SUPPORTING INFORMATION

Section 2.2.3

Comparison of the relative polydispersity index \( \frac{D}{D_0} \) for distribution of the number of E-units bonded to A units in various reaction states calculated kinetically (solving corresponding systems of differential aquations) and as convolution of distribution function for a single chain (Eq. (A1-5)).

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<th>ratio A1:E</th>
<th>reaction state of unit</th>
<th>( \frac{D}{D_0} )_{kine}</th>
<th>( \frac{D}{D_0} )_{convol}</th>
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<tr>
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Section 2.2.3

Distributions of units in E-branches of polyfunctional cores with substitution effect – kinetic approach via generating function

Example:

Bifunctional core with groups A1 reacts with E, according to the following scheme

...
The corresponding sets of differential equations

\[
\begin{align*}
\frac{d[A20]}{dt} &= -2k_{20}[A20][E] \\
\frac{d[A11(1)]}{dt} &= 2k_{20}[A20][E] - (k_{11} + k_2)[A11(1)][E] \\
\frac{d[A11(2)]}{dt} &= k_2[A11(1)][E] - (k_{11} + k_2)[A11(2)][E] \\
\frac{d[A11(3)]}{dt} &= k_2[A11(2)][E] - (k_{11} + k_2)[A11(3)][E] \\
\vdots \\
\frac{d[A02(2)]}{dt} &= k_{11}[A11(1)][E] - 2k_2[A02(2)][E] \\
\frac{d[A02(3)]}{dt} &= (k_{11}[A11(2)] + 2k_2[A02(2)][E]) - 2k_2[A02(3)][E] \\
\frac{d[A02(4)]}{dt} &= (k_{11}[A11(3)] + 2k_2[A02(3)][E]) - 2k_2[A02(3)][E] \\
\vdots
\end{align*}
\]
The differential equations read

\[
\frac{\partial g_{A_{11}}(Z)}{[E]\partial t} = 2k_{20}[A_{20}] + [k_1Z - (k_{11} + k_2)]g_{A_{11}}(Z) \\
\frac{\partial g_{A_{02}}(Z)}{[E]\partial t} = k_{11}Zg_{A_{11}}(Z) + k_2(Z - 1)g_{A_{02}}(Z)
\]  

(SI2-4)

The first equation can be solved when the time \( t \) is replaced by the concentration \([A_{20}]\). The solution is substituted in the second equation. Also the method of moments can be used if appropriate. Alternatively, the distribution of degrees of polymerization of E-branches can easily be obtained by numerical solution of sets of equation (SI-2) because \( P_{en} \) is usually low.

It is seen that in the case of substitution effect, the distribution of E-sequences on f-functional core is no longer equal to the f-fold convolution. The distribution of A02 of the example discussed above depends on how E is consumed in the branch of A11 and what is left if formation of A02 is strongly delayed.

For \( k_{20} = k_{11} = k_1 \) (no substitution effect) it is not obvious how to prove that the distribution of the number of E-units in two branches of A02 is equal to the convolution of two distributions for one branch. For that case, one has to consider separately the build-up of each branch (i.e., all possible ways of combination) based on the following scheme.
Section 2.3.2
Formulation of recursive functions $u$ and equations for values of their derivatives used for calculation of $M_w$. 
\[ u_{\text{BAP}} = Z_A^E (1 - \xi_{\text{APE}} (1 - \alpha_{\text{APB}} + \alpha_{\text{APB}} u_{\text{APB}}) + \xi_{\text{APE}} (1 - \alpha_{\text{ASB}} + \alpha_{\text{ASB}} u_{\text{ASB}}) W_E (Z_E^E)^{n-1}) \]

\[ u_{\text{BAS}} = u_{\text{BAP}} \]

\[ u_{\text{APB}} = Z_B^E (1 - \alpha_B + \alpha_B (\psi_B u_{\text{BAP}} + (1 - \psi_B) u_{\text{BAS}})) W_{n-1} \]

\[ u_{\text{ASB}} = u_{\text{APB}} \]

\[ u_{\text{BAP}}^A = M_A + (f_A - 1) \left[ (1 - \xi_{\text{APE}}) \alpha_{\text{APB}} u_{\text{APB}}^A + \xi_{\text{APE}} \alpha_{\text{ASB}} u_{\text{ASB}}^A \right] \]

\[ u_{\text{BAP}}^E = (f_A - 1) \left[ (1 - \xi_{\text{APE}}) \alpha_{\text{APB}} u_{\text{APB}}^E + \xi_{\text{APE}} \alpha_{\text{ASB}} u_{\text{ASB}}^E + M_B W_E (1) \right] \]

\[ u_{\text{BAS}}^E = u_{\text{BAP}}^E \]

\[ u_{\text{BAP}}^B = (f_A - 1) \left[ (1 - \xi_{\text{APE}}) \alpha_{\text{APB}} u_{\text{APB}}^B + \xi_{\text{APE}} \alpha_{\text{ASB}} u_{\text{ASB}}^B \right] \]

\[ u_{\text{BAS}}^B = u_{\text{BAP}}^B \]

\[ u_{\text{APB}}^A = (f_B - 1) \left[ \alpha_B \psi_B u_{\text{BAP}}^A + \alpha_B (1 - \psi_B) u_{\text{BAS}}^A \right] \]

\[ u_{\text{APB}}^E = (f_B - 1) \left[ \alpha_B \psi_B u_{\text{BAP}}^E + \alpha_B (1 - \psi_B) u_{\text{BAS}}^E \right] \]

\[ u_{\text{APB}}^B = M_B + (f_B - 1) \left[ \alpha_B \psi_B u_{\text{BAP}}^B + \alpha_B (1 - \psi_B) u_{\text{BAS}}^B \right] \]

Results of solution

| \( u_{\text{BA1}}^A = M_A / D \) | \( u_{\text{BA1}}^B = M_B (f_A - 1) (1 - \xi_{\text{A1E}}) \alpha_{\text{A1}} + \xi_{\text{A1E}} \alpha_{\text{A2}}) / D \) | \( u_{\text{BA2}}^A = u_{\text{BA1}}^A \) |
| \( u_{\text{BA1}}^E = M_{\text{EW}} / D \) | \( u_{\text{BA2}}^E = u_{\text{BA1}}^E \) |
| \( u_{\text{BA1}}^B = u_{\text{BA2}}^B \) |

| \( u_{\text{A1B}}^A = M_A (f_B - 1) \alpha_B / D \) | \( u_{\text{A1B}}^B = M_B / D \) | \( u_{\text{A2B}}^A = u_{\text{A1B}}^A \) |
| \( u_{\text{A1B}}^E = M_{\text{EW}} (f_B - 1) \alpha_B / D \) | \( u_{\text{A2B}}^E = u_{\text{A1B}}^E \) |
| \( u_{\text{A1B}}^B = u_{\text{A2B}}^B \) |

Section 2.3.3

Explicit relations for contributions to the number of elastically active network chains
$$
T_A(z_{\text{inf}}) = [(1 - \xi_{A1E})\alpha_A1 + \alpha_A1\nu_{AIB} + (1 - \nu_{AIB})z_{\text{inf}}] + \\
\xi_{A1E}(1 - \alpha_A2 + \alpha_A2\nu_{A2B} + (1 - \nu_{A2B})z_{\text{inf}})]^\lambda
$$

$$
T_B(z_{\text{inf}}) = [1 - \alpha_B + \alpha_B(\nu_{BA1} + (1 - \nu_{BA1})z_{\text{inf}})]^\mu
$$

$$
T_A'(z_{\text{inf}}) = f_A(1 - \nu_{AIB})[(1 - \xi_{A1E})\alpha_A1 + \xi_{A1E}\alpha_A2(1 - \nu_{A2B})]
$$

$$
T_A'(0) = f_A[(1 - \xi_{A1E})\alpha_A1 + \xi_{A1E}\alpha_A2(1 - \nu_{A2B})] \\
[(1 - \xi_{A1E})(1 - \alpha_A1 + \alpha_A1\nu_{AIB}) + \xi_{A1E}(1 - \alpha_A2 + \alpha_A2\nu_{A2B})]^\lambda = \\
f_A(1 - \nu_{AIB})[(1 - \xi_{A1E})\alpha_A1 + \xi_{A1E}\alpha_A2]\nu_{BA1}
$$

$$
T_A''(0) = f_A(f_A - 1)(1 - \nu_{AIB})[(1 - \xi_{A1E})\alpha_A1 + \xi_{A1E}\alpha_A2(1 - \nu_{A2B})]^2 \\
[(1 - \xi_{A1E})(1 - \alpha_A1 + \alpha_A1\nu_{AIB}) + \xi_{A1E}(1 - \alpha_A2 + \alpha_A2\nu_{A2B})]^\lambda = \\
f_A(f_A - 1)(1 - \nu_{AIB})^2[(1 - \xi_{A1E})\alpha_A1 + \xi_{A1E}\alpha_A2]^2 \nu_{BA1}^{(f_A - 2)/(f_A - 1)}
$$

$$
T_A'(1) - T_A'(0) = f_A[(1 - \nu_{AIB})[(1 - \xi_{A1E})\alpha_A1 + \xi_{A1E}\alpha_A2] \\
[1 - \nu_{BA1} - (f_A - 1)(1 - \nu_{AIB})[(1 - \xi_{A1E})\alpha_A1 + \xi_{A1E}\alpha_A2]\nu_{BA1}^{(f_A - 2)/(f_A - 1)}]
$$

$$
T_B(z_{\text{inf}}) = [1 - \alpha_B + \alpha_B(\nu_{BA1} + (1 - \nu_{BA1})z_{\text{inf}})]^\mu
$$

$$
T_B'(z_{\text{inf}}) = f_B[\alpha_B(1 - \nu_{BA1})][1 - \alpha_B + \alpha_B(\nu_{BA1} + (1 - \nu_{BA1})z_{\text{inf}})]^\mu
$$

$$
T_B'(0) = f_B[\alpha_B(1 - \nu_{BA1})][1 - \alpha_B + \alpha_B\nu_{BA1}]^\mu = f_B[\alpha_B(1 - \nu_{BA1})]\nu_{AIB}
$$

$$
T_B''(0) = f_B[(f_B - 1)[\alpha_B(1 - \nu_{BA1})]^2 \nu_{AIB}^{(f_B - 2)/(f_B - 1)}
$$

$$
T_B'(1) - T_B'(0) - T_B''(0) = f_B[\alpha_B(1 - \nu_{BA1})][1 - \nu_{AIB} - (f_B - 1)[\alpha_B(1 - \nu_{BA1})]\nu_{AIB}^{(f_B - 2)/(f_B - 1)}]
$$

**Section 3**

**Experimental**

**Materials**
The materials used in the preparation of the polyether star oligomers were commercially available: neopentyl glycol (NPG), monopentaerythritol (MPE) and dipentaerythritol (DPE) were purchased from Perstorp, trimethylolethane (TME) from GEO Specialty Chemicals. Other chemicals from Aldrich were used as received.

**Preparation of glycidyl pivalate.** Epichlorohydrine (1770 g) was reacted with pivalic acid (650 g) in the presence of 0.1% ethyltriphenylphosphonium chloride at 110 °C under nitrogen for > 100 min until the acid number dropped below 1 mg KOH. After cooling to 30 °C, NaOH (306 g) in the form of solution (50 wt.-%) is gradually added during 120 min. keeping the temperature constant. After 60 min., water was added and the aqueous bottom layer was separated. The second portion of NaOH (53 g) in solution was added and the solution was stirred for 30 min. The reaction mixture was neutralized with CO₂ and the aqueous layer removed. The remaining epichlorohydrine with water was distilled off under reduced pressure. The mixture of epichlorohydrine and glycidyl pivalate and epichlorohydrine was distilled off at higher temperature. The remaining glycidyl pivalate was cooled down to 40 °C and filtered. The product was analyzed by GC/MS. It contained 90% glycidyl pivalate, the byproducts were composed of di- and triesters of glycerol and pivalic acid and glycidyl ether of glycidyl pivalate. Their possible activity in chain extension of polyols was taken into account.

For curing of the polyols, the trimer of 1,6-hexamethylenediisocyanate Desmodur N3600 (Bayer) was used. Its composition with respect to functionality distribution was determined by MALDI-TOF FTIR MS of the triisocyanate deactivated before the measurement with n-butanol as described in detail in ref. 33. The first- and second-moment functionality averages (number of NCO groups per molecule of cross-linker), \( \langle f \rangle_1 \) and \( \langle f \rangle_2 \), are defined as

\[
\langle f \rangle_1 = \sum f_n \frac{n_f}{n_f}, \quad \langle f \rangle_2 = \sum \frac{f_n^2 n_f}{n_f}
\]

where \( n_f \) is the number fraction of molecules having \( f \) NCO groups. For triisocyanate used in this work \( \langle f \rangle_1 = 3.22 \) and \( \langle f \rangle_2 = 3.29 \).

**Preparation of precursors**

The polyether oligomers were prepared by ring-opening polyaddition of the mono epoxy ester glycidyl pivalate, (GLPI (I)), with polyols – neopentyl glycol (1,3-dihydroxy-2,2-dimethylpropane), NPG (IIa), trimethylolethane (1,1,1-trihydroxymethylethane), TME (IIb), monopentaerythritol, tetrahydroxymethylmethane, MPE (IIc), and dipentaerythritol, DPE (IId). The synthesis of the polyether oligomers was done in methyl isobutyl ketone at about 90% solids content using 0.2% of tin II octoate as a catalyst. The mixture was kept at reflux temperature of about 160° C until ≥99% glycidyl pivalate was converted (about 8 hours reaction time). The reaction products were analyzed by MS and SEC and used for further cross-linking studies with the triisocyanate.

**Preparation of networks**

The hydroxy-functional oligoethers were either used as prepared or further diluted with the same or similar solvent. Dibutyltin dilaurate (500 ppm based on solids) was used as catalyst and Desmodur N3600 was added. Always, the mixtures were stirred approximately for three minutes. The initial molar ratio [NCO]/[OH] was kept equal to one. For preparation of the sheets, the solution was poured into a glass mold (about 2 mm thick). The samples were kept at room temperature for about 2 days, and later at
elevated temperature (50°C) for 1 day to achieve full conversion of NCO groups. The absence of unreacted NCO groups (below 1 %) was confirmed by FTIR ATR.

**Characterization methods**

**Mass spectrometry**
Dried droplet-method was used. Each sample was dissolved in THF (10 mg/mL) and mixed with THF solution of 2,5-dihydroxybenzoic acid as a matrix (20 mg/mL), in volumetric ratio 1:4 (sample:matrix). 1 µL of the mixture was deposited on the target and let to dry at ambient atmosphere. The addition of ionization agent was not necessary. MALDI-TOF mass spectra were measured in the positive ion mode using the mass spectrometer Bruker BiFlex III equipped with a nitrogen laser (337 nm, 3 ns pulse width, 3 Hz). The spectra were obtained by sampling whole area of the spot. The reflector mode and the external calibration on poly(ethylene glycol) were used.

**Determination of NCO and OH groups**
The decrease of the concentration of NCO groups was determined by FTIR spectroscopy. The decrease in the intensities of the stretching band at 2273 cm\(^{-1}\) was monitored. The intensity of NCO group band was related to the intensity of the reference C-H stretching band at 2930 cm\(^{-1}\), which remains practically constant during the reaction.

**SEC analysis**
SEC analysis was performed with a Waters Alliance 2695 instrument using tetrahydrofurane as eluent. The instrument was calibrated with polystyrene standards.

**Determination of gel point**
The reactants, solvent and catalyst were mixed for about 3 minutes and small portions of the material were placed into closed vials and kept at 25°C. At selected reaction times close to the gel time, the solution of dibutylamine in THF was added to the reaction mixture in the vials followed by addition of a small amount of dichloromethane after a few seconds. The critical (gel) time was the first time at which an insoluble fraction was visually registered. In parallel, the conversion of NCO groups at critical time (critical conversion) was determined by FTIR spectroscopy.

**Determination of the swelling degree**
Pieces (0.1–0.2 g) of cross-linked polymer were swollen in a large excess of solvent. After the full swelling at constant temperature, the solvent was exchanged several times until the samples weights reached constant values. The weight fractions of sol, \(w_s\), were determined from the difference of the dry samples before and after extraction. For all fully cured samples, \(w_s \leq 0.1\ %\). The volume fraction of polymer in the swollen sample (\(\phi_2\)) was calculated from weights of the swollen \((m_{sw})\) sample and dry sample after extraction \((m_d)\) and specific gravities of the polymer \((\rho_{pol})\) and solvent \((\rho_{solv})\)

\[
\phi_2 = \frac{m_d / \rho_{pol}}{m_d / \rho_{pol} + (m_{sw} - m_d) / \rho_{solv}}
\]

(2)

The volume fraction of polymerizable material during network formation \(\phi_2^0\) is equal to

\[
\phi_2^0 = \frac{m_d / \rho_{pol}}{m_{pol,0} / \rho_{pol} + m_{dil} / \rho_{dil}}
\]

(3)
where \( m_{\text{pol},0} \) is the weight of polymerizable material, and \( m_{\text{dil}} \) and \( \rho_{\text{dil}} \) are the weight and specific gravity of the added diluent, respectively.

**Determination of shear modulus**

Dynamic mechanical measurements (DMA) were performed using the Dynamic Mechanical Analyser Tritec 2000 (Triton Technology Ltd.). Rectangular samples (a free, unclamped specimen of length 5 mm, thickness from 1.5 to 3 mm and width 10 mm), were used in fully clamped bending mode. Samples were measured in the equilibrium swollen state at frequency 0.1 Hz at which the storage modulus \( E' \) was much larger than the loss modulus, \( E'' \), and practically equal to values determined at lower frequencies.

**Section 3.1.1**

Abundance for chain-extended NPG precursor

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<td>( f_2 )</td>
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abundances relative to compound NPG-PI\(_2\)-GL\(_3\) (= 100)

**Section 3.1.2**
Compositional distributions of the precursors by transesterification and alcoholysis and comparison with MS analysis: Compositional distribution of hydroxy-functional precursors prior to transesterification and hydrolysis from the basic pgf

The distribution of molar fractions of reaction products of GLPI addition to the polyol, transesterification and alcoholysis is equal to the coefficients $x_{ij}$ of eq. (39) expanded into power series of $Z_{GL}^{i}Z_{PI}^{j}$. The $N_{ETH}(Z_{PI}, Z_{GL})$ part is a sum over GLPI chains of all possible lengths given by number fractions $n_i$ defined by eq. (4). In reality, only a few of them have to be considered; for $r_e = 1$, consideration of $i$ and $j$ equal to 1, 2, 3 is sufficient.

The basic pgf for the number of GLPI units in polyether branches (cf., eq. (4))

$$N(Z) = \frac{Z}{\kappa_{2}(Z-1)+1} \left( \frac{1}{\xi_{AIE}} \left( \frac{1}{1-\xi_{AIE}} \right)^{\kappa_{1}(Z-1)} - \frac{1-\xi_{AIE}}{\xi_{AIE}} \right) \equiv \sum_{i} n_{i} Z^{i} \quad \text{(SI3-1)}$$

$Z$ counts the number of glycidyl pivalate units, i.e. $Z \rightarrow Z_{PI}Z_{GL}$. For counting low-molecular-weight oligomers, one makes use of the postulate of independent growth of branches on the polyether core. The number fraction the reads

$$n_{j} = \frac{1}{i!} \left[ \frac{\partial N^{i}(Z)}{\partial Z^{i}} \right]_{Z=0} \quad \text{(SI3-2)}$$

where $\left[ \frac{\partial N^{i}(Z)}{\partial Z^{i}} \right]_{Z=0}$ is the value of the $i$-th derivative of $N(Z)$. To obtain the $n_{i}$ values, $N(Z)$ is split into two functions

$$N(Z) = N_{1}(Z) N_{2}(Z)$$

$$N_{1}(Z) = \frac{Z}{\kappa_{2}(Z-1)+1}; \quad N_{2}(Z) = \frac{1}{\xi_{AIE}} \left( \frac{1}{1-\xi_{AIE}} \right)^{\kappa_{1}(Z-1)} - \frac{1-\xi_{AIE}}{\xi_{AIE}} = ab^{\kappa_{1}(Z-1)} - a / b$$

The values of a few derivatives are summarized below
The values of derivatives of $N$ are summarized below (eq. (SI3-2)):

\[
\begin{align*}
N^{(1)}(0) &= N_1^{(1)}(0)N_2(0) + N_1(0)N_2^{(1)}(0) \\
N^{(2)}(0) &= N_1^{(2)}(0)N_2(0) + 2N_1^{(1)}(0)N_2^{(1)}(0) + N_1(0)N_2^{(2)}(0) \\
N^{(3)}(0) &= N_1^{(3)}(0)N_2(0) + 3N_1^{(2)}(0)N_2^{(2)}(0) + 3N_1^{(1)}(0)N_2^{(3)}(0) + N_1(0)N_2^{(3)}(0) \\
N^{(4)}(0) &= N_1^{(4)}(0)N_2(0) + 4N_1^{(3)}(0)N_2^{(3)}(0) + 6N_1^{(2)}(0)N_2^{(4)}(0) + 4N_1^{(1)}(0)N_2^{(3)}(0) + N_1(0)N_2^{(4)}(0)
\end{align*}
\]

**Section 3.2.1**

Derivation of the gel point condition for cross-linking of hydroxy-functional precursors affected by transesterification and alcoholysis with polyisocyanates
The gel point condition is derived from the pgfs for additional number of bonds issuing from units already connected by one bond. They characterize bond propagation ability of the units. These functions and their derivatives read

\[
F_{BA1}(z) = \frac{((1 - \xi_{A1E})\beta_{A1} + \xi_{A1E}\beta_{A2}N_{ETH}(z_{A1B}))^{x-1}[(1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}\beta_{A2}\sum m_i(i^{-1})]}{(1 - \xi_{A1E})(1 - x_{TH}) + x_{TH}\xi_{A1E}P_n}
\]

\[
\frac{\partial F_{BA1}(z)}{\partial z_{A1B}} \bigg|_{z=1} = (f_A - 1)\alpha_A((1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}P_n) + \frac{\alpha_{A2}\xi_{A1E}x_{TH}P_n(P_w - 1)}{(1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}P_n}
\]

\[
\frac{\partial F_{BA1}(z)}{\partial z_{A2B}} \bigg|_{z=1} = (f_A - 1)\alpha_A\xi_{A1E}(1 - x_{TH}) + \frac{\xi_{A1E}x_{TH}(1 - x_{TH})\alpha_{A2}P_n}{(1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}P_n}
\]

\[
\frac{\partial F_{BA1}(z)}{\partial z_{A1B}} \bigg|_{z=1} = (f_A - 1)\alpha_A((1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}P_n) + \frac{\alpha_{A2}\xi_{A1E}x_{TH}P_n(P_w - 1)}{(1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}P_n}
\]

\[
\frac{\partial F_{BA1}(z)}{\partial z_{A2B}} \bigg|_{z=1} = (f_A - 1)\alpha_A\xi_{A1E}(1 - x_{TH}) + \frac{\xi_{A1E}x_{TH}(1 - x_{TH})\alpha_{A2}P_n}{(1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}P_n}
\]

\[
\frac{\partial F_{BA1}(z)}{\partial z_{A1B}} \bigg|_{z=1} = (f_A - 1)\alpha_A((1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}P_n) + \frac{\alpha_{A2}\xi_{A1E}x_{TH}P_n(P_w - 1)}{(1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}P_n}
\]

\[
\frac{\partial F_{BA1}(z)}{\partial z_{A2B}} \bigg|_{z=1} = (f_A - 1)\alpha_A\xi_{A1E}(1 - x_{TH}) + \frac{\xi_{A1E}x_{TH}(1 - x_{TH})\alpha_{A2}P_n}{(1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}P_n}
\]

\[
\frac{\partial F_{BA1}(z)}{\partial z_{A1B}} \bigg|_{z=1} = (f_A - 1)\alpha_A((1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}P_n) + \frac{\alpha_{A2}\xi_{A1E}x_{TH}P_n(P_w - 1)}{(1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}P_n}
\]

\[
\frac{\partial F_{BA1}(z)}{\partial z_{A2B}} \bigg|_{z=1} = (f_A - 1)\alpha_A\xi_{A1E}(1 - x_{TH}) + \frac{\xi_{A1E}x_{TH}(1 - x_{TH})\alpha_{A2}P_n}{(1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}x_{TH}P_n}
\]

\[
F_{A1B}(z) = [1 - \alpha_B + \alpha_B(\xi_{BA1}z_{BA1} + (1 - \xi_{BA1})z_{BA2})]^{x_{B-1}}
\]

\[
F_{A2B}(z) = F_{A1B}(z)
\]

\[
F_{A1B} = (f_B - 1)\alpha_B\xi_{BA1}
\]

\[
F_{A2B} = (f_B - 1)\alpha_B(1 - \xi_{BA1})
\]

\[
F_{A1B} = (f_B - 1)\alpha_B\xi_{BA1}
\]

\[
F_{A2B} = (f_B - 1)\alpha_B(1 - \xi_{BA1})
\]
the gel point condition is given equality of the determinant to 0, which means that there must be at least 1 sequence of bonds propagating to infinity

\[
D = \begin{vmatrix}
1 & 0 & -F_{A1B}^{BA1} & -F_{A2B}^{BA1} \\
0 & 1 & -F_{A1B}^{BA2} & -F_{A2B}^{BA2} \\
-F_{A1B}^{BA1} & -F_{A1B}^{BA2} & 1 & 0 \\
-F_{A2B}^{BA1} & -F_{A2B}^{BA2} & 0 & 1 \\
\end{vmatrix} = 0
\]

After simplification, the gel point condition is obtained in the form

\[
D = 1 - b(F_{BA2}^{A2B} + F_{BA2}^{A1B}) - a(F_{BA1}^{A1B} + F_{BA1}^{A2B}) = 0
\]

There are 3 unknown variables: critical conversions of primary and secondary hydroxy groups and conversion of isocyanate groups, they are interconnected by two equations: one between \( \alpha_{A1} \) and \( \alpha_{A2} \) and between \( \alpha_a = (1 - \xi_{A1}) \alpha_{A1} + \xi_{A1} \alpha_{A2} \) and \( \alpha_b \). The summary of relations is shown below for \( \alpha_a = \alpha_b \).
\[ \alpha_{A2} = 1 - (1 - \alpha_{A1})^5; \]
\[ \zeta = \frac{(1 - \xi_{A1E})(1 - x_{TH}) + \Theta_{A1E}P_n^2 \alpha_{A1}}{(1 - \xi_{A1E})(1 - x_{TH}) + \Theta_{A1E}P_n^2 \alpha_{A1} + \xi_{A1E}(1 - x_{TH}) \alpha_{A2}} \]
\[ \Theta = (1 - x_{H})x_{TE} + x_{H}(1 - x_{TE}) \]
\[ x_{TE} = \frac{1 + x_{H}\xi_{A1E}P_n}{(1 - x_{H})\xi_{A1E}P_n} x_{TH} \]
\[ F_{BA1}^{A1B} = \alpha_{A1}(f_A - 1)((1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}\Theta P_n) + \frac{\alpha_{A1}\xi_{A1E}\Theta^2 P_n(P_w - 1)}{(1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}\Theta P_n} \]
\[ F_{BA2}^{A1B} = (f_A - 1)\alpha_{A1}(1 - x_{TH}) + \frac{\xi_{A1E}(1 - x_{TH}) \alpha_{A2}P_n}{(1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}\Theta P_n} \]
\[ F_{BA1}^{A2B} = (f_A - 1)\alpha_{A2}\xi_{A1E}(1 - x_{TH}) + \frac{\alpha_{A1}\xi_{A1E}\Theta P_n}{(1 - \xi_{A1E})(1 - x_{TH}) + \xi_{A1E}\Theta P_n} \]
\[ F_{BA2}^{A2B} = (f_A - 1)\alpha_{A2}\xi_{A1E}(1 - x_{TH}) \]
\[ F_{A1B}^{B1A} = (f_B - 1)\alpha_{B}\zeta \]
\[ F_{A2B}^{B1B} = (f_B - 1)\alpha_{B}(1 - \zeta) \]
\[ F_{A1B}^{A1B} = F_{BA1} \]
\[ F_{A2B}^{A2B} = F_{BA2} \]
\[ F_{A1B}^{A2B} = F_{BA1} \]

Equation y to be solved reads:
\[ y = (f_B - 1)\alpha_B \left[ \zeta(F_{BA2}^{A1B} + F_{BA2}^{A2B}) + (1 - \zeta)(F_{BA1}^{A1B} + F_{BA1}^{A2B}) \right] - 1 = 0 \]

**Section 3.3.1**

Concentration of elastically active chains for conversion \( \alpha_B, \alpha_{A1}, \alpha_{A2} \rightarrow 1 \)

The probability generating functions for bonds with infinite continuation, \( T_A(z) \) and \( T_B(z) \) read
\[ T_A(z) = F_{A0a}(z = v_A + (1 - v_A)z) = ((1 - \xi_{A1E})\beta_{A1} + \xi_{A1E}\beta_{A2}N_{ETH}(z))^A \]
\[ T_A(z) = F_{B0b}(z = v_B + (1 - v_B)z) = [1 - \alpha_B + \alpha_B(\xi_{BA1}(v_{BA1} + (1 - v_{BA1})z) + (1 - \xi_{BA1})(v_{BA2} + (1 - v_{BA2})z))]^b \]
\[ (SI33-1) \]

where \( v_A = v_{A1B}, v_{A2B}; \ v_B = v_{BA1}, v_{BA2} \)
\[ \beta_{A1} = (1 - x_{TH})(1 - \alpha_{A1} + \alpha_{A1}(v_{A1B} + (1 - v_{A1B})z) + x_{TH} \]
\[ \beta_{A2} = (1 - x_{TH})(1 - \alpha_{A2} + \alpha_{A2}(v_{A2B} + (1 - v_{A2B})z) + x_{TH} \]
\[ (SI33-2) \]
\[ N_{\text{ETH}}(z) = \sum_{i=1}^{\infty} n_i \left[ (1-x_h)(1-x_{\text{TE}} + x_{\text{TE}}(1-\alpha_A + \alpha_A(\nu_{\text{AIB}} + (1-\nu_{\text{AIB}})z)) \right]^i \]

\[ X = (1-x_h)x_{\text{TE}} + x_h(1-x_{\text{TH}}) \]

\[ \zeta_{\text{BAI}} = \frac{(1-x_{\text{TE}}(1-x_{\text{TH}}) + X\xi_{\text{AIE}}P_{\phi})\alpha_A}{((1-x_{\text{TE}}(1-x_{\text{TH}}) + X\xi_{\text{AIE1}}P_{\phi})\alpha_A + \xi_{\text{AIE1}}(1-x_{\text{TH}}))\alpha_{A2}} \]

In the limit of full conversion of functional groups

\[ \alpha_B, \alpha_A, \alpha_{A2} \rightarrow 1 \quad \nu_{\text{AIB}}, \nu_{\text{A2B}}, \nu_{\text{BA1}}, \nu_{\text{BA2}} \rightarrow 0 \]

The convergence of extinction probability to zero is well fulfilled for \( f_A > 3, 4, 6 \), but should be checked for \( f_A = 2 \). For \( \nu = 0 \),

\[ T_A(z) = ((1-\xi_{\text{AIE1}})\beta_A + \xi_{\text{AIE1}}\beta_{A2}N_{\text{ETH}}(z))^f_A \]  

\[ T_B(z) = z^{f_B} \]

\[ \beta_{A1} = \beta_{A2} = \beta = (1-x_{\text{TH}})z + x_{\text{TH}} \]

\[ N_{\text{ETH}}(z) = \sum_{i=1}^{\infty} n_i \left[ (1-x_h)(1-x_{\text{TE}} + x_{\text{TE}}z) + x_h(1-x_{\text{TH}})z \right]^i \]

The generating function \( N_{\text{E}}(\zeta) = \sum_{i=1}^{\infty} n_i \zeta^i \) describes the number fraction distribution \( (n_i) \) of number of GLPI units of polyol branches that have reacted with GLPI (cf. eq. (1) of Part I). The number of OH groups per branch after transesterification and hydrolysis is determined by \( N_{\text{ETH}}(z) \)

\[ N_{\text{ETH}}(z) = \left[ \frac{\zeta}{\kappa_2(\zeta - 1) + 1} \left( \frac{1}{\xi_{\text{AIE}}} \left( \frac{1}{1 - \xi_{\text{AIE}}} \right)^{\kappa_2(\zeta - 1)} - \frac{1-\xi_{\text{AIE}}}{\xi_{\text{AIE}}} \right) \right] = \sum_{i=1}^{\infty} n_i (\zeta)^i \]  

The derivatives with respect to the variable \( z \) and their values for \( z = 1 \) and \( z = 0 \) are summarized below.

The \( \text{NETH} \) functions is for convenience into 3 factors \( A, B, \) and \( C \)

\[ N_{\text{ETH}}(\zeta(z)) = [A(\zeta(z))(B(\zeta(z)) - C)] \]

The first and second derivatives are as follows

\[ N_{\text{ETH}}'(\zeta(z)) = [A'(\zeta(z))(B(\zeta(z)) - C) + A(\zeta(z))B'(\zeta(z))]\zeta' \]

\[ N_{\text{ETH}}''(\zeta(z)) = [A''(\zeta(z))(B(\zeta(z)) - C) + 2A'(\zeta(z))B'(\zeta(z)) + A(\zeta(z))B''(\zeta(z))](\zeta')^2 + O(\zeta''(z)) \]

\[ \zeta = (1-x_h)(1-x_{\text{TE}} + x_{\text{TE}}z) + x_h((1-x_{\text{TH}})z + x_{\text{TH}}) \]
\[ \zeta' = (1 - x_H) x_{TE} + x_H (1 - x_{TH}); \quad \zeta'' = 0 \]

\[ A'(\zeta) = \frac{\zeta}{\kappa_2 (\zeta - 1) + 1}; \quad A''(\zeta) = \frac{1 - \kappa_2}{(\kappa_2 (\zeta - 1) + 1)^2}; \quad A'''(\zeta) = \frac{-2\kappa_2 (1 - \kappa_2)}{(\kappa_2 (\zeta - 1) + 1)^3} \]

\[ B'(\zeta) = \kappa_2 \left( \frac{1}{\xi_{A1E}} \left[ \frac{1}{1 - \xi_{A1E}} \right]^{\kappa_2 (\zeta - 1)} \right) \ln \left( \frac{1}{1 - \xi_{A1E}} \right); \quad \text{(SI33-8)} \]

\[ B''(\zeta) = \kappa_2 \left( \frac{1}{\xi_{A1E}} \left[ \frac{1}{1 - \xi_{A1E}} \right]^{\kappa_2 (\zeta - 1)} \right) \ln^2 \left( \frac{1}{1 - \xi_{A1E}} \right) \]

The values of the function \( N_{eth}(\zeta) \) and its derivatives are obtained by substitution of values of the function \( \zeta(z) \) and its first derivative \( \zeta'(1), \zeta'(0) \), \( \zeta''(0) \)

\[ \zeta(1) = 1; \quad \zeta(0) = (1 - x_H) (1 - x_{TE}) + x_H x_{TH} \]

\[ \zeta'(1) = \zeta'(0) = (1 - x_H) x_{TE} + x_H (1 - x_{TH}) \]

The concentration of EANCs is given by (cf. Pt. I)

\[ V_c = \frac{N_c \rho}{n_A (M_A + f_A \rho \rho M_E) + n_B M_{Bn}} \quad \text{(SI33-9)} \]

where \( M_A \) and \( M_E \) are molecular weights of polyol and GLPI, respectively, \( n_A \) and \( n_B \) are molar fractions of polyol and polyisocyanate, and \( M_{Bn} \) is the number-average molecular weight of polyisocyanate; \( r_e \) is the initial ratio of of epoxy groups to primary hydroxy-groups of polyol; \( \rho \) is specific gravity of the polymer. \( M_e \) should be corrected for a possible loss of PI groups by hydrolysis.

The number of EANCs per building unit, \( N_e \) is given by contributions of units A and B issuing at least three paths to infinity

\[ N_e = \frac{1}{2} \left( n_A \sum_{i=3}^{6} iT_{Ai} + n_A \sum_{i=3}^{6} iT_{Bi} \right) = \]

\[ \frac{1}{2} \left( n_A (T_A '(1) - T_A '(0) - T_A ''(0)) + n_B (T_B '(1) - T_B '(0)) - T_B ''(0)) \right) \quad \text{(SI33-10)} \]

The values of derivatives of the pgf \( T_A \) and \( T_B \) (eq. (S3-4))
\[ T_A'(z) = f_A \alpha^{\frac{1}{\alpha}} \beta'(1 - \xi_{AIE} + \xi_{AIE} N_{ETH}(z))^{\frac{1}{\alpha}} + \]
\[ f_A \alpha^{\frac{1}{\alpha}} \beta'(1 - \xi_{AIE} + \xi_{AIE} N_{ETH}(z))^{\frac{1}{\alpha} - 1} \xi_{AIE} N_{ETH}'(z) \]
\[ T_A'(1) = f_A(1 - x_{TH}) + f_A \xi_{AIE} P_n \]  
\[ (SI33-11) \]
\[ T_A'(0) = f_A x_{TH}^{\alpha - 1} (1 - x_{TH}) \left( 1 - \xi_{AIE} + \xi_{AIE} N_{ETH}(0) \right)^{\frac{1}{\alpha}} + \]
\[ f_A x_{TH}^{\alpha - 1} \left( 1 - \xi_{AIE} + \xi_{AIE} N_{ETH}(0) \right)^{\frac{1}{\alpha} - 1} \xi_{AIE} N_{ETH}'(0) \]
\[ T_A''(0) = f_A (f_A - 1) x_{TH}^{\alpha - 2} (1 - x_{TH})^{2} (1 - \xi_{AIE} + \xi_{AIE} N_{ETH}(0))^{\frac{1}{\alpha}} + \]
\[ 2 f_A x_{TH}^{\alpha - 1} (1 - x_{TH}) (1 - \xi_{AIE} + \xi_{AIE} N_{ETH}(0))^{\frac{1}{\alpha} - 1} \xi_{AIE} N_{ETH}'(0) + \]
\[ f_A (f_A - 1) x_{TH}^{\alpha - 1} (1 - \xi_{AIE} + \xi_{AIE} N_{ETH}(0))^{\frac{1}{\alpha} - 2} \xi_{AIE}^{2} N_{ETH}'(0)^{2} + \]
\[ f_A x_{TH}^{\alpha - 1} ((1 - \xi_{AIE}) + \xi_{AIE} N_{ETH}(0))^{\frac{1}{\alpha} - 1} \xi_{AIE} N_{ETH}''(0) \]  
\[ (SI33-12) \]

For component B, \( T_B(z) = z^{f_B/(f_B - 1)} \)
\[ T_B'(z) = f_B z^{f_B/(f_B - 1) - 1}, \quad T_B''(z) = f_B (f_B - 1) z^{f_B/(f_B - 1) - 2} \]
\[ T_B'(1) = f_B, \quad T_B'(0) = 0, \quad T_B''(0) = 0, \quad \text{for} \quad f_B = 2 \quad T_B''(0) = 2 \]  
\[ (S3-14) \]