Practical Chemistry of
Polyurethanes and Diisocyanates

PRACTICAL CHEMISTRY OF POLYURETHANES & DIISOCYANATES

Section #1: Basic Concepts in Polymer Chemistry and Technology

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TESTING & DEVELOPMENT SERVICES

PRACTICAL CHEMISTRY OF POLYURETHANES

AND DIISOCYANATES

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CONTENTS

SLIDE 1

SLIDE 2A

BASIC CONCEPTS IN POLYMER CHEMISTRY AND TECHNOLOGY

I. **OVERVIEW:**

Polymers are extremely large and complex molecules produced by combining a large number of simple molecules. The simple molecules which combine to form polymers are called monomers. Monomers, like most chemical compounds, are compounds whose properties (molecular weight, boiling point, melting point, and etc.) are discrete. Polymers, on the other hand, typically do not have discrete properties but have average properties which represent a range of molecules with differing molecular weight and often slightly differing structure.

PROPERTIES OF SMALL MOLECULES vs POLYMERS

SMALL MOLECULES	POLYMER MOLECULES
Three Discrete States solid, liquid, gas	**Continuum of Two States** solid → quasi solid → liquid
Discrete Formula	Average Formula
Discrete Molecular Wt.	Average Molecular Wt.
Discrete Properties mp density crystalline /glass	Ranges of Properties mp range density range microcrystalline mechanical properties
	Topography

SLIDE 3

The average molecular weight can greatly affect the physical properties of a polymer. Molecular weight distribution can also have a significant effect upon a polymer's properties, especially processing and rheological characteristics.

PROPERTIES vs MOLECULAR WT.

MELT VISCOSITY

TENSILE STRENGTH
TEAR STRENGTH

50   100   150   200

$\overline{DP}$

1
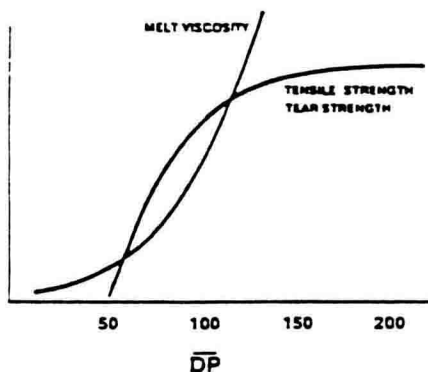
The polymer chains have a spacial architecture. They may be linear, branched, or networked. Polymers have tacticity and stereo microstructure. Polymers exist as homopolymers and copolymers. Copolymers may be random, alternating, segmented, block, graft types.

STRUCTURAL CHARACTERISTIC of POLYMERS

MW, MWD

LINEAR, BRANCHED, or CROSSLINKED

ORIENTATION of MONOMER UNITS
- H-H
- H-T
- T-T

MICROSTRUCTURE
- 1,2 or 1,4
- TRANS
- CIS

TACTICITY
- ATACTIC
- SYNDIOTACTIC
- ISOTACTIC

HOMOPOLYMER, COPOLYMER, TERPOLYMER
- RANDOM   SLIDE 5
- ALTERNATING
- TAPERED   SLIDE 5A
- SEGMENTED
- BLOCK
- GRAFT

Polymers can be crystaline solids, amorphous glasses, viscoelastic fluids, or viscoelastic solids. With respect to mechanical properties, polymers are non-ideal solids. The mechanical properties of polymers are time dependent. For every excitation there are two responses; a viscous response and an elastic response, i.e. a time dependent and a non-time dependent response. The properties of polymers are also very temperature dependent.

MODULUS vs TEMPERATURE
(t = constant)

E'

TEMP

SLIDE 6
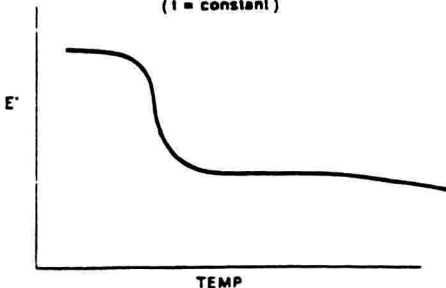
MODULUS vs FREQUENCY
(T = constant)

E'

Frequency¹ (or t)

SLIDE 6A

II. CLASSIFICATION OF POLYMERS:

A. General:

Polymers were for many years classified according to their polymerization method as either addition type or condensation type polymer. More recently the distinction between polymer types has been drawn along the lines of the major differences in the kinetics of polymerization. Here the terms chain polymerization and step growth polymerization replace the terms addition polymerization and condensation polymerization.

CLASSIFICATION SYSTEMS for POLYMERS

CLASSIFICATION by MODE of PZN
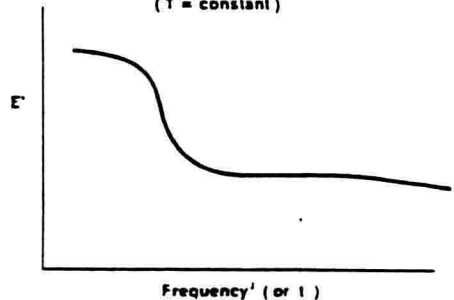Addition Polymers
Condensation Polymers

CLASSIFICATION by KINETICS of PZN
Chain Addition Polymers
Step Addition Polymers

SLIDE 7

The major differences between the kinetics of chain and step polymerizations are that in chain polymerization the high polymer is formed very early in the polymerization. The locus of the polymerization is only on those few chains containing an active propogating center. In step polymerization all species present can react with all other species present. Polymerization proceeds as dimer, trimer, tetramer, and etc. High molecular weight polymer doesn't result until very late in the reaction.

CHAIN ADDITION vs STEP ADDITION

CHAIN   IONIC (LIVING)

AVE MW of POLYMER FRACTION

STEP

% CONVERSION
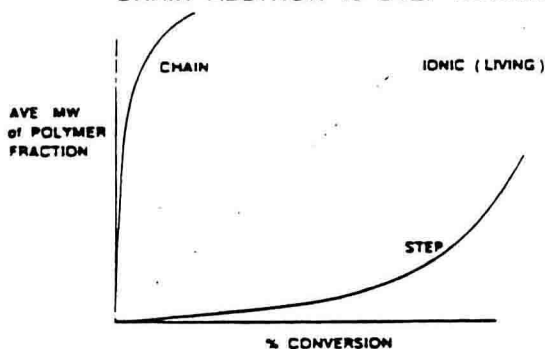
SLIDE 8

	STEP ADDITION	CHAIN ADDITION
Reactions	Single Reaction	Initiation, Propogation, Transfer, Termination
Locus of Pzn	All Molecules	Only Activated Ends
MW Dev.	Slowly, Dimer – Trimer Tetramer – Etc High MW Only @ High Conversion	High MW Early In Pzn
Monomer Conc.	Depleted Early In Pzn	High Throughout Pzn
MWD	Relative Broad Throughout Pzn	Relative Narrow From Outset
Rxn Rate	Propogation Rxn Relatively Slow	Propogation Rxn Relatively Fast

SLIDE 9

B. Chain Addition Polymerization:

The most common forms of chain polymerization are those occuring for monomer containing C=C. Ring opening polymerizations also commonly propogate by chain kinetics.   By their nature chain addition polymerizations typically involve four distinct reactions; initiation, propogation, chain transfer, and termination.   The primary distinguishing feature of chain polymerization is that the sole propogation reaction is that which results from the addition of an active chain end to a monomer molecule.

Chain addition polymerizations are classified according to the nature of the active species on the growing chain end, i.e. radical, anionic, cationic, and Ziegler-Natta coordination polymerization:

NATURE of ACTIVE CHAIN ENDS

MECHANISM   PROPOGATING SPECIES

FREE RADICAL   ⎯⎰⎰⎰⎰⎯ •

ANIONIC   ⎯⎰⎰⎰⎰⎯ ⊖

CATIONIC   ⎯⎰⎰⎰⎯ ⊖

COORDINATION   ⎯⎰⎰⎰⎯ C – Z
                                   M

Z = Coordination Cat.
M = Monomer

SLIDE 10

4

The figure below describes a number of commercial polymers made by chain polymerization:

CHAIN ADDITION POLYMERS

PZN MECHANISM	INITIATORS	EXAMPLES
Radical	Peroxides, Redox, Azo, UV	SBR, PVC, NBR, CR, PS, PTFE
Anionic	Alkali Metals, Lewis Bases, Organo-alkali	SBS, PEO, PMMA QM, POM, PBd
Cationic	Protons, Lewis Acids, Carbocations, Oxoniums	IR, IIR, ECO, PTHF, POM
Z-N Coordination	Transition Metal Halides, Alkyl Aluminums, Alkyl Aluminum Halides	PP, HDPE, LLDPE EPDM, CIS 1,4
Olefin Metathesis	$MoCl_5$, WCl_6	PNORBORNENE
Group Transfer	$(CH_3)_3 Si^{\ominus}$	PMMA

SLIDE ...

C. Step Addition Polymers:

In step polymerization monomers are typically difunctional or trifunctional. In a typical step polymerization a single reaction, the propogation reaction, is responsible for the formation of polymer.

Step polymerization typically occurs in systems of two or more difunctional or trifunctional monomers which bear two dintinctly different functionalities. A single chemical mechanism is responsible for the formation of the polymer. Chain transfer and termination reactions are inherently absent in step polymerizations, though side reactions and reactions with contaminants can have similar effects as transfer or termination.

In a step system all monomer units and growing polymer chain ends participate in propogation throughout the polymerization process. Initially, monomer reacts with monomer to form dimer, dimer with monomer or dimer with dimer to form trimer or tetramer and so on. Monomer is depleted very early in the polymerization and high polymer is not formed until late in the reaction. Figure X above summarizes the characteristic features of step polymerization.

The following provides examples of some typical step addition polymerizations:

STEP ADDITION POLYMERS
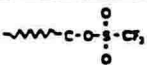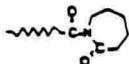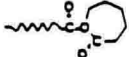
RXN TYPE	GROUP A	GROUP B	EXAMPLE
Condensation	R- OH	R'- COOH	Polyester
	R- OH	R'- COCl	Polyester
	R- OH	R'- COOR'	Polyester
	R- OH	COCl$_2$	Polyester
	R- OH	R'- NCO	Polyurethane
	R- NH$_2$	R'- NCO	Polyurea
	R- NH$_2$	R'- COOH	Polyamide
	R- NH$_2$	R'- COCl	Polyamide
	Si-R$_2$-Cl$_2$	H$_2$O	Polysiloxane
	Ar- OH	COH$_2$	Phenolic Resin
	Ar- OH	R-CH-O-CH$_2$	Epoxy Resin
Oxidative Cplg	Ar- OH	O$_2$	PPO
	Ar- H	Ar- H	
Diels - Alder	R-C≡C-C≡C-R'	R-C-C≡C-C-R'	
Friedel - Crafts	O-CH$_3$	O-CH$_3$	

SLIDE 12

6

D. Ring Opening Polymerizations:

Ring opening polymerizations is a special classification of polymerization comprised almost entirely of reactions proceeding with chain kinetics. This class encompasses anionic, cationic, and coordination type active chain ends. Figure X below provides some examples of ring opening polymerizations.

RING OPENING POLYMER SYSTEMS

MONOMER	ACTIVE CHAIN END	POLYMER
THF	~~~C-O-S-CF₃	POLY (THF) / PTMEG
CAPROLACTAM		NYLON 6
PROPLYENE OXIDE		PPG
CAPROLACTONE		POLYCAPRO-LACTONE

SLIDE 13

III.   METHODS OF POLYMERIZATION:

A.   Homogeneous:

Polymerization methods may be classified in several ways. First we may divide polymerizations into either heterogeneous or homogeneous systems. In homogeneous systems there is generally a single phase present. These may be as bulk systems, i.e. only monomer and forming polymer present, or solution systems, i.e. monomer, forming polymer, and solvent present. In bulk systems, polymerization invariable begins in a solution of polymer in monomer and as monomer is depleted and molecular weight increases polymerization may ultimately be in a solid state or as a melt.

Bulk systems are used when polymerization is relatively slow, exothermic heat is low and manageable, where polymerization mass is small, and/or when final part or shape can be produced "as polymerized". Figure X below provides examples of homogeneous polymerization systems.

HOMOGENEOUS PZN SYSTEMS

BULK SYSTEMS:

Polycondensation—Polyester or Polyamide

Cast Polystyrene or Polyacrylic

Cast Nylon—Caprolactam or Laurylactam

TPU Polymerization

Castable Urethane

SOLUTION SYSTEMS:

Polyurethanes

Cationic Pzn of IR, IIR

Anionic Pzn of SBR, SBS

Coordination Pzn of PP, EPDM

SLIDE 14

B. **Heterogeneous:**

In heterogeneous systems there are two distinct phases are present. Four common heterogeneous systems commonly employed; emulsion, suspension, interfacial, and gas phase.

1. Emulsion and Suspension:

In emulsion and suspension systems monomer is dispersed into small droplets in a media in which the monomer has little or no solubility. Due to cost and ease of disposed or recycle water is a favorite median. A major advantage of suspension and emulsion polymerization is that bulk viscosity is kept low and the heat of polymerization can be readily removed thereby allowing rapid polymerization without excessive heat build up.

8

HETEOGENEOUS PZN SYSTEMS

POLYMERS by EMULSION PZN:

SBR, NBR, PVC, EVA, CR,
Acrylics, Acrylates, PTFE

POLYMERS by SUSPENSION PZN:

PVC, PS, Acrylic

SLIDE 13

In suspension polymerization the initiator is
soluble in the monomer, polymerization within the
droplet behaves according to the same kinetics as
bulk polymerization. Emulsion polymerization has
two major differences from suspension
polymerization: the initiator is soluble only in
the medium and the monomer is emulsified into very
small droplets. Because the droplet's size is very
small and the initiator has low solubility in the
droplet the kinetics of polymerization for emulsion
polymerization is uniquely different from other
polymerizations. Because of low polymerization
temperatures and absence of solvent, chain
transfer, and spontaneous termination rates are
low. Termination due to coupling is kept low by
low radical concentration within the particle. The
result is very favorable: high reaction rates with
high molecular weight.

2. Interfacial Polymerization:

This is a method of step polymerization which is
possible when monomers are highly reactive and
uniquely and individually soluble in immiscile
solvents. A further requirement is that the
forming high polymer must be insoluble in both
solvents. Polymerization then occurs at the
interface of the solutions. This method, like
other heterogeneous methods of polymerization,
allows control of exotherm but its most attractive
feature is the ability to form condensation
polymers of very high molecular weight due to high
reactivity and intrinsic stochiometric control.

9

3. Gas Phase Polymerization:

Here particulate catalyst and forming particles of solid polymer are suspended in a fluidized bed of monomer gas. Again excellent control of temperature is possible. This method of producing polyethylene is very attractive as it operates at low pressures and without solvent.

IV. RADICAL POLYMERIZATION:

A. General:

The fundamental reaction involved in radical polymerization is free radical addition of a carbon-carbon double bond. Among all polymerization types free radical accommodates by far the greatest number of possible monomers. Nearly all vinyl compounds are polymerizable to some extent; the key issue is that it is desirable to have a substituent on the double bond so as to provide sufficient resonance stabilization so that monomer radical will first be more stable than initiator radical so as to allow efficient initiation and that propogating radical is sufficiently stabilized so as to allow propogation reaction to compete favorably with chain termination and chain transfer reactions.

On the other hand, the monomer radical cannot be so highly stabilized as to impede propogation (such as allylic structures) and substituents to the carbon carbon bond cannot be so bulky as to cause stearic hinderance to polymerization. Figure X below depicts the general scheme of the propogation reaction in radical polymerization.

RADICAL PZN OF VINYL MONOMERS
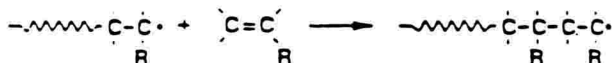
COMMON POLYMERIZABLE MONOMERS

Styrene	1,3 Chloroprene	Methyl Acrylate
Ethylene	Methyl Methacrylate	Vinyl Acetate
1,3 Dienes	Vinylidene Fluoride	Vinylidene Chloride
Vinyl Chloride	Tetrafluoro Ethylene	Acrylonitrile

SLIDE 10

10

TYPICAL FREE RADICAL INITIATORS

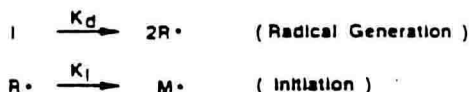| CLASS	EXAMPLE
Peroxides	t-Butyl Peroxide
	Cumyl Peroxide
	Benzoyl Peroxide
Azo Compounds	2, 2'-Azobisisobutyronitrile
Redox	H_2O_2 Fe^{2+}
Ionizing Radiation	*UV*

As a result of both resonance stabilization and stearic hinderance polymerizations typically proceed head to tail (H-T). Radical polymerization is generally not stereo selective so polymers prepared by radical polymerization are usually attactic.

Radical polymerization proceeds in four distinct steps: initiation, propogation, chain transfer, and termination. Initiator and propogating chain radicals are in general very reactive. In order to produce polymers of high molecular weight and with minimum branding, great attention must be given to the polymerization system in order to minimize chain transfer and termination reactions.

RADICAL PZN — 4 STEPS

1. INITIATION:

$$I \xrightarrow{K_d} 2R\cdot \quad \text{(Radical Generation)}$$

$$R\cdot \xrightarrow{K_I} M\cdot \quad \text{(Initiation)}$$

2. PROPOGATION:

$$M\cdot + M \xrightarrow{K_p} MM\cdot$$

3. CHAIN TRANSFER:
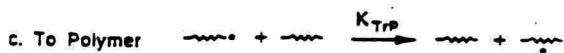
a. To Monomer $\sim\!\!\bullet$ + M $\xrightarrow{K_{TrM}}$ $\sim\!\!\sim$ + M$\bullet$

b. To Solvent $\sim\!\!\bullet$ + S $\xrightarrow{K_{Trs}}$ $\sim\!\!\sim$ + S$\bullet$

c. To Polymer $\sim\!\!\bullet$ + $\sim\!\!\sim$ $\xrightarrow{K_{TrP}}$ $\sim\!\!\sim$ + $\underset{\bullet}{\sim\!\!\sim}$

4. TERMINATION:

a. $\sim\!\!\bullet$ + $\sim\!\!\bullet$ $\xrightarrow{K_{Tc}}$ $\sim\!\!\sim\!\!\sim$ (By Combination)

b. $\sim\!\!\bullet$ + $\sim\!\!\bullet$ $\xrightarrow{K_{Tdis}}$ $\sim\!\!\sim$ + $\sim\!\!\sim$

                 (By Dissproportionation
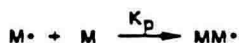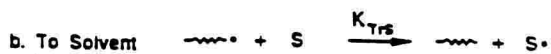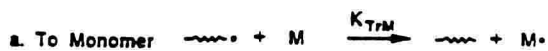
V. IONIC POLYMERIZATION:

A. General:

Monomers polymerizable by ionic polymerization (anionic or cationic) are very limited compared to radical polymerization. None the less, ionic polymerization is a very important class. Ionic mechanics are available for polymerization of both vinyl monomers and a number of cyclic monomers. For ring monomers it is important that sufficient ring strain be present to favor ring opening and there must be an atom capable of bearing a positive or negative charge (e.g. N or O). For both ring and vinyl monomers it is essential that there be an adjacent group capable of stabilizing the charge; for anionic polymerization an e-withdrawing and for cationic an e-donator group, or in the general case an electron system.

TYPES of POLYMERIZATIONS UNDERGONE by VARIOUS VINYL MONOMERS

MONOMER	TYPE of INITIATOR			
	RADICAL	CATIONIC	ANIONIC	Z-N
Ethyene	+	-	+	+
1-Alkyl Olefins	-	+	-	+
1,1-Dialkyl Olefins	-	+	-	-
1,3-Dienes	+	+	+	+
Styrene	+	+	+	+
Halogenated Olefins	+	-	-	-
Vinyl Esters	+	-	-	-
Acrylates	+	+	+	-
n-Vinyl Carbazole	+	+	-	-
n-Vinyl Pyrrolidone	+	+	-	-
Acrylonitrile	+	-	+	-
Acrylamide	+	-	+	-
Vinyl Ether	-	+	-	-

SLIDE 18A

The special features which make ionic polymerization so valuable are the ability to control molecular weight, molecular weight distribution, to provide functional end groups and to control microstructure. Certain high polymers such as poly isobutylene can be made only by ionic means.