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Quantitative Aspects of Chain Extension of Telechelics

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Summary

Quantitative aspects of chain extension of telechelics have been studied. Molecular weight independent characteristic terms were defined and simple expressions were derived for number average extension, $\overline{E}_n = \overline{F}_n/(2-\overline{F}_n)$, and number average degree of extension, $\overline{DE}_n = 2/(2-\overline{F}_n)$, as a function of number average functionality ($\overline{F}_n$) of telechelic prepolymers. Analysis of these expressions indicate that $\overline{E}_n$ and $\overline{DE}_n$ are enormously sensitive to insignificant changes in $\overline{F}_n$ close to ideal $\overline{F}_n = 2.0$. Molecular weight of the extended polymer ($\overline{M}_r$) has also been calculated considering $\overline{F}_n$, number average molecular weight of the prepolymer ($\overline{M}_n$), and molecular weight of the extender (M_e).

Introduction

Telechelic polymers are α,ω-difunctional prepolymers (URANECK et al. 1960) the usefulness of which resides in their chain extension ability. In practice, however, telechelic polymers are mixtures of α,ω-difunctional polymers containing non-negligible amounts of monofunctional components. Previous authors (BALDWIN et al. 1969) derived an equation for number average molecular weight of the extended polymer ($\overline{M}_r$) as a function of number average functionality ($\overline{F}_n$) and number average molecular weight of the prepolymer ($\overline{M}_n$). Later this equation was modified (ATHEY, 1974) considering the molecular weight of extender molecules.

This paper concerns some quantitative aspects of chain extension, specifically derivation of simple,

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characteristic molecular weight independent expressions for number average extension ($\bar{E}_n$) and number average degree of extension ($\overline{DE}_n$).

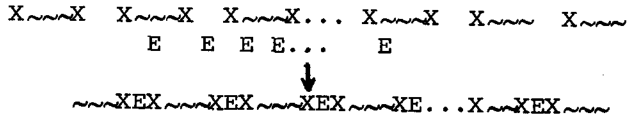
Derivation of Equations for Extension of Telechelics

Recently we have prepared and characterized a variety of telechelic polyisobutylene prepolymers, X-PIB-X, where X = tert.-chloro (KENNEDY and SMITH 1980, IVÁN et al. 1980a), $-CH_2C(CH_3)=CH_2$ (KENNEDY et al. 1979), $-CH_2OH$ (IVÁN et al. 1980b) and epoxy (CHANG 1980) which may also contain monofunctional chains (IVÁN et al. 1980c) and have investigated aspects of their extension chemistries (IVÁN 1980). In view of the well known extreme sensitivity of the degree of extension to degree of terminal functionality, $\bar{F}_n$, need arose to determine this quantity by methods far more sensitive than possible by conventional analytical techniques. In the course of these investigations several simple relationships useful for the quantitative characterization of telechelic prepolymer systems have been derived and are described as follows.

The telechelic polymer system under consideration contains n_1 monofunctional and n_2 difunctional species. The number average functionality of such a system is

$$\bar{F}_n = \frac{n_1 + 2n_2}{n_1 + n_2} \qquad (1)$$

Chain extension or "extension" for short is the process by which telechelic (usually liquid) prepolymers are linked to high molecular weight polymer. Chain extension usually employs "extenders" i.e., low molecular weight species whose sole function it is to connect the prepolymers. Chain extensions considered in our calculations are irreversible, do not lead to cyclic products, and self-addition of extenders or prepolymers is absent. Further, in the telechelic polymer systems under consideration $n_1 \neq 0$ but $n_1 << n_2$ and every polymer that is formed by extension contains many α,ω-difunctional species plus two monofunctional species at the extremities. The following scheme illustrates the formation of one polymer:



where X~~~X, ~~~X and E stand for α,ω-difunctional species, monofunctional species and extender, respectively.

The number of polymers formed after extension will be $n_1/2$.

In a molecule containing n_{2i} difunctional species, the number of extensions i.e., the links arising between prepolymers (~XEX~ in the above scheme) is

$$e_i = n_{2i} + 1 \tag{2}$$

and the total number of extensions in the system:

$$e = \sum_{i=1}^{n_1/2} e_i = \sum_{i=1}^{n_1/2} (n_{2i} + 1) = n_2 + \frac{n_1}{2} \tag{3}$$

The number average extension is defined as

$$\overline{E}_n = \frac{\text{number of extensions}}{\text{number of polymers formed after extension}} \tag{4}$$

so that

$$\overline{E}_n = \frac{e}{n_1/2} = 1 + \frac{n_2}{n_1/2} \tag{5}$$

Combining eqs. (1) and (5) yields

$$\overline{E}_n = \frac{\overline{F}_n}{2 - \overline{F}_n} \tag{6}$$

Similarly, the number average degree of extension:

$$\overline{DE}_n = \frac{\text{number of prepolymers}}{\text{number of polymers formed after extension}} \tag{7}$$

so that

$$\overline{DE}_n = \frac{n_1 + n_2}{n_1/2} \tag{8}$$

Combining eqs. (1) and (8) yields

$$\overline{DE}_n = \frac{2}{2 - \overline{F}_n} \tag{9}$$

and with eq. (6)

$$\overline{DE}_n = \overline{E}_n + 1 \tag{10}$$

As Figure 1 and the data in Table I show $\overline{DE}_n$ is very sensitive to small changes in $\overline{F}_n$ close to $\overline{F}_n$ = 2.0. For example, a change in $\overline{F}_n$ from 1.98 to 1.998 (i.e. less than 1% change in $\overline{F}_n$) leads to an order of magnitude difference in $\overline{DE}_n$, or else, even an insignificant deviation from the ideal (0.001 unit drop from ideal, $\overline{F}_n = 2.0$) results in an enormous drop in $\overline{DE}_n$ (from ∞ to 2,000). Evidently extension is an extremely sensitive function of $\overline{F}_n$.

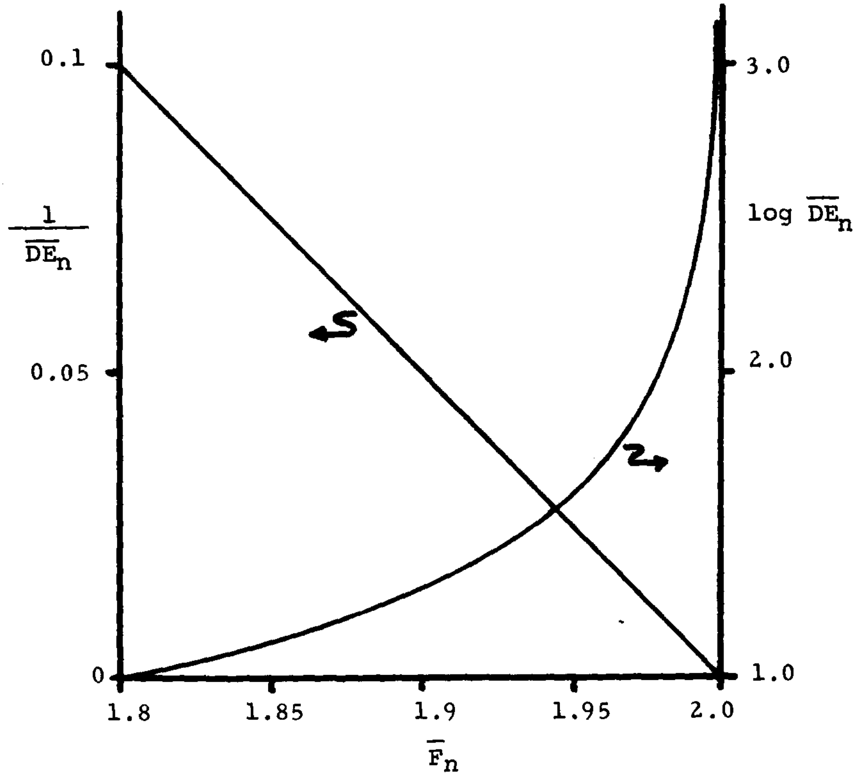


Figure 1. Logarithm and reciprocal of number averaverage degree of extension ($\overline{DE}_n$) as a function of number average functionality ($\overline{F}_n$) near to the ideal ($\overline{F}_n$ = 2.0).

Table I. Number average degree of extension ($\overline{DE}_n$) as a function of number average functionality ($\overline{F}_n$).

$\overline{F}_n$	$\overline{DE}_n$
2.0	∞
1.999	2000
1.998	1000
1.996	500
1.99	200
1.98	100
1.96	50
1.90	20
1.80	10

In regards to molecular weight dependent parameters

$$\overline{M}_r = \overline{DE}_n \cdot \overline{M}_n + \overline{E}_n \cdot M_e, \qquad (11)$$

where $\overline{M}_r$ is the number average molecular weight of the resulting polymer, $\overline{M}_n$ is the number average molecular weight of the prepolymer, and M_e is the molecular weight of the extender. From eqs. (6) and (9)

$$\overline{M}_r = \frac{2}{2-\overline{F}_n}\,\overline{M}_n + \frac{\overline{F}_n}{2-\overline{F}_n}\,M_e \qquad (12)$$

Inspection of eq. (12) reveals fundamental similarity with the Baldwin-equation (BALDWIN et al. 1969), except the latter authors have not considered M_e, i.e. the second member on the right of eq. (12). However M_e must be considered, particularly in systems in which $\overline{M}_n$ is relatively low.

From eq. (12)

$$\overline{F}_n = 2\,\frac{\overline{M}_r - \overline{M}_n}{\overline{M}_r + M_e} \qquad (13)$$

This equation can be conveniently used to calculate $\overline{F}_n$ provided $\overline{M}_n$ and M_e are known, and $\overline{M}_r$ is determined after chain extension. Comparison of $\overline{F}_n$ of prepolymer determined independently and $\overline{F}_n$ calculated by eq. (13) would give a valuable insight into chain extension process.

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