Industrial Polymers Handbook Volume 1

Industrial Polymers Handbook

Products, Processes, Applications

Edward S. Wilks (Editor)

Volume 1

Polymerization Processes
Synthetic Polymers

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Cover Illustration: Poly{5-[phenoxtytris(ethoxy)carbonyl]bicyclo[2.2.1]hept-2ene} was prepared via ring-opening metathesis polymerization of the corresponding monomer in the presence of bis(tricyclohexylphosphine)benzylideneruthenium(IV) dichloride. This thermally stable functionalized polynorbornene has a thermogravimetric decomposition temperature of 431°C. Reproduced by courtesy of Professor Alaa S. Abd-El-Aziz, University of Winnipeg, Canada.

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Volume 1	Polymerization Processes Synthetic Polymers
Volume 2	Synthetic Polymers (Continued)
Volume 3	Synthetic Polymers (Continued) Biopolymers and their Derivatives
Volume 4	Biopolymers and their Derivatives (Continued) Indexes

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Preface

In the last 50 years, many comprehensive books on polymers have been published, but few have been dedicated to detailed treatment of those polymers that are industrially important. Only a small percentage of polymers discovered through laboratory research reach commercial status. Many potential candidates for commercialization are rejected for scale-up because of the many tests that each candidate must pass before a decision is made to manufacture and sell it. Therefore, publications offering in-depth coverage of commercially significant polymers and their manufacturing processes are valuable to those whose careers are focused on industrial polymer manufacture.

Since 1998, the sixth edition of *Ullmann's Encyclopedia of Industrial Chemistry*, a comprehensive multi-volume treatise devoted solely to both polymeric and non-polymeric chemicals encountered in the industrial world, has been the standard reference text. Inevitably, one drawback of the accumulation of all of this information in a single, massive work was that its acquisition required considerable expenditure. This problem is now being addressed by Wiley-VCH. The "Industrial Polymers Handbook: Products, Processes, Applications" is being created as a separate publication for the first time by extraction from the complete multi-volume encyclopedia of selected chapters on polymers. Basic principles and fundamental processes associated with industrial polymer manufacture are being discussed. Chapters on polymer nomenclature and on polyureas have been written especially for this book.

The first section of the book describes polymerization processes in detail, addresses trends in polymer reaction engineering, polymerization mechanisms and kinetics, and polymerization processes and reactor modeling. The next section includes a comprehensive presentation of source-based and structure-based polymer nomenclature and covers descriptions of the syntheses and characteristics of the industrially important polymer classes: step-growth polymers (polyamides, polycarbonates, polyesters, polyimides, polyureas, and polyurethanes); chain-growth polymers (acrylic, ethylenic, and vinyl); polyoxymethylenes; polymers formed by ring-opening reactions; resins (including alkyd, amino, epoxy, phenolic, and unsaturated polyester types); and miscellaneous types [electrically conducting polymers, inorganic polymers, poly(phenylene oxides), and silicones]. Also included are biopolymers and their derivatives: cellulose and its esters and ethers; chitin and chitosan; gelatin; nucleic acids, polysaccharides, proteins, natural resins, silk, starch, and wool.

Each chapter begins with an introduction to the subject under discussion, which is followed by a detailed description of the basic principles of the subject. For the synthetic polymer classes covered by the book, the practical aspects of manufacture are discussed in a wealth of detail. For the biopolymers and their derivatives, there is information on manufacture (where appropriate), and extensive treatment of their properties and industrial processing.

My thanks go to all contributing authors, especially to Professor Constantin I. Chiriac and researcher Mrs. Fulga M. Tanasa, both of the Institute of Molecular Chemistry "Petru Poni", Iasi (Jassy), Romania, for their prompt contribution to the chapter on polyureas, to the Wiley-VCH team for their support, and to my wife for her unending patience, encouragement, and understanding.

Wilmington, Delaware, September, 2000 Edward S. Wilks

Contents

Part I: Polymerization Processes 1

1 Polymerization Processes 3

Part II: Synthetic Polymers 201

1 Nomenclature 203

1 Polymer Nomenclature 205

2 Step-Growth Polymers 245

1 Polyamides 247

2 Polycarbonates 291

3 Polyesters 305

4 Polyimides 349

5 Polyureas 383

6 Polyurethanes 419

3 Chain-Growth Polymers 503

1 Fluoropolymers 505

2 Polyacrylamides and Poly(Acrylic Acids) 565

3 Polyacrylates 587

Part I: Polymerization Processes

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I. Polymerization Processes

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Sections 3.3.3.1 – 3.3.3.5 and 3.3.6.1 were based on the article Polymerisationstechnik in Ullmann's Encyclopedia of Industrial Chemistry, 4th ed. written by HEINZ GERRENS

List of symbols

A	chemical species; vacant adsorption site
[A]	concentration of species A
$[A]_0$	initial concentration of species A
A_1, A_2, A_3	adjustable parameters
ABS	acrylonitrile – butadiene – styrene rubber-modified copolymer
ACA	aminocaproic acid
$A(h)$	energy required to separate to a distance h=∞, two drops of diameter d=1 initially separated by a distance h_0
A_m	surface area of micelles
A_p	surface area of polymer particles

B	chemical species
BHET	bis-hydroxyethyl terephthalate
BR	batch reactor
C_{pi}	dimensionless moments of polymer distribution for chain transfer to polymer [$= K_{fp} Q_i/(K_p[M])$]
C_S	surfactant concentration
CCD	chemical composition distribution
CMC	critical micelle concentration
CPFR	continuous plug flow reactor
CSTR	continuous stirred-tank reactor with an ideal residence-time distribution
CTA	chain-transfer agent
d	particle diameter
$\bar{d}$	average particle diameter
d_{32}	Sauter mean diameter of a spherical-particle suspension
d_{50}	diameter at which 50 wt % of particles pass through a sieve
d_{min}	minimum particle diameter
d_{max}	maximum particle diameter
D	stirrer diameter
D_{op}	mean diffusion coefficient for oligomeric radicals and latex particles
DMT	dimethyl terephthalate
E_d	activation energy for initiator decomposition
E/E_0	mass fraction of material passing out of reactor with a residence time t to $t + dt$
E_f	activation energy for chain-transfer reaction
E_L	activation energy for average chain lengths
E_N	activation energy for polymer particle nucleation
E_p	activation energy for propagation
E_R	activation energy for polymerization
$E(t)$	residence-time distribution for a flow reactor at steady state
E_t	activation energy for bimolecular termination
Eu	modified power number
EG	ethylene glycol
EGDMA	ethylene glycol dimethacrylate
EPS	expandable polystyrene
ESR	electron spin resonance spectroscopy
f	initiator efficiency; functionality of monomer
f_j	mole fraction of monomer of type j
$F_{i,in}$	molar flow rate of monomer of type i into the reactor
F_{in}	total molar flow rate (of all monomer types) into the reactor
$F_{Ii,in}$	molar flow rate of initiator of type i into the reactor
F_j	mole fraction of monomer of type j, chemically bound in polymer produced instantaneously
$\bar{F}_j$	mole fraction of monomer of type j chemically bound in accumulated polymer
$\bar{F}_1$	mole fraction of monomer 1 (containing an abstractable atom) in accumulated polymer
$\bar{F}_2$	mole fraction of monomer 2 (containing a reactive carbon – carbon bond
$F_{pi,in}$	molar flow rate of monomer of type i chemically bound in polymer into the reactor
Fr	Froude number

$F_{T,in}$	molar flow rate of chain-transfer agent T into the reactor
G^+	counterion
GPC	gel permeation chromatography
HCSTR	homogeneous CSTR
HDPE	high-density polyethylene
H – H	Hui – Hamielec styrene polymerization model
HIPS	high-impact polystyrene
I	initiator or catalyst
[I]	concentration of initiator or catalyst
K	chemical rate constant; equilibrium constant
K_a	absorption constant for oligomeric radicals entering polymer particles
K_A	adsorption rate constant
K_d	initiator decomposition constant
K_{dp}	depropagation constant
K_D	desorption rate constant
$K_{f_{ij}}$	rate constant for polymeric radical of type i abstracting an atom from monomer of type j chemically bound in polymer
K_{fm}	transfer to monomer rate constant
K_{fp}	rate constant for chain transfer to polymer
K_{fT}	rate constant for chain transfer to CTA
K_{fT^i}	rate constant for chain transfer from polymeric radical of type i to CTA
K_{fX}	transfer to small molecule X rate constant
K_i	rate constant for monomer adding to a primary radical
K_p	propagation rate constant
K'_p	propagation rate constant for transfer radical
K_p^-	propagation rate constant for free ion
$K_p^{\pm}$	propagation rate constant for ion pair
$K_p{}^*$	rate constant for polymeric radicals adding to pendant double bonds on polymer chains
$K_{p_{ij}}$, K_{ij}	propagation rate constant for monomer of type j adding to polymeric active center of type i
$K_{p_{ij}}$	rate constant for polymeric radical of type i adding to a double bond on a monomer unit of type j chemically bound in the polymer
$K_{p_{ijk}}$	propagation rate constant for monomer of type k adding to a polymeric active center of type ij
K_t	total bimolecular termination constant ($K_{tc} + K_{td}$)
K_{t0}	total bimolecular termination constant at zero conversion of monomer
K_{tc}	rate constant for bimolecular termination by combination
$K_{tc_{ij}}$	termination by combination rate constant for polymeric radicals of types i and j (chemical control)
$\bar{K}_{tcN}$	number-average bimolecular termination constant by combination
K_{td}	rate constant for bimolecular termination by disproportionation
$K_{td_{ij}}$	termination by disproportionation rate constant for polymeric radicals of types i and j (chemical control)
$\bar{K}_{tdN}$	number-average bimolecular termination constant by disproportionation
$\bar{K}_{tN}$	total number-average bimolecular termination constant
K_{tp}	termination rate constant in polymer particles

$K_t(r, s)$	total bivariate distribution for diffusion-controlled bimolecular termination of polymeric species of chain lengths r and s
K_{tw}	termination rate constant in aqueous phase
$\bar{K}_{tW}, \bar{K}_{tZ}$	total weight- and z-average bimolecular termination constants
L	characteristic length of energy-containing large eddies
L	length of path traversed by a growing radical from its point of origin to the point where it precipitates
L	reactor length
LALLS	low-angle laser light scattering
LCB	long-chain branching
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
m_i	number of moles of monomer i in terpolymer (Eq. 3.101)
M_c	average molecular mass between cross-links
M_i	monomer of type i
M_m	aggregation number for emulsifier molecules in micelles
M_{mi}	molecular mass of monomer of type$i$
$\bar{M}_N, \bar{M}_W, \bar{M}_Z, \bar{M}_{Z+1}$	number-, weight-, Z and $Z+1$-average molar mass (molecular mass, respectively)
[M]	total monomer concentration
$[M]_0$	initial monomer concentration; monomer concentration in feed
$[M]_c$	equilibrium concentration of monomer at the ceiling temperature
$[M_i]$	concentration of monomer of type i
$[M]_p$	concentration of monomer in the polymer particles
M – H	Marten – Hamielec polymerization model
MMA	methyl methacrylate
MWD	molecular mass distribution (molar mass distribution)
n	number of monomer types
n	order of reaction
$\bar{n}$	average number of radicals per particle
N_0, N	number of functional groups at time zero and t
N	total number of moles in the reactor; stirrer speed
N_A	number of moles of A-functional groups; Avogadro number
N_{A_0}	initial number of moles of A-functional groups
N_B	number of moles of B-functional groups
N_{B_0}	initial number of moles of B-functional groups
N_i	moles of monomer of type i in the reactor
N_I	number of moles of initiator in the reactor; number of growing chains
N_{I0}	initial number of moles of initiator in the reactor
N_{Ii}	moles of initiator of type i in the reactor
$N(r)$	number chain length distribution (number-fraction of polymer molecules of chain length r)
N_M	number of monomer units; number of micelles; number of monomer molecules consumed
N_n	number of polymer particles containing n radicals
N_p	number of polymer particles per unit volume
N_T	moles of CTA in reactor

NBR	nitrile – butadiene rubber
NIRS	near infrared spectroscopy
p	conversion of functional groups
p_c	critical threshold
P	growing polymer particle; polymer
P_c	conversion of functional groups at gelation point
P_{cr}	critical chain length for precipitation
P_i	moles of monomer of type i chemically bound in polymer in the reactor
P_{ij}	polymer containing i units of monomer of type 1 and j units of monomer of type 2
$[P_m]$	concentration of polymer with chain length m
$P_{m,n}$	dead polymer chain containing m units of monomer 1 and n units of monomer 2
P_N	number-average chain length of polymer produced instantaneously
$\bar{P}_N$	number-average chain length of accumulated polymer
$\bar{P}_N^{sol}$	number-average chain length of sol molecules
P_r	polymer molecule of chain length r
P_W	weight-average chain length of polymer produced instantaneously
$\bar{P}_W$	weight-average chain length of accumulated polymer
$\bar{P}_W^{sol}$	weight-average chain length of sol molecules
PDI	polydispersity index of polymer produced instantaneously
$\overline{\text{PDI}}$	polydispersity index of accumulated polymer
PE	polyethylene
PEK	polyetherketone
PES	polyethersulfone
PETP	poly(ethylene terephthalate)
PFR	plug-flow reactor
PMMA	poly(methyl methacrylate)
PP	polypropylene
PPS	poly(phenylene sulfide)
PS	polystyrene
PSD	particle size distribution
PVAL	poly(vinyl alcohol), partially hydrolyzed
PVC	poly(vinyl chloride)
P^*	polymeric active center
$[P^*]$	concentration of polymeric active centers (ionic or radical type)
P^*_i	polymeric active center with active center located on monomer of type i chemically bound in the polymer chain
P^*_{ij}	polymeric active center with active center located on monomer of type j which is adjacent to monomer of type i chemically bound in the polymer chain
$P^*_{m,n,i}$	polymer chain containing m units of monomer 1, n units of monomer 2, with active center on monomer i
Q_i	i-th moment of the dead polymer distribution
r	polymer chain length
r	polymer particle radius
r_M	micelle radius
r_p	polymer particle radius
r_1, r_2	reactivity ratios
R	gas constant

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