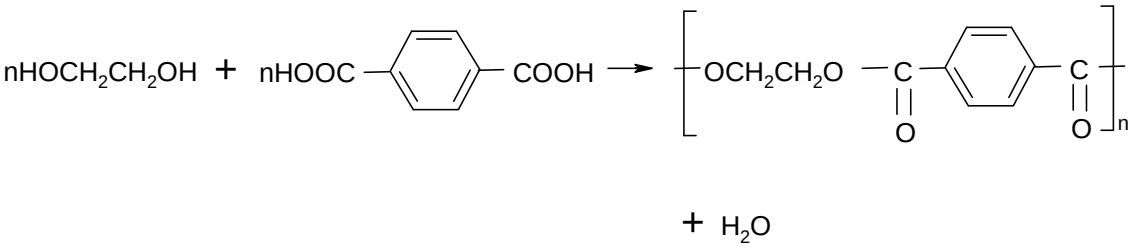
Chapter 9 . Polycondensation reactions or Step-Growth Polymerizations

Condensation polymers - nylon6, nylon 6,6 , PET
Addition polymers – PS, PE, PP

-The requirements of satisfactory step -growth polymerization

(1) At a reasonably fast reaction rate
(2) No side reactions which produce cyclic or undesirable products
(3) No harmful impurities in monomers
(4) Almost complete reaction of the functional groups
(5) Stoichometry of the reactantants must be controlled carefully.
(6) Control of molecular weightsand MWD

ex > Ethylene Glycol + Terephthalic acid → PET



-Number Average Degree of Polymerization (Xn)

functionality : the number of polsition in the monomer that is available for reaction under the specified condition

$$f_{av} = \sum N_i f / \sum N_i$$

f_i : functionality of monometric species I
N_i : number of moles of species I

only good for equal conc. of A and B , $n_A = n_B$

when , $n_A < n_B$

where n_i : number of equivalents of functional groups of type i

-the number of B equivalents which can react cannot exceed n_A

$$\therefore f_{av} = \frac{\sum n_A}{\sum N_i} = \frac{2n_A}{N_A + N_B}$$

We also can define P : the extent of reaction $0 \leq P \leq 1$

$$P = \frac{no.\ functional\ groups\ used}{no.\ functional\ groups\ initially} = \frac{2(N_0 - N)}{N_O f_{av}}$$

where

$N_O = \sum N_i$ (initial number of monomers)

N : total number of moles of molecules when the reaction has proceeded to an extent P

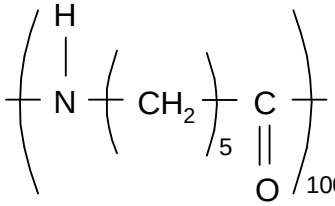
$2(N_0 - N)$: two functional groups to form a linkage

$$N = \frac{1}{2}(2N_0 - N_0 P f_{av})$$

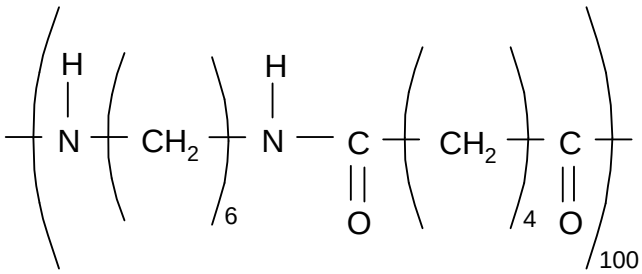
$\therefore X_n = \frac{N_0}{N}$ (number average degree of polymerization of the reaction mixture)

$$= \frac{N_0}{\frac{1}{2}(2N_0 - N_0 P f_{av})} = \frac{2}{2 - P f_{av}}$$ "Carothers equ. "

ex > Nylon -6 ($DP_n = X_n = 100$)



Nylon -6,6 ($DP_n = 100$, $X_n = 200$)



ex > For Nylon -6,6 (Hexamethylene diame + adipic acid)

-bifunctional monomers and equal conc. present

$$X_n = \frac{2}{2 - 2P} = \frac{1}{1 - P}$$

if the reaction extent

P=0.95 , X_n=20 P=0.98, X_n=50 P=0.995, X_n=200

“This is the reason step-growth polymerization require very high conversion of functional groups.”