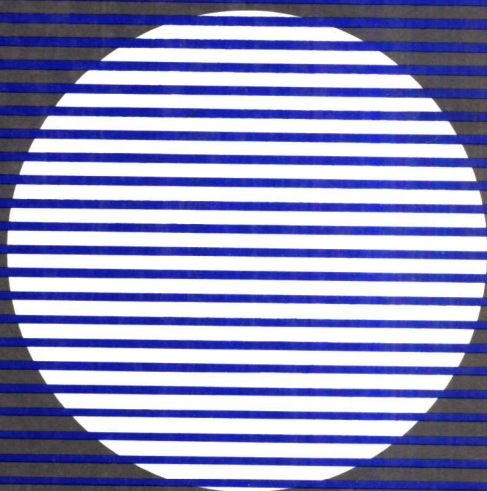


# SURFACE COATINGS

Science and  
Technology

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SWARAJ PAUL



*Surface Coatings*  
*Science and Technology*

SWARAJ PAUL

JOHN WILEY & SONS

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*To my parents,  
Dr Prafulla Chandra and Mrs. Arati Paul  
and to  
my wife Ann-Christin and my son Amit*

the published literature and go through it. While screening the literature I found similar information in several papers. In order to keep the total number of references low, I have mentioned only those references which contained some new information. I am sure that there are errors and omissions in this book. I regret these, assume responsibility for them and would appreciate having them called to my attention.

Piteå, 1983

*Swaraj Paul*

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# **Part I**

## **Binders**



# Chapter 1

## Synthesis of polymeric binders

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## 1.1 CLASSIFICATION OF POLYMERS

### 1.1.1 Introduction

Carothers (1929) proposed the first classification and according to him polymers could be divided mainly into two groups, the condensation and the addition polymers. Condensation polymers are those in which the molecular formula of the structural unit lacks certain atoms that are present in the monomer from which it is prepared or to which it may be degraded. On the other hand, addition polymers are those in which the molecular formula of the structural unit is identical with that of the monomer from which the polymer is derived.

This definition has been shown to be very confusing since polymers with desired structural units could be prepared by both the methods. Alternative

definitions were proposed by Flory (1953) and Lenz (1967). Flory suggested that the differentiation between the condensation and the addition polymers should be based on two grounds: firstly the mechanisms by which the two types of polymers are formed, and secondly by the difference in the chain structure instead of the structure of the repeating units. So far as mechanisms are concerned condensation polymerization proceeds by stepwise intermolecular condensation of functional groups; whereas the addition polymerization usually proceeds by a chain mechanism involving active centres of one sort or another. As far as the chain structures are concerned, structural units of condensation polymers usually are joined by inter-unit functional groups (e.g. ester or amide) of one sort or another whereas most addition polymers do not possess functional groups within the polymer chain, although they may be present as lateral substituents. Lenz (1967) placed emphasis on the molecular weight of the polymers obtained by the two routes. Lenz showed that molecular weight is dependent on the polymerization mechanism. It has been shown that addition polymerization yields significantly higher molecular-weight polymers than condensation polymerization. Thus addition polymerization results in polymers with significantly better physical or mechanical properties than does condensation polymerization. Summarizing, polymerization processes can be classified into two main groups, namely step-growth polymerization and chain-growth polymerization on the basis of several criteria such as:

- (1) growth mechanism;
- (2) relationship between monomer structure and repeating unit structure;
- (3) molecular weight of the polymers formed.

Thus most of the condensation reactions proposed by Carothers are of the step-growth type, whereas most of the addition polymerization reactions are of the chain-growth type. The characteristic features of the step-growth and the chain-growth polymerization reactions can be summarized as follows.

#### *Chain-growth polymerization*

- (a) Comprises of initiation, propagation and termination reactions significantly different in rate and mechanism.
- (b) Needs reactive species either generated *in situ* or added externally.
- (c) Monomers can react with relatively few reactive species.
- (d) By addition of monomers at the few active centres on a polymer chain the chain molecules grow very rapidly until they reach their definitive length by chain termination.
- (e) Once the growth has been terminated, the formed macromolecules do not participate in the polymerization reaction any more (except where chain transfer reaction occur).
- (f) The length of the polymer chain is more or less independent on the degree of conversion.

### *Step-growth polymerization*

- (a) No preferred reaction centre exists. Functional group reactivity is same no matter if it is present on the polymer molecules or on the monomer molecules. This results in slow growth rate over a long period of time.
- (b) Chain growth consists of a continuous succession of starts and stops and it can be interrupted at any time without affecting the reactivity of oligomers or polymers.
- (c) Length of the polymer chain is very strongly dependent on the degree of conversion. Only at high conversions, above 98–99.9%, are long polymer chains formed.

A few examples of condensation and addition polymerization belonging to both step-growth and chain-growth mechanisms have been reviewed by Lenz (1967).

## **1.2 STEP-GROWTH POLYMERIZATION**

It has been mentioned earlier that the characteristic feature of the step-growth polymerization is that its chain length is strongly dependent on the degree of conversion. This suggests that the basic requirement for the step-growth polymerization reactions leading to high molecular-weight linear polymers is that they should give high yields. For example, a reaction conversion of 98% leads to a degree of polymerization (DP) of 50. In general, linear polymers begins to show interesting physical properties at an average DP of  $> 50$ . Another important condition in order to attain high DP is that the side reactions should not prevent the attainment of high theoretical yields to any appreciable extent. However, in the case of nonlinear polymers, reaction conversions need not be very high. In this case, reaction of a few functional groups per macromolecular chain is enough to bind the linear polymer chains together, resulting in high molecular-weight polymers. The above-mentioned limitations in the case of linear polymers restricts the number of organic reactions employed to just four. These reactions are:

1. Esterification by ester interchange.
2. Esterification and amidation by the Schotten–Baumann reaction of acid chlorides.
3. Amidation by the thermal dehydration of an ammonium salt.
4. The formation of urethanes from isocyanates and alcohols.

The theoretical aspects of step-growth polymerization have been extensively discussed earlier by several workers (Flory 1953, Howard 1961, Morgan 1965, Ham 1967, Lee *et al.* 1967, Margerison *et al.* 1967, Solomon 1967, Sokolov 1968, Solomon 1972, Stille *et al.* 1972, Elias 1977, Bamford *et al.* 1976, Ravve 1967, Odian 1970, Billmeyer 1971). The general underlying principles of step-growth polymerization will be treated briefly in this section. Reaction mechanisms for

each of the specific polymers will be discussed separately in details later, under the synthesis of each of the individual commercial binders. To understand the importance of the above-mentioned limitations, relations between degree of polymerization and conversion, and conversion and molecular weight distribution will be derived first for the bifunctional polycondensations and then will be generalized for multifunctional polycondensations. Reaction kinetics of the step-growth reaction will also be discussed in brief.

## 1.2.1 Bifunctional polycondensation

### 1.2.1.1 Conversion and degree of polymerization

The number-average degree of polymerization for such a reaction can be expressed as follows:

$$X_n = \frac{\text{amount of monomeric units in the system}}{\text{amount of molecules in the system}} \\ = \frac{n_{\text{mer}}}{n_{\text{mol}}} = \frac{N_{\text{mer}}}{N_{\text{mol}}} \quad (1.1)$$

Thus it is obvious that  $X_n$  is related to the monomeric unit and not to the repeating unit.

In order to derive a relation between  $X_n$  and conversion  $p$ , it is assumed that functional groups are consumed only through polycondensation and not through side reactions, volatility, etc. If it is assumed that the initial concentrations of functional groups A and B are  $(n_A)_0$  and  $(n_B)_0$  moles respectively, such that the ratio,  $r_0 = [n_A/n_B]_0$  is never greater than 1, and that the extent for reaction for A and B can be expressed as  $p_A$  and  $p_B$ , where A and B are bifunctional compounds,  $X_n$  can be expressed according to

$$\bar{X}_n = \frac{r_0 + 1}{2r_0(1 - p_A) + 1 - r_0} \quad (1.2)$$

Thus the number-average degree of polymerization in the case of bifunctional polycondensation reactions is dependent on initial mole ratio  $r_0$  and the extent of reaction  $p_A$ . Based on eqn (1.2), a few special cases can be derived as follows:

*Case 1:* When  $r_0 = 1$ , i.e. the functional groups are present in equivalent amount and  $p_A = 1$ , i.e. functional groups are converted to 100%,  $X_n = \infty$ .

*Case 2:* When  $p_A = 1$  and  $r_0 < 1$ , i.e. A groups are present at a lower concentration than B groups,

$$\bar{X}_n = \frac{1 + r_0}{1 - r_0} \quad (1.3)$$

Thus the optimum DP that can be achieved is given by the initial molar ratio of groups. As  $r_0$  approaches unity, the higher will be  $X_n$ . Commercially available

step-growth polymers have DP of  $\sim 200$ . This can be achieved either by having an excess of about 1 mol% in one group, or by replacing an equivalent amount of bifunctional reactant with a monofunctional impurity.

Case 3: When  $r_0 = 1$ ,

$$\bar{X}_n = \frac{1}{1 - p_A} \quad (1.4)$$

and is thus dependent only on the extent of reaction  $p_A$ .

When functional groups are present in equivalent amounts in the initial mixture, the functional groups present in the resulting polymer are capable of undergoing further polycondensation. This post-polycondensation reaction may raise the melt viscosity of the polymers in an undesirable way during their processing. This can, however, be eliminated in one of the following two ways:

1. By using a slight excess of one of the two initial monomers. This will result in polymer chains containing identical end groups which in turn are unable to react with one another, and will thus eliminate post-polycondensation. This measure is not always effective because the end groups may sometime be converted to volatile products as a result of side reactions disturbing the equilibrium. This later phenomenon can be illustrated by the hydroxyl excess polymers obtained by using a slight excess of ethylene glycol. The terminal hydroxyl groups in these polymers, which otherwise are unreactive, undergo glycolysis resulting in volatile glycol molecules.
2. By the addition of monofunctional compounds that are able to condense and thus act as 'chain stabilizers' or 'molecular weight stabilizers'. This method is usually used on an industrial scale and especially in the case of polyamides where the reaction rates are  $\sim 100$  times greater than in polyesters. In this case,  $\bar{X}_n$  can be expressed as

$$\bar{X}_n = \frac{1 + (n_1/n_A)_0}{1 - p_A + (n_1/n_A)_0} \quad (1.5)$$

where  $(n_1)_0$  is the initial mole fraction of monofunctional compound.

### 1.2.1.2 Molecular weight distribution (MWD) and conversion

In deriving these relations, it is assumed that all the functional groups are equally reactive in the step-growth polymerization no matter whether they are present on monomeric or polymeric units, and therefore a mixture of a different DPs result during this type of polymerization. However, some deviations from the concept of equal reactivity of functional groups occur if the following conditions are not fulfilled:

1. The polymer formed does not exist in true solution.



2. The functional groups are not present in a similar environment in terms of adjacent groups and steric interactions.
3. The viscosity of the system is such that removal of reaction products (e.g. water) which set up equilibrium reactions is not hindered.

The case of unequal reactivity has been reviewed by Alfrey (1964) and has mainly been attributed to the neighbouring groups interaction. Solomon *et al.* (1966a–d) showed in the case of alkyd resins that particularly hydroxyl groups are not necessarily available for reaction. The reason for the deviation from the principle of equal reactivity has been shown to be due to the fact that alkyd resins are not in true solutions (Solomon *et al.* 1966a–d; Bobalek *et al.* 1964; Solomon 1967; Solomon *et al.* 1967) but instead are present as dispersed particles, termed microgels, of size 0.05 to 1.0  $\mu$  in diameter. The functional groups within these microgels are bound and are unreactive.

Since physical properties of polymers are dependent on MWD, it is essential to derive the dependence of MWD on conversion. Such a relation has been elegantly derived from probability calculations. Thus the number average,  $\bar{x}_x$ , and the weight average,  $w_x$ , molecular weights can be expressed as follows:

$$\bar{x}_x = \frac{N_x}{N_{\text{mol}}} = p^{x-1}(1-p) \quad (1.6)$$

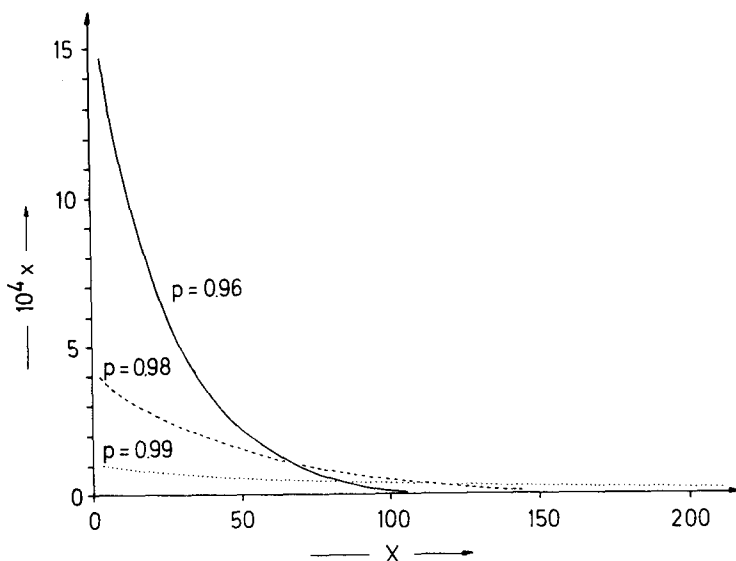


Figure 1.1 Dependence of the mole fraction  $x_x$  on the degree of polymerization  $X$  in the polycondensation of equivalent quantities of bifunctional monomer. The numbers give the extent of reaction  $p$ . (Elias 1977. Reproduced by permission of Hüthig & Wept Verlag and Plenum Publishing Corp.)