Physical Chemistry at the University of Greenwich in South East London. Barbara returned to Australia in 1995, joining the staff of the Department of Materials Science at the University of Technology, Sydney, where she is currently a Senior Lecturer. She is presently conducting research in the fields of polymer spectroscopy, materials conservation and forensic science. Barbara is the author of two other books published by John Wiley and Sons, Ltd, namely *Modern Infrared Spectroscopy* and *Biological Applications of Infrared Spectroscopy*, both of these titles in the ACOL Series of open learning texts.

Chapter 1

Introduction

Learning Objectives

- To understand the basic definitions used to describe polymers.
- To understand the different categories of polymers as based on their structures.
- To appreciate the history of the development of synthetic polymers.
- To recognize common thermoplastics, thermosets and elastomers, and their specific properties.
- To recognize the structures and properties of high-performance polymers.
- To understand the nature and types of copolymers.
- To understand the characteristics of polymer blends.
- To understand the nature and composition of polymer composites.
- To recognize the types of additives used in polymers.
- To understand the nature of speciality polymeric materials, such as liquid crystalline polymers, conducting polymers, thermoplastic elastomers, bio-medical polymers and biodegradable polymers.

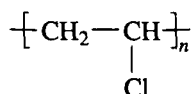
1.1 Introduction

Polymers play an enormously important role in modern society. The significance of these materials is often taken for granted, yet polymers are fundamental to most aspects of modern life such as building, communication, transportation, clothing and packaging. Thus, an understanding of the structures and properties of polymeric materials is vital.

What is a polymer? Polymers are large molecules consisting of a large number of small component molecules. In fact, the name polymer derives from the

Greek 'polys' meaning 'many' and 'meros' meaning 'part.' Many polymers are synthesized from their constituent *monomers* via a *polymerization* process. Most commercial polymers are based on covalent compounds of carbon, although certain synthetic polymers may also be based on inorganic atoms such as silicon.

Vinyl polymers have names which are derived from the names of their particular monomers. For example, poly(vinyl chloride) (PVC) is made from vinyl chloride ($\text{CH}_2=\text{CHCl}$). PVC is usually denoted as follows:



illustrating the structural repeat unit of the polymer. The repeat unit in a polymer is often referred to as a *mer*. The n in the polymer structure is known as the *degree of polymerization* (DP) and refers to the number of 'mers' in a polymer structure.

SAQ 1.1

What is the degree of polymerization of a sample of polyethylene, $[\text{CH}_2-\text{CH}_2]_n$, which has a molecular weight of $100\,000 \text{ g mol}^{-1}$?

Polymers can display a range of different structures (see Figure 1.1). In the simplest case, they possess a simple *linear* structure. However, polymers can also be *branched*, depending on the method of polymerization. They may also display a *cross-linked* structure. Some more unusual polymer structures include *star* polymers, which contain three or more polymer chains connected to a central unit, *ladder* polymers, which consist of repeating ring structures, and *dendrimers*, which show a star-like structure with branching. These different sorts of microstructures have an effect on the properties of the polymer; this aspect will be discussed further in Chapter 5.

Polymers are often commonly referred to as 'plastics'. However, this is somewhat of a misnomer. The term 'plastic' refers to one class of polymers known as *thermoplastics*. Polymers in this category show a range of different properties, but a simple definition is to describe these as polymers that melt when heated and re-solidify when cooled. Thermoplastics tend to be made up of linear or lightly branched molecules, as such structures enable the polymer chains enough freedom of movement to change form as a function of temperature. However, not all polymers are capable of being melted. For example, *thermosets* are polymers that do not melt when heated, but decompose irreversibly at high temperatures. Thermosets are cross-linked, with the restrictive structure preventing melting behaviour. Some cross-linked polymers may show rubber-like characteristics and these are known as *elastomers*. Such materials can be extensively stretched but will rapidly recover their original dimensions.

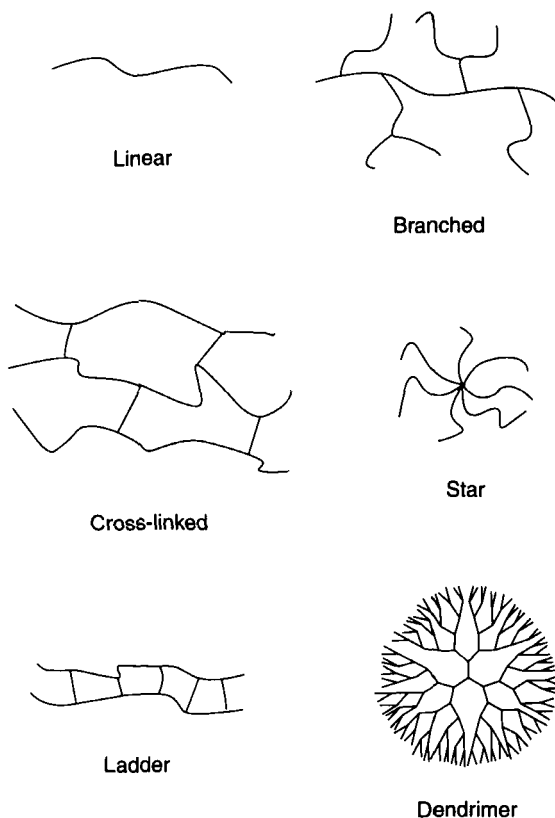


Figure 1.1 Various types of polymer structures.

1.2 History

The modern polymer industry evolved from the modification of the properties of certain natural polymers [1]. In the 19th century, the latex extracted from a tropical rubber tree was used to produce a rubbery material. The US chemist, Charles Goodyear, was able to improve the elastic properties of natural rubber by heating with sulfur, a process known as *vulcanization*.

Cellulose nitrate, derived from cellulose, was developed by Christian Schoenbein in Switzerland during 1846. Although initially recognized as an explosive, it was soon realized that cellulose nitrate was also a hard elastic material which could be readily moulded into different shapes. The development of *celluloid*, a plasticized version of cellulose nitrate, soon followed and was a commercial success, leading to the development of photography. By the late 19th century, other modifications of cellulose, such as viscose rayon fibres and cellophane, had been developed.

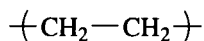
The first decade of the 20th century saw the development of the first synthetic plastics. In the United States, Leo Baekeland reacted phenol and formaldehyde to obtain a heat-resistant material that was marketed as 'Bakelite'. This polymer soon achieved broad commercial success and became widely used for household goods, and in the developing electronic and car industries. Despite the success of Bakelite, one disadvantage was its dark colour. Consequently, in the 1920s, urea-formaldehyde polymers were introduced, with such materials being available in a wide range of colours.

The 1930s saw the development of the commercially important material, *polyethylene*. Chemists at ICI in the UK, while experimenting with ethylene at different temperatures and pressures, stumbled upon this important polymer. The development of *nylon* was a more deliberate process. Wallace Carothers of the DuPont Company in the United States set about producing a material which could replace silk. The 2nd World War was responsible for the development of many synthetic polymers, with war-time needs forcing the production of low-cost plastics. By the 1950s, polyethylene, polystyrene and poly(vinyl chloride) had become widely available materials and very much a part of everyday life. Since this period, polymers have been developed and incorporated into many aspects of life – everything from engineering to medicine.

1.3 Thermoplastics

Thermoplastics are polymers that require heat to make them processable. After cooling, such materials retain their shape. In addition, these polymers may be reheated and reformed, often without significant changes to their properties. Many thermoplastics contain long main chains consisting of covalently bonded carbon atoms. Table 1.1 summarizes the properties and applications of some common thermoplastics [2].

Polyethylene (PE) is the major general purpose thermoplastic and is widely used for packaging, containers, tubing and household goods. The structural repeat unit of PE is as follows:



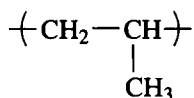
The main reasons for the popularity of PE is its low cost, easy processability and good mechanical properties. A susceptibility to weathering is a limitation, but this is not usually a problem with routine applications of PE. There are two main types of mass-produced polyethylene. *Low-density polyethylene* (LDPE) has a branched chain structure and tends to be used for bags and packaging, while *high-density polyethylene* (HDPE) has a mostly linear structure and finds uses in bottles and containers. *Linear low-density polyethylene* (LLDPE) has also been developed for its good processing properties. This PE has a linear chain structure with short side branches and is used for bags. Another class of PE of note is

Table 1.1 The properties and applications of some common thermoplastics

Name	Trade names	Properties	Applications
Polyethylene (PE)	Polythene, Rigidex, Alkathene, Hostalen, Lupolen, Alathon	Inexpensive, easily processed, good chemical resistance, poor resistance to weathering	Household goods, packaging, containers
Polypropylene (PP)	Propathene, Appryl, Novolen	Inexpensive, good chemical resistance, poor ultraviolet resistance	Packaging, containers, furniture, pipes
Poly(vinyl chloride) (PVC)	Darvic, Corvic, Geon, Evipol, Vinnolit, Hostalit	Inexpensive, rigid, good chemical resistance, limited thermal stability, additives required for processing	Packaging, cable insulation, pipes, toys
Polystyrene (PS)	Styron, Polystyrol, Novacor	Inexpensive, transparent, rigid, good insulating properties, low water absorption, flammable, brittle	Food containers, packaging, appliance housings
Poly(methyl methacrylate) (PMMA)	Perspex, Plexiglas, Lucite, Acrylite	Transparent, good weathering properties, tough, rigid, poor insulating properties, poor resistance to organic solvents	Transparent sheets and mouldings, aeroplane windows, street lamps, display signs
Polyamide (PA)	Nylon, Ultramid, Zytel, Caprolan, Stanyl, Capron, Akulon, Rilsan, Vestamid	Tough, flexible, abrasion resistant, good wear and frictional properties, absorbs water	Textiles, brushes, surgical applications, bearings, gears
Polytetrafluoroethylene (PTFE)	Teflon, Fluon, Halon, Hostaflon	Low friction, good electrical insulation, excellent chemical resistance, cannot be dissolved, relatively expensive	Non-stick surfaces, insulation tape, engineering applications
Polyacrylonitrile (PAN)	Barex, Orlon	Strong, good chemical resistance	Wool-type applications
Cellulose acetate	Tenite, Acetate, Clarifoil, Dixel	Crease resistance, moisture resistance, dyeability	Textile fibres, moulded products, film, packaging
Poly(vinyl acetate) (PVA)	Elvacet, Vinylite	Good general stability, quick drying, inexpensive	Surface coatings, adhesives, paint
Poly(vinyl alcohol) (PVAI)	Vinex	Water-soluble	Fibres, adhesives, thickening agents
Poly(ethylene terephthalate) (PET)	Terylene, Dacron, Melinex, Mylar	Low short-term water absorption, fibres are crease resistant, strong, high processing temperatures required	Textile fibres, film, packaging, magnetic tapes
Poly(butylene terephthalate) (PBT)	Celanex, Tenite, Rynite, Valox	Strong, good chemical resistance, good electrical insulation	Electrical, electronic and automotive engineering

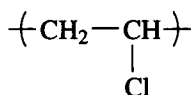
ultra-high-molecular-weight polyethylene (UHMWPE), a linear PE with a high molecular weight of the order of $4 \times 10^6 \text{ g mol}^{-1}$. This form of polyethylene shows excellent wear and abrasion resistance, high impact resistance and a very low friction coefficient. UHMWPE also possesses good chemical resistance and a self-lubricating and non-stick surface. This combination of properties leads to its use in diverse applications such as medical prostheses, blood filters, bullet-proof vests and fishing lines.

Polypropylene (PP) shows a similar structure to PE, but with a substituted methyl group, as follows:



The presence of the methyl group restricts the rotation of the PP chain and produces a less flexible, but stronger polymer. Like polyethylene, polypropylene shows several attractive properties such as good chemical and moisture resistance and high dimensional stability. These characteristics make this polymer suitable for a wide range of applications, such as bottles, carpets, casings and packaging.

Poly(vinyl chloride) (PVC) is the second largest volume thermoplastic polymer. PVC has a structure which contains a chlorine atom on alternate main chain carbons, as follows:



There are strong dipole interactions between the PVC chains and steric hindrance reduces the flexibility of the molecules. This lack of flexibility in PVC molecules means that this polymer can only be processed when compounded with various *plasticizers*. PVC is widely used because of its excellent chemical resistance and its ability to be modified with additives. In its rigid form, PVC is commonly used in construction as piping, guttering, siding and electrical conduit. Plasticized PVC is also used widely as electrical wire insulation and in household and automotive applications.

Polystyrene (PS) is another widely used thermoplastic, being the fourth most produced polymer by weight. PS is a clear, rigid and brittle material, unless it is modified with rubber. The polymer molecule contains a benzene ring attached to alternate carbon atoms on the backbone, as follows: