

Modeling of Unsaturated Polyester Prepolymer Structures. I. Chain Branches and Overall Chain End Numbers

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ABSTRACT: A review on the synthesis of unsaturated polyester (UP) prepolymers showed that Ordelt saturation (reaction of hydroxyl groups with double bonds) is the major effect that may cause formation of chain branches and then result in an uncertainty of chain end number or functionality. A model has been derived in this work to estimate the number of chain branches and the number of chain ends of UP prepolymers from several fundamental molecular parameters, including hydroxyl and carboxyl indexes, Ordelt saturation extent, short- and long-chain branch distribution, molecular polydispersity, and starting reactant composition and also reasonable assumptions concerning the chain-branch lengths. Simulation results were compared with experimental ones. The influences of the mentioned molecular parameters on the chain branches and on the overall molecular chain ends are discussed in this work. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 133–145, 1997

INTRODUCTION

Unsaturated polyester prepolymers are macromolecules obtained by polycondensation of unsaturated and saturated diacids or anhydrides with diols. For most of the applications, they are diluted with one or several vinyl monomers, e.g., styrene or methyl methacrylate, which are capable of free-radical copolymerization with unsaturation bondings on polyester chains. These solutions are called unsaturated polyester (UP) resins.

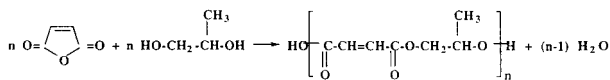
UP resins can be compounded with fillers and/or glass fibers and be cured in the presence of free-radical initiators to yield thermoset articles with a very wide range of mechanical and chemical properties. Currently, the glass fiber-reinforced UP composites are widely used in a large number of industries, such as transportation, electrics, electronics, and housing as well as in

the manufacture of sport and leisure articles, furniture, and sanitary and domestic appliances. In all the applications, semifinished compounds, such as sheet-molding compounds (SMC) and bulk-molding compounds (BMC), have been developed for high-temperature molding processes. They exhibit an excellent range of molding reactivity, physical properties, dimensional stability, surface appearance, and temperature and corrosion resistance. They have become increasingly important, particularly in automotive and marine applications for mass and cost reduction.

SMC technology always employs chemical thickening of UP resins during maturation. BMC technology currently is also increasingly employing the same approach. The purpose of the chemical thickening is to provide a tack-free prepreg which is stiff enough to permit easy material handling and also to provide sufficient resin viscosity to carry the glass fibers to the extremities of the mold during the mold-filling stage in a curing process. The most used thickening reaction involves an interaction of carboxyl groups of UP pre-

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Scheme 1 Overall synthesis reaction of UP prepolymer from maleic anhydride and 1,2-propanediol.

polymers with alkaline earth oxides,^{1,2} such as MgO and CaO, or hydroxides to increase the viscosity of uncrosslinked reactive systems during maturation, just after compound mixing. This thickening reaction requires a time period from 1 day to 1 week, depending on the formulation, to reach an optimum viscosity ($\approx 10^5$ Pa-s) for a given application.^{3,4} The optimization of compound viscosity depends on several parameters. They include molar mass and molar mass polydispersity of UP prepolymers, acid functionality of UP prepolymers, type and amount of alkaline earth oxide, solvent extent, and amounts of fillers and fibers. Most of those parameters can be controlled except the acid functionality of UP prepolymers (which is different from the acid index which is easy to measure). It is caused by the side reactions occurring during the synthesis stage.

The alternative thickening process may be a pure isocyanate thickening system⁵ or a dual isocyanate-alkaline earth oxide/hydroxide thickener system.^{6,7} Both thickening processes involve an addition reaction between an alcohol and an isocyanate to form covalent urethane bonds. The reaction between the hydroxyl chain ends and the isocyanate groups of a di- or polyisocyanate will result in a molar mass increase and, consequently, in a viscosity increase. Similar to the alkaline earth oxide thickening process, the control of compound viscosity by isocyanate thickening strongly depends on the following parameters: molar mass and molar mass polydispersity of UP prepolymers,⁸ hydroxyl functionality of UP prepolymers,⁸ type and amount of polyisocyanate, solvent extent, additives,⁹ and amounts of fillers and fibers. Similarly, the hydroxyl functionality of UP prepolymers is the principal parameter that cannot be well controlled, to date, due to the side reactions occurring during the synthesis stage.

In fact, the molecular hydroxyl functionality of UP prepolymers may be experimentally determined by an observation of gel formation during the hydroxyl-isocyanate reaction.⁸ However, so far, there is still no adequate experimental method to determine the molecular acid functionality of UP prepolymers. It is still difficult to control the compound viscosity in the alkaline earth oxide thickening process. Therefore, it should be

worth developing a simulation method from molecular characteristics of UP prepolymers experimentally available to estimate the molecular functionality of UP prepolymers.

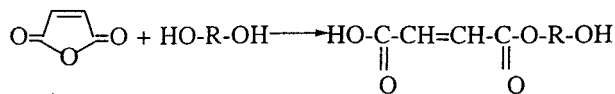
BACKGROUND AND MODELING

Synthesis

The synthesis of unsaturated polyesters usually involves a bulk reaction at elevated temperature between diacids or anhydrides and diols. For a synthesis from maleic anhydride and 1,2-propanediol, the overall reaction scheme is illustrated in Scheme 1.

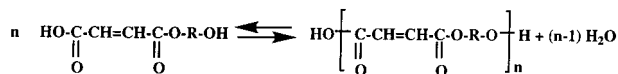
In fact, Scheme 1 involves two main reactions: the monoester formation reaction and the polycondensation reaction, illustrated in the following schemes:

(i) Monoester formation:



Scheme 2 Monoester formation.

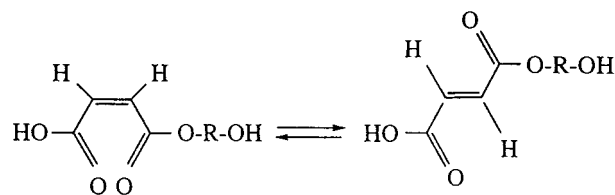
(ii) Polycondensation (polyesterification):



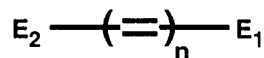
Scheme 3 Polycondensation from monoester.

The monoester formation reaction takes place in a temperature range between 60 and 130°C, while the polyesterification occurs in a higher-temperature range between 160 and 220°C. The extent of polycondensation depends on the residual water content since esterification is a reversible process.

In addition to the main reactions, there are several side reactions occurring during the synthesis of unsaturated polyesters. A well-documented review of these reactions can be obtained in Ref. 10. They are listed and discussed briefly here.



Scheme 4 Maleate-fumarate isomerization.



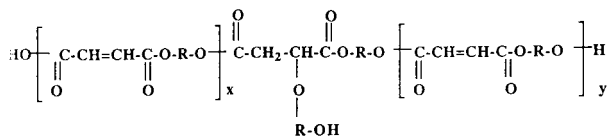
Scheme 8 Ideal linear UP prepolymer structure.

where the number of double bonds, arbitrary given for illustration, depends upon the acid or anhydride ingredients used for the synthesis and prepolymer molecular mass.

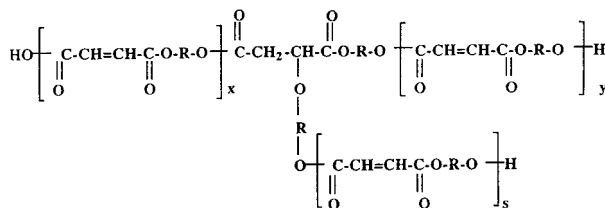
The first side reaction 1 (maleate–fumarate isomerization, shown in Scheme 4), in fact, should not change the molecular structures except the isomer form of double bonds. The partition of the three types of molecular structures in the synthesized product depends on the nature of reactants, ratio of acid and glycol, and reaction conditions. If the stoichiometric ratio is equal to 1 and if there is no diol loss during the synthesis and no side reactions, the partition should be 50% S1, 25% S2, and 25% S3. Those linear molecular structures may be presented as a simplified form illustrated as Scheme 8, where E_1 and E_2 are chain ends. Corresponding to Schemes 2 and 3, they may be a hydroxyl group or a carboxyl group independently; n is number of double bonds on the polyester chain and is dependent of polycondensation degree.

The α -diol dehydration, side reaction 4, would deviate the reactant ratio such as the ratio of diol to acid. Consequently, it would change the partition of the structures S1, S2, and S3 in the final synthesized product. However, the linear structure would not be changed, remaining as Scheme 8.

The only side reaction that may deviate the linear structure is the Ordelt reaction (side reaction 2). The Ordelt reaction leads to the formation of branched monoesters either by Scheme 5 or by Scheme 6. As mentioned before, the reaction of Scheme 6 may be neglected, in certain cases, with respect to the reaction of Scheme 5. The saturated and branched monoester shown in Scheme 5 may proceed as the polyesterification reaction, as shown in Scheme 3, with unsaturated monoesters. It may result in UP molecules having side-chain branches, short ones and long ones. The short-chain branch, shown in Scheme 9, contains only one diol molecule in the side chain, while



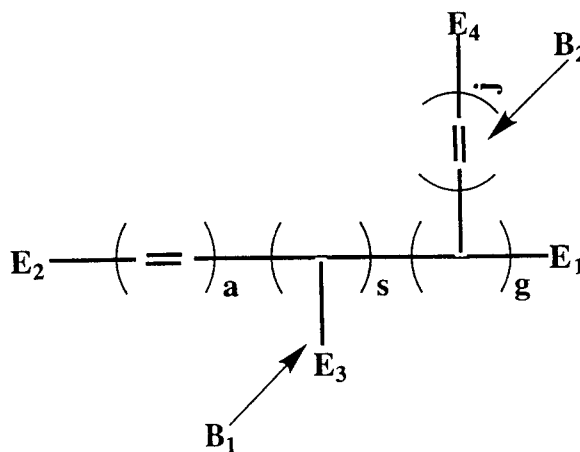
Scheme 9 UP prepolymer structure with short chain branch.



Scheme 10 UP prepolymer structure with long-chain branch.

the long-chain branch (Scheme 10, where $z \geq 1$) contains more than one diol molecule.

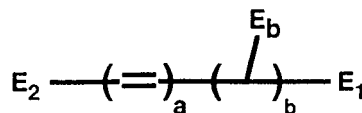
The Ordelt reaction may be also taken place on the unsaturation points of the long-chain branches of Scheme 10. It is, however, not likely to happen because when it could happen, it results in really small quantity of free diol in the polycondensation stage. Therefore, by neglecting the secondary Ordelt saturation on long-chain branches (Scheme 11), one may obtain a general molecular structure for the UP prepolymers as follows:



Scheme 11 General UP prepolymer structure.

where E_1 and E_2 are the main-chain end groups, hydroxyl or carboxyl groups; E_3 and E_4 , the branch-chain end groups, mainly hydroxyl groups (Scheme 9); B_1 , the short-chain branch; B_2 , the long-chain branch; and a, s, g, j , the number of constitutive units, $a > 0, b \geq 0, g \geq 0, j > 0$; $a + s + g$ is approximately equal to n in the Scheme 8.

It is clearly shown in Scheme 11 that the average molar mass of UP prepolymers increases and



Scheme 12 Simplified UP prepolymer structure.

that their number of chain ends, including hydroxyl and carboxyl groups, is, in fact, larger than two, which is the theoretical number for linear chains. The real chain end number should be two plus the overall branch number which is the sum of short-chain branch number (s) and long-chain branch number (g).

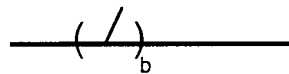
Since UP prepolymers from Scheme 1 have either hydroxyl or carboxyl groups on the chain ends (including main chain and chain branches), the chain end number should be equal to their overall hydroxy and carboxy functionality. This is not always true; for example, if some monoacid (like methacrylic acid) or dicyclopentadiene molecules are introduced in the UP synthesis, other types of chain ends can be present.

MODEL DERIVATION

The constitutive unit number, j , of unsaturation points on the long branches of Scheme 11, in reality, is a variable rather than a constant. This variable strongly depends on the acids and diols used for synthesis and also on the reaction conditions such as temperature and pressure. It has not, however, been systematically well studied yet. There is a general trend to believe that the probability to form a longer chain branch is strictly decreased by increasing the constitutive unit number, j . It means, in most of cases, that most of the long-chain branches have only one unsaturation point. For simplification, one may consider “ j ” as a constant, not far away from unity.

Piras²⁰ showed that a 2-dimensional NMR technique could help to determine the partition of short- and long-chain branches of UP prepolymers. The partition of short- and long-chain branches depends also on the acids and diols used for synthesis and on the reaction process. Since it is measurable, it can be classified as an experimental parameter, t , the ratio of the long-chain branch number to the short-chain branch number. Consequently, the molecular structure shown in Scheme 11 can be further simplified to the structure of Scheme 12, where b is the sum of short-chain branch number (s) and long-chain branch number (g), i.e., $b = s + g = s(1 + t)$; t , the ratio of the long-chain branch number to the short-chain branch number, $t = g/s$; E_b , the branch-chain end group; and E_1 , E_2 , and a , the same as in Scheme 11.

For model derivation, the structure shown on Scheme 12 can be further simplified by expressing



Scheme 13 UP prepolymer structure for model derivation.

the linear backbone chain and branched chains as shown in Scheme 13. In Scheme 13, the linear backbone has molar mass, M_1 , and the chain branch has molar mass, m . The branch molar mass, m , could be calculated by the following equation:

$$m = (m_s s + m_g g)/(s + g) \\ = (m_s + m_g t)/(1 + t) \quad (1)$$

where m_s is the molar mass of the short-chain branch; m_g , the molar mass of the long-chain branch; and τ , the ratio of the long-chain branch number (g) to the short-chain branch number (s).

For each species i , the molar mass of the linear backbone, M_i , is $(M_i)_l$; the number of branched units is b_i . An average molar mass, m , is taken for all the chain branches on all species. Then, the molar mass of the species i , M_i , and the numbers of its end groups, f_i , can be calculated by the following equations:

$$M_i = (M_i)_l + b_i m \quad (2)$$

$$f_i = 2 + b_i \quad (3)$$

Furthermore, if one assumes an equal probability of the Ordelt reaction on every double bond, the branch number, b_i , of species i can be calculated by

$$b_i = \frac{(M_i)_l}{M_{c=c}} X_{\text{Ordelt}} = K(M_i)_l \quad (4)$$

where $K = X_{\text{Ordelt}}/M_{c=c}$; $M_{c=c}$ = molar mass per mole of double bond on UP prepolymer chains; X_{Ordelt} = ratio of moles of saturated double bonds to moles of initially introduced double bonds, or Ordelt saturation degree of the UP prepolymer.

One important assumption is that τ and X_{Ordelt} are constant, meaning that there is not a distribution with average values, $\bar{\tau}$ and \bar{X}_{Ordelt} . By substituting eq. (4) into eq. (2), one obtains

$$M_i = (1 + Km)(M_i)_l \quad (6)$$

$$B_i = \frac{KM_i}{1 + Km} \quad (7)$$

According to classical definitions, the number-average and mass-average molar mass of UP prepolymers are determined as follows:

$$\overline{M}_n = \frac{\sum_i A_i M_i}{\sum_i A_i} \quad (8)$$

$$\overline{M}_w = \frac{\sum_i A_i M_i^2}{\sum_i A_i M_i} \quad (9)$$

where A_i is the fraction of species i in the prepolymer.

Similar to eqs. (8) and (9), the number-average and mass-average molar mass of linear prepolymer backbones are defined as follows:

$$(\overline{M}_n)_l = \frac{\sum_i A_i (M_i)_l}{\sum_i A_i} \quad (10)$$

$$(\overline{M}_w)_l = \frac{\sum_i A_i (M_i)_l^2}{\sum_i A_i (M_i)_l} \quad (11)$$

The number-average branch number, \overline{b}_n , could be found as

$$\overline{b}_n = \frac{\sum_i A_i b_i}{\sum_i A_i} = \frac{K\overline{M}_n}{1 + Km}$$

or

$$\overline{b}_n = \frac{(\overline{M}_n)_l}{\overline{M}_{c=c}} X_{\text{Ordelt}} = K(\overline{M}_n)_l \quad (12)$$

By substituting eq. (6) into eqs. (8)–(11), one obtains

$$\overline{M}_n = (1 + Km)(\overline{M}_n)_l = (\overline{M}_n)_l + \overline{b}_n m \quad (13)$$

and

$$\overline{M}_w = (1 + Km)(\overline{M}_w)_l \quad (14)$$

Consequently, one has

$$\frac{\overline{M}_w}{\overline{M}_n} = \frac{(\overline{M}_w)_l}{(\overline{M}_n)_l} = I_p \quad (15)$$

where I_p is the mass polydispersity index of the UP prepolymer.

In eq. (15), it is found that the polydispersity of linear chains is the same as that of real molecules containing chain branches. It results from the assumption that τ and X_{Ordelt} are constant values for all chains.

One may also define number-average chain ends, \overline{f}_n , of the prepolymers as follows:

$$\overline{f}_n = \frac{\sum_i A_i f_i}{\sum_i A_i} \quad (16)$$

By using eqs. (3), (4), and (12), eq. (16) can be derived into eq. (17):

$$\begin{aligned} \overline{f}_n &= 2 + \overline{b}_n = 2 + K(\overline{M}_n)_l \\ \overline{f}_n &= 2 + \left(\frac{K\overline{M}_n}{1 + Km} \right) \end{aligned} \quad (17)$$

Therefore, it is clear that one can determine the chain end number of the UP prepolymers by eq. (17) if one has the experimental number-average molar mass, \overline{M}_n , K , and m values.

Generally, there are two classical methods to measure the number-average molar mass of UP prepolymers. They are chemical titration and size-exclusion chromatography (SEC) methods. The molar mass measured by chemical titration method, $\overline{M}_{n,\text{index}}$, is calculated from carboxyl (I_C) and hydroxyl (I_H) indexes of UP prepolymers, with a theoretical approach of two chain ends per molecule (based on Scheme 8), by the following equation:

$$\overline{M}_{n,\text{index}} = 112,200/(I_H + I_C) \quad (18)$$

while the molar mass measured by the SEC method, $\overline{M}_{n,\text{SEC}}$, is determined by a calibration curve based on linear polystyrene standard or linear polyester standard. Unfortunately, due to branching chains caused by the Ordelt reaction, it is clear that the number-average molar masses measured by both methods, $\overline{M}_{n,\text{index}}$ and $\overline{M}_{n,\text{SEC}}$, are not the real number-average molar mass, \overline{M}_n , in eq. (12) or eq. (17). Nevertheless, there is an approach to estimate the real number-average molar masses, \overline{M}_n . By the definition of $\overline{M}_{n,\text{index}}$ measured by the chemical titration method and by the more realistic Scheme 13 instead of Scheme 8, one may have following relationship:

$$\begin{aligned}\overline{M}_{n,\text{index}} &= \overline{M}_n \frac{2}{(2 + \overline{b}_n)} \\ &= [(\overline{M}_n)_l + \overline{b}_n m] \left(\frac{2}{2 + \overline{b}_n} \right) \quad (19)\end{aligned}$$

By eqs. (12) and (19), one has

$$\begin{aligned}(\overline{M}_n)_l &= \frac{2\overline{M}_{n,\text{index}}}{2 + 2Km - K\overline{M}_{n,\text{index}}} \\ &= \frac{2\overline{M}_{n,\text{index}}M_{c=c}}{2M_{c=c} + 2mX_{\text{Ordelt}} - \overline{M}_{n,\text{index}}X_{\text{Ordelt}}} \quad (20)\end{aligned}$$

Consequently, one obtains

$$\overline{b}_n = \frac{2\overline{M}_{n,\text{index}}X_{\text{Ordelt}}}{2M_{c=c} + 2mX_{\text{Ordelt}} - \overline{M}_{n,\text{index}}X_{\text{Ordelt}}} \quad (21)$$

In eqs. (20) and (21), $\overline{M}_{n,\text{index}}$ and X_{Ordelt} are experimental values, and $M_{c=c}$ is a molecular constant depending on type of prepolymers. The chain branch molecular mass, m , can be estimated by eq. (1). Therefore, the number-average chain end, \overline{f}_n , of UP prepolymers can be estimated by eqs. (17) and (20) from experimental results. It is expressed as follows:

$$\overline{f}_n = 2 + \frac{2\overline{M}_{n,\text{index}}X_{\text{Ordelt}}}{2M_{c=c} + 2mX_{\text{Ordelt}} - \overline{M}_{n,\text{index}}X_{\text{Ordelt}}} \quad (22)$$

Similar to the first moment of the chain end distribution, \overline{f}_n , the second moment, called the "chain end average chain end," \overline{f}_w is defined as follows:

$$\overline{f}_w = \frac{\sum A_i f_i^2}{\sum A_i f_i} \quad (23)$$

By using eqs. (3) and (4), eq. (23) can be derived into eq. (24):

$$\overline{f}_w = 2 + K(\overline{M}_n)_l \left(\frac{2 + K(\overline{M}_w)_l}{2 + K(\overline{M}_n)_l} \right) \quad (24)$$

Applying eqs. (14) and (20) into eq. (13), one obtains

$$\begin{aligned}\overline{f}_w &= 2 \\ &+ \left[\frac{\overline{M}_{n,\text{index}}X_{\text{Ordelt}}}{2M_{c=c} + 2mX_{\text{Ordelt}} - \overline{M}_{n,\text{index}}X_{\text{Ordelt}}} \right] \\ &\times \left[\frac{2M_{c=c} + 2mX_{\text{Ordelt}} - \overline{M}_{n,\text{index}}X_{\text{Ordelt}}(1 - I_p)}{M_{c=c} + mX_{\text{Ordelt}}} \right] \quad (25)\end{aligned}$$

In the case discussed here, the chain ends of the UP prepolymers are only hydroxyl or carboxyl groups. It means that \overline{f}_n is also the number-average functionality, and \overline{f}_w , the "functionality"-average functionality of the UP prepolymer.

In eq. (25), if the prepolymer has a perfect molar mass polydispersity, i.e., $I_p = 1$, it means that $\overline{M}_n = \overline{M}_w$; then, eq. (25) is identical to eq. (22), i.e., $\overline{f}_n = \overline{f}_w$. Generally, I_p is higher than 1 and it can be obtained experimentally by SEC measurements, whatever is the calibration (assuming only few branching).

In eqs. (21) and (24), the number-average and the functionality-average of functionality of UP prepolymers can be estimated directly from experimental data such as I_C and I_H , Ordelt saturation degree (X_{Ordelt}), molar mass of unsaturation unit ($M_{c=c}$), molar mass of branches (m), and polydispersity index (I_p).

From eq. (4), the mass-average branch ends can be obtained as

$$\begin{aligned}\overline{b}_w &= \frac{\sum A_i b_i^2}{\sum A_i b_i} = \frac{\sum A_i K^2 (M_i)_l^2}{\sum A_i K (M_i)_l} = K \frac{\sum A_i (M_i)_l^2}{\sum A_i (M_i)_l} \\ \overline{b}_w &= K(\overline{M}_w)_l \quad \text{or} \quad KI_p(\overline{M}_n)_l \quad (26)\end{aligned}$$

By using eqs. (13) and (14), eq. (26) can be transformed into eq. (27):

$$\overline{b}_w = \frac{K\overline{M}_w}{1 + Km} \quad \text{or} \quad \frac{KI_p\overline{M}_n}{1 + Km} \quad (27)$$

Consequently, one obtains the following relationship:

$$\frac{\overline{b}_w}{\overline{b}_n} = \frac{\overline{M}_w}{\overline{M}_n} = \frac{(\overline{M}_w)_l}{(\overline{M}_n)_l} = I_p \quad (28)$$

It is interesting to conclude that the polydispersity of chain branches is the same as that of real molar masses or linear chain molar masses. Again, it is due to the assumption that $\overline{\tau}$ and X_{Ordelt} are constant values.

Substituting eq. (20) into eq. (26), one may have mass-average branch ends in terms of experimental parameters as shown in eq. (29):

$$\begin{aligned} \overline{b_w} &= \frac{2I_p \overline{M_{n,\text{index}}} X_{\text{Ordelt}}}{2M_{c=c} + 2m X_{\text{Ordelt}} - \overline{M_{n,\text{index}}} X_{\text{Ordelt}}} \\ &= I_p \overline{b_n} \quad (29) \end{aligned}$$

The estimation of functionality-average functionality, $\overline{f_w}$, can be further simplified by substituting eqs. (21) and (29) into eq. (24):

$$\overline{f_w} = 2 + \overline{b_n} \left(\frac{2 + I_p \overline{b_n}}{2 + \overline{b_n}} \right) \quad (30)$$

RESULTS AND DISCUSSION

Lecoite et al.⁸ prepared and characterized different UP prepolymers with different molecular structures. Both UP prepolymers were 1 : 1 copolymers of fumaric acid with combination of two diols, diethylene glycol (DEG) and neopentyl glycol (NPG). The diol composition of F90 is NPG/DEG equal to 90/10 by mol, while that of F80 is 80/20. The fact that they were prepared for isocyanate thickening explains why I_H is higher than is I_C . As we have much information concerning these UP prepolymers, they were first chosen as base materials to do simulation and to compare them with some experimental results of Lecoite et al.⁸ The basic molecular parameters such as X_{Ordelt} , I_C , I_H , $\overline{M_{n,\text{index}}}$, and $\overline{M_{n,\text{SEC}}}$ and the polydispersity index, I_p , are listed in Table I.

Table I also lists several other calculated or estimated molecular parameters, such as $M_{c=c}$, m_s , m_g , τ , and m , which are necessary to describe the molecular structures of UP prepolymers. An internal study from Cray Valley²³ showed that the chain branches caused by Ordelt saturation are mostly either monomer short-chain branches or trimer long-chain branches. Moreover, the fraction of short- and long-chain branches is around 70/30 for UP prepolymers based on fumaric acid and diols with primary hydroxyl groups. Therefore, m_s is assigned to be the molar mass of a one-diol-molecule short-chain branch, and m_g is the molar mass of a trimer (diol–acid–diol) long-chain branch. Both depend on the composition of the acid and diols (Table I). In addition, the ratio

Table I Molecular Parameters of UP Prepolymers for Model Simulation

Reference	Experimental Molecular Parameters					Other Molecular Parameters ^d					
	X_{Ordelt} ^a (%)	I_H ^a (mg KOH/g)	I_C ^a (mg KOH/g)	$\overline{M_{n,\text{index}}}$ ^{a,b} (g/mol)	$\overline{M_{n,\text{SEC}}}$ ^{a,b} (g/mol)	$(\overline{M_w}/\overline{M_n})_{\text{SEC}}$ ^{a,c}	$M_{c=c}$ (g/mol)	m_s (g/mol)	m_g (g/mol)	τ	m (g/mol)
F80-1	4.0	71.8	17.5	1260	2470	2.0	185.6	104.6	290.2	0.4286	160.3
F80-2	5.5	87.3	17.5	1070	2340	5.2	185.6	104.6	290.2	0.4286	160.3
F90-1	3.8	72.4	17.7	1245	2450	1.9	185.8	104.8	290.6	0.4286	160.5
F90-3	3.2	42.5	7.8	2230	4370	8.0	185.8	104.8	290.6	0.4286	160.5

^a Data from Lecoite et al.⁸

^b $\overline{M_{n,\text{index}}} = 112,200/(I_H + I_C)$.

^c Measured by SEC with polystyrene standard.

^d See text.

Table II Simulation Results for F80 and F90 UP Prepolymers (See Text)

Reference	$(\overline{M}_n)_l$	(\overline{M}_n)	\overline{b}_n	\overline{b}_w	\overline{f}_n	\overline{f}_w
F80-1	1402	1450	0.30	0.60	2.30	2.34
F80-2	1204	1461	0.36	1.87	2.36	2.59
F90-1	1357	1420	0.28	0.53	2.28	2.31
F90-3	2669	2743	0.46	3.68	2.46	3.06

of long-chain branches to short-chain branches (t) in this study is fixed at $3/7$.^{20,23}

All the simulation results including linear and whole molar masses [$(\overline{M}_n)_l$, \overline{M}_n], number- and mass-average chain branches (\overline{b}_n , \overline{b}_w), and number- and mass-average chain ends (\overline{f}_n , \overline{f}_w) are listed in Table II. $(\overline{M}_n)_l$ is estimated by eq. (20), while \overline{M}_n is by eq. (13). \overline{b}_n , \overline{b}_w , \overline{f}_n , and \overline{f}_w are calculated by eqs. (21), (29), (22), and (25), respectively.

First of all, Table II shows the estimated molar masses, \overline{M}_n , of UP prepolymers including chain branches. Comparing with the molar masses measured by chemical titration or by SEC methods,

shown in Table I, one could find that the estimated values are always located between $\overline{M}_{n,\text{index}}$ and $\overline{M}_{n,\text{SEC}}$. The chemical titration method underestimates the molar mass due to the neglect of the chain branches, while the SEC measurement is wrong due to the use of a linear polystyrene sample as the calibration standard. Nevertheless, the estimated molar masses are closer to the values obtained by the chemical titration method.

The simulation results also show that the number-average chain branches are in the range between 0.28 and 0.40 per UP molecule, depending on molecular parameters. The overall chain end number, i.e., the overall average functionality in this case, is then calculated in number, \overline{f}_n , and functionality, \overline{f}_w , averages (Table II). The difference between \overline{f}_n and \overline{f}_w is enlarged by the Ordelt saturation extent and molar mass polydispersity. It is not possible to compare \overline{f}_n and \overline{f}_w to experimental results, but it can be seen in Table II that the calculated values are higher than 2. In Part II, we will give a method to separate the —OH and —COOH contributions to the overall chain end number (\overline{f}_n and \overline{f}_w) and, thus, an experimental comparison with the calculated values would be possible.

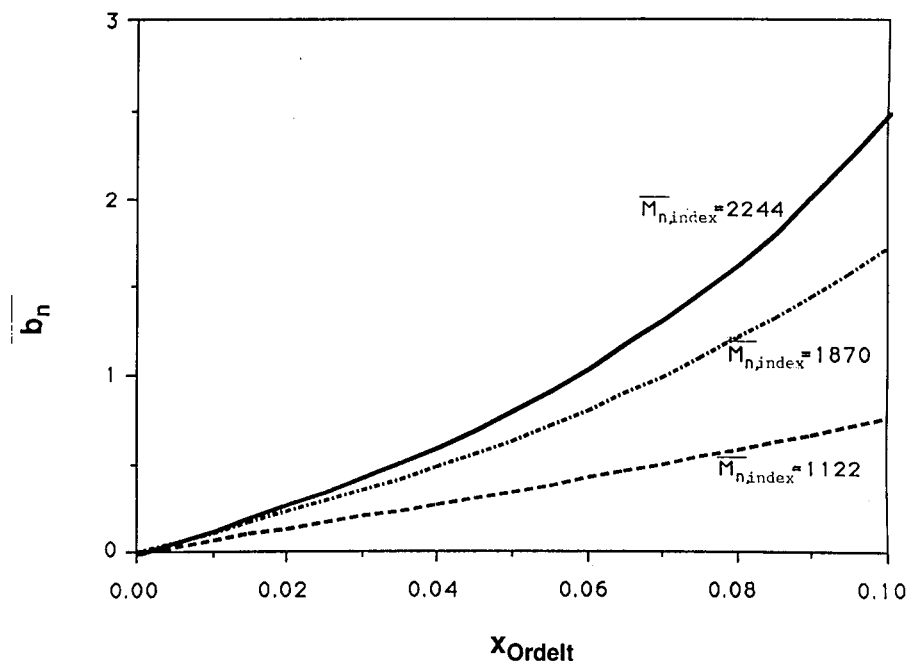


Figure 1 Influences of Ordelt saturation extent (X_{Ordelt}) and molar mass ($\overline{M}_{n,\text{theo}}$) on number-average chain branches (\overline{b}_n) for an FA-DEG UP prepolymer: (—) $\overline{M}_{n,\text{index}} = 2244$ ($I_C + I_H = 50$); (· · · ·) $\overline{M}_{n,\text{index}} = 1870$ ($I_C + I_H = 60$); (-----) $\overline{M}_{n,\text{index}} = 1122$ ($I_C + I_H = 100$).

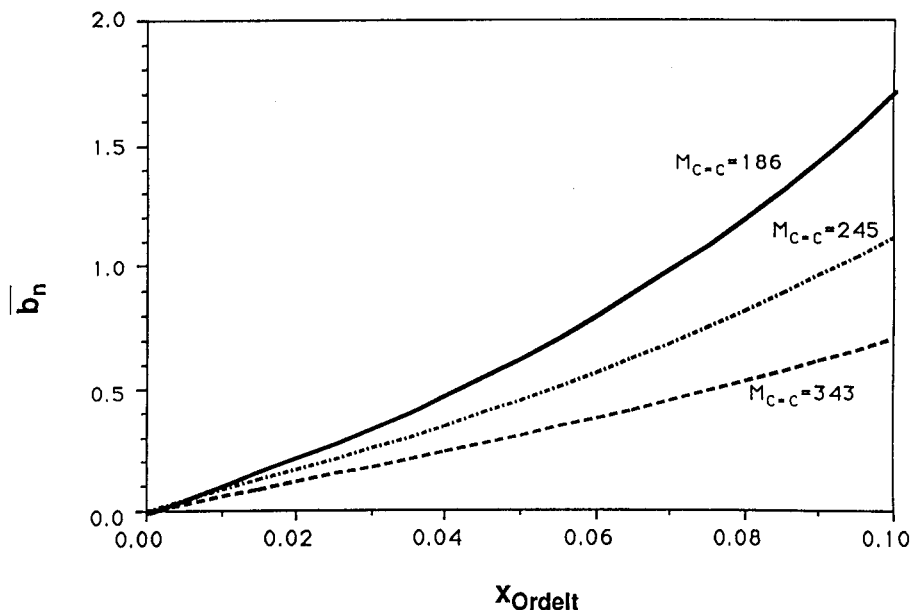


Figure 2 Influences of Ordelt saturation extent (X_{Ordelt}) and unit unsaturation molecular mass ($M_{c=c}$) on number-average chain branches (\bar{b}_n) for an FA-IPA-DEG UP prepolymer: (—) $M_{c=c} = 186$ for FA/IPA = 100/0; (-·-·-) $M_{c=c} = 245$ for FA/IPA = 80/20; (----) $M_{c=c} = 343$ for FA/IPA = 60/40.

In eq. (21), it is shown that the number-average of the chain branch number is a function of the Ordelt saturation (X_{Ordelt}), index molar mass ($\bar{M}_{n,\text{index}}$, obtained from chemical titration, I_C and I_H), unit unsaturation molar mass ($M_{c=c}$), and branching molar mass (m). If one takes a more classical UP prepolymer than those presented in Table I, i.e., prepared from maleic anhydride [(MA) instead of fumaric acid] and diethylene glycol (DEG) as another example, two of the parameters could be fixed as $M_{c=c} = 186$ and $m = 160$. With these conditions, Figure 1 shows the influence of X_{Ordelt} and $\bar{M}_{n,\text{index}}$ on the chain branch number, \bar{b}_n . The results reveal that \bar{b}_n increases as the X_{Ordelt} or $\bar{M}_{n,\text{index}}$ of UP prepolymers increases. In the case of $X_{\text{Ordelt}} = 0.10$ (which is more usual than 0.05) and $I_C + I_H = 50$, i.e., $\bar{M}_{n,\text{index}} = 2244$, \bar{b}_n could be as high as 2.4. It means that the number-average functionality, \bar{f}_n , could be up to 4.4, far from the value $\bar{f}_n = 2$ if no Ordelt reaction occurs.

The unit unsaturation molecular mass ($M_{c=c}$) is also an important factor influencing \bar{b}_n as shown in eq. (21). In fact, $M_{c=c}$ could be influenced by introduction in the synthesis of saturated diacids or anhydrides and/or higher molar masses diols. In the case that UP prepolymers are made of maleic anhydride, isophthalic anhydride

(IPA), and diethylene glycol, $M_{c=c}$ could be changed from 186 through 245 to 343 for the acid mixtures with MA/IPA ratio from 100/0 through 80/20 to 60/40, respectively, in which $I_C + I_H$ is fixed at 60 and m is 160. Figure 2 shows simulation results of the influence of $M_{c=c}$ as well as X_{Ordelt} on \bar{b}_n . It reveals that one may considerably decrease the chain branch number by increasing the isophthalic content in UP prepolymers.

In both Figures 1 and 2, the influences of $\bar{M}_{n,\text{index}}$ and $M_{c=c}$ on \bar{b}_n are less important when X_{Ordelt} is small. Only in the high Ordelt saturation extent range would the UP prepolymers be very sensitive to the variation of $\bar{M}_{n,\text{index}}$ and $M_{c=c}$ on the number-average of chain branches. One may conclude that the key point to decrease the chain branch number is to maintain an Ordelt saturation extent as low as possible.

Figure 3 shows the influence of number-average chain branches (\bar{b}_n) and the molecular polydispersity (I_p) on the functionality-average functionality (\bar{f}_w), according to eq. (30). The results reveal that, for a normally polydispersed UP prepolymer (i.e., $I_p = 2$), the increase of \bar{f}_w is nearly equal to the increase of \bar{b}_n , while for a highly polydispersed prepolymer, e.g., $I_p = 8$, \bar{f}_w may be exponentially increased by an increase of \bar{b}_n .

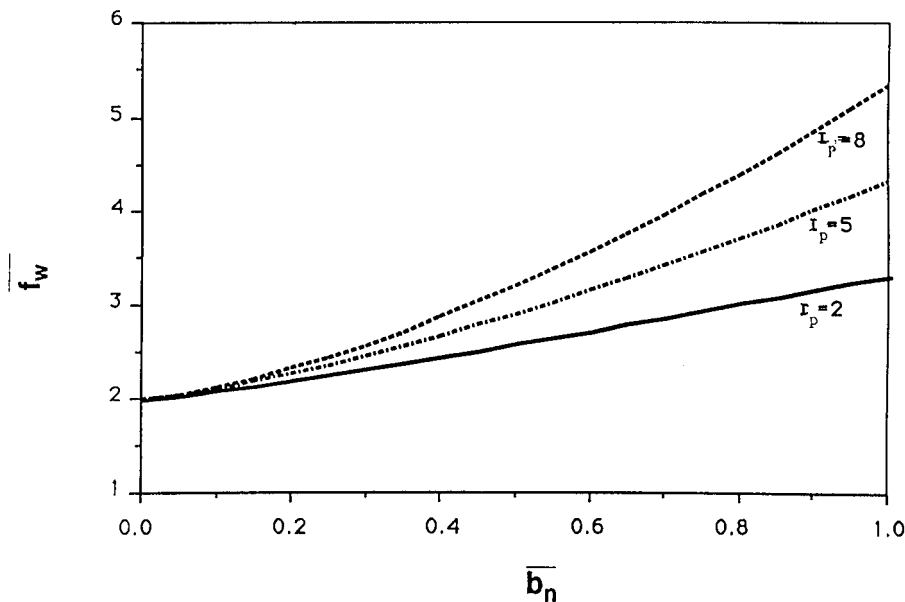


Figure 3 Influences of number-average chain branches (\bar{b}_n) and molar mass polydispersity (I_p) on functionality-average functionality (\bar{f}_w) for UP prepolymers: (—) $I_p = 2$; (- · - · -) $I_p = 5$; (-----) $I_p = 8$.

From eqs. (22) and (30), one may obtain a polydispersity index for the functionality

$$\frac{\bar{f}_w}{\bar{f}_n} = \frac{2 + \bar{b}_n \left(\frac{2 + I_p \bar{b}_n}{2 + \bar{b}_n} \right)}{2 + \bar{b}_n} \quad (31)$$

Rearranging eq. (31), one obtains

$$\frac{\bar{f}_w}{\bar{f}_n} = 1 + \frac{\bar{b}_n^2}{(2 + \bar{b}_n)^2} (I_p - 1) \quad (32)$$

It is clearly shown that the functionality polydispersity index is a function of \bar{b}_n and molecular mass polydispersity (I_p). Figure 4 illustrates the influences of \bar{b}_n and I_p on \bar{f}_w/\bar{f}_n . In the high \bar{b}_n range, \bar{f}_w/\bar{f}_n becomes very dependent on the molecular mass polydispersity. It indicates that, in order to reduce overall chain ends, one should put efforts on decreasing the prepolymer's molar mass polydispersity as well as on the decrease of \bar{b}_n by reducing X_{Ordelt} .

CONCLUSION

During the synthesis of UP prepolymers, there are always side reactions occurring in addition

to polyesterification. The side reactions include maleate-fumarate isomerization, Ordelt saturation, transesterification, and α -diol dehydration. Those side reactions may either alter reaction stoichiometry or randomly change the prepolymers' molecular structure. Among them, the Ordelt saturation is the major effect that may cause formation of chain branches and then results in an uncertainty concerning the chain end number or molar prepolymer functionality. An unknown functionality may lead to serious problems in the SMC thickening process for final applications.

A model with few and reasonable assumptions was derived in this work to estimate the average numbers of branches and of reactive chain ends of UP prepolymers from several fundamental molecular parameters. Those molecular parameters include hydroxyl and carboxyl indexes, Ordelt saturation extent, short- and long-chain branch distribution, mass polydispersity index, and starting reactant composition. The assumptions concern the length and the polydispersity in length of branches introduced by the Ordelt reaction. The molecular parameters are either known from the reactant composition or are measurable after synthesis.

The results show that the determination of real molar mass of UP prepolymers is the key point to develop the following model derivation. Classical

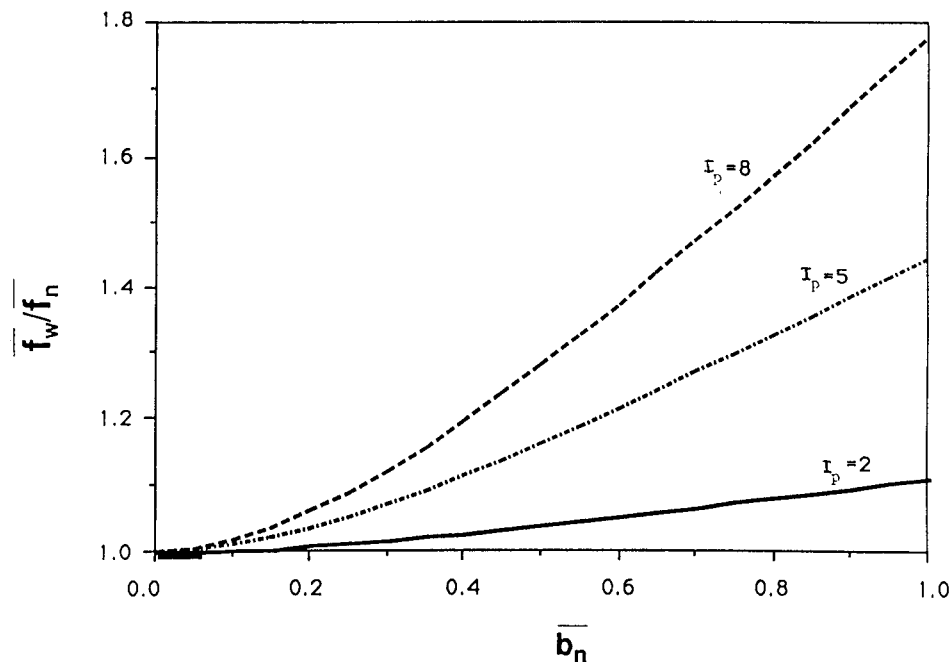


Figure 4 Influences of number-average chain branches (\bar{b}_n) and molar mass polydispersity (I_p) on polydispersity index of overall chain ends (\bar{f}_w/\bar{f}_n) for UP: (—) $I_p = 2$; (- · - · -) $I_p = 5$; (----) $I_p = 8$.

molar mass measurements such as chemical titration and SEC methods are found not accurate enough. Nevertheless, the real molar mass, especially the molecular mass of linear backbone chain, could be estimated by molecular parameters by the model.

Simulation results reveal that the higher the Ordelt saturation extent is the greater is the number of chain branches. In the high X_{Ordelt} range, the chain branch number becomes very sensitive to the increase of hydroxyl/carboxyl indexes and unit unsaturation molecular mass. Furthermore, the polydispersity index of overall reactive chain ends is highly dependent on the molecular polydispersity, particularly in the high chain-branch range.

In conclusion, to decrease the chain-branch number (or the overall reactive chain ends), and the polydispersity of molecular chain ends, one should put all efforts on the decrease of Ordelt saturation extent and molecular mass polydispersity. Other minor factors are (i) to introduce saturated acids or longer-chain diols to increase the unit unsaturation molecular mass and (ii) to maintain molecular mass in a reasonable range rather than toward a high molar mass range. A comparison between the simulation of the average

functionalities, \bar{f}_n and \bar{f}_w , and the experimental results will be given in the Part II in which we propose a method to separate the hydroxyl and carboxyl contributions to the overall reactive chain-end number.

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