

Supplemental information

REVISED

To the manuscript:

Kinetics of non-ideal Hyperbranched Polymerizations, 1. Simulation of the Structural Units and the Diads.

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1. Further plots of the ratio of the different structural units of an AB₂-system as function of the conversion depending on the different kinetic situations

In the following section we like to present additional plots how a single structural unit changes its ratio with the conversion when for a given kinetic situation the ratio of the k-values is varied.

1.1. Situation 1

(figures 1-6)

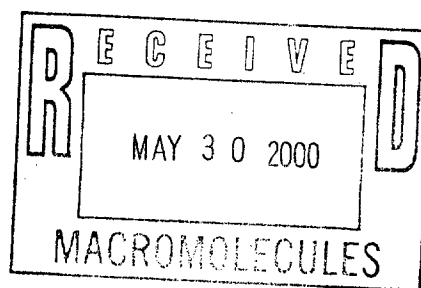
1.2. Situation 2

(figures 7-12)

1.3. Situation 3

(figures 13-18)

2. AB₃-system, ideal situation



Since it has not been published before, we will only give the ratios of the structural units as function of the conversion p_A for the ideal situation. A more extended discussion of the different kinetic situation is beyond the scope of this paper.

(figure 19)

3. The kinetic situations for the self-condensing vinyl polymerization (SCVP)

In this section the kinetics of the SCVP will be analyzed in more detail (compare table 5, scheme 5).

For a more convenient notation, we change the 4x8-matrix into a 2x5-matrix by omitting the k -values, which are equal to zero due to the special reaction mechanism of the SCVP:

$$(44) \quad \underline{\underline{K}} = \begin{bmatrix} 0 & k_{21} & 0 & k_{61} & k_{1'1} & k_{2'1} & 0 & k_{5'1} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & k_{24} & 0 & k_{64} & k_{1'4} & k_{2'4} & 0 & k_{5'4} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$(A1) \quad \Rightarrow \underline{\underline{K'}} = \begin{bmatrix} k_{21} & k_{61} & k_{1'1} & k_{2'1} & k_{5'1} \\ k_{24} & k_{64} & k_{1'4} & k_{2'4} & k_{5'4} \end{bmatrix}$$

The different kinetic situations are:

3.1. Different reactivities of the two B/B'-groups

The B'-group has a different reactivity than the B-group.

$$(A2) \quad \underline{\underline{K'}} = \begin{bmatrix} k_1 & k_1 & k_2 & k_2 & k_2 \\ k_1 & k_1 & k_2 & k_2 & k_2 \end{bmatrix}$$

This situation describes in the case of *p*-(chloromethyl)styrene different chemical functionalities. It can be addressed to the situation described by Müller et al.¹ using the parameter $r = k_1/k_2$. Müller et al. gave several plots on this situation; therefore we do not discuss this situation any further.

3.2. Effect of one group on another

¹ D. Yan, A.H.E. Müller, K. Matyjaszewski, *Macromolecules* 1997, 30, 7024-7033 (Supplemental information)

All other kinetic situations are due to different environments; one group is effecting the reactivity of the others.

a) The active B'-group activates/deactivates the A-group

$$(A3) \quad \underline{\underline{K'}} = \begin{bmatrix} k_1 & k_1 & k_1 & k_1 & k_1 \\ k_2 & k_2 & k_2 & k_2 & k_2 \end{bmatrix}$$

(figures 20, 21)

b) The active A-group activates/deactivates the B'-group

$$(A4) \quad \underline{\underline{K'}} = \begin{bmatrix} k_1 & k_1 & k_2 & k_1 & k_1 \\ k_1 & k_1 & k_2 & k_1 & k_1 \end{bmatrix}$$

(figures 22, 23)

c) The active B-group activates/deactivates the B'-group

$$(A5) \quad \underline{\underline{K'}} = \begin{bmatrix} k_1 & k_1 & k_1 & k_2 & k_1 \\ k_1 & k_1 & k_1 & k_2 & k_1 \end{bmatrix}$$

d) The reacted b-group activates/deactivates the B'-group

$$(A6) \quad \underline{\underline{K'}} = \begin{bmatrix} k_1 & k_1 & k_1 & k_1 & k_2 \\ k_1 & k_1 & k_1 & k_1 & k_2 \end{bmatrix}$$

e) The active B'-group activates/deactivates the B-group

$$(A7) \quad \underline{\underline{K'}} = \begin{bmatrix} k_2 & k_1 & k_1 & k_1 & k_1 \\ k_2 & k_1 & k_1 & k_1 & k_1 \end{bmatrix}$$

f) The reacted b'-group activates/deactivates the B-group

$$(A8) \quad \underline{\underline{K'}} = \begin{bmatrix} k_1 & k_2 & k_1 & k_1 & k_1 \\ k_1 & k_2 & k_1 & k_1 & k_1 \end{bmatrix}$$

Captions to the figures

- Figure 1: Simulation of conversion dependence of the structural unit 1t (situation 1).
- Figure 2: Simulation of conversion dependence of the structural unit 1l (situation 1).
- Figure 3: Simulation of conversion dependence of the structural unit 1d (situation 1).
- Figure 4: Simulation of conversion dependence of the structural unit 2t (situation 1).
- Figure 5: Simulation of conversion dependence of the structural unit 2l (situation 1).
- Figure 6: Simulation of conversion dependence of the structural unit 2d (situation 1).
- Figure 7: Simulation of conversion dependence of the structural unit 1t (situation 2).
- Figure 8: Simulation of conversion dependence of the structural unit 1l (situation 2).
- Figure 9: Simulation of conversion dependence of the structural unit 1d (situation 2).
- Figure 10: Simulation of conversion dependence of the structural unit 2t (situation 2).
- Figure 11: Simulation of conversion dependence of the structural unit 2l (situation 2).
- Figure 12: Simulation of conversion dependence of the structural unit 2d (situation 2).
- Figure 13: Simulation of conversion dependence of the structural unit 1t (situation 3).
- Figure 14: Simulation of conversion dependence of the structural unit 1l (situation 3).
- Figure 15: Simulation of conversion dependence of the structural unit 1d (situation 3).

Figure 16: Simulation of conversion dependence of the structural unit 2t (situation 3).

Figure 17: Simulation of conversion dependence of the structural unit 2l (situation 3).

Figure 18: Simulation of conversion dependence of the structural unit 2d (situation 3).

Figure 19: Simulation of conversion dependence of the structural units 1t, 1l, 1s, 1d, 2t, 2l, 2s and 2d: AB₃-system at ideal statistical kinetics.

Figure 20: Simulation of conversion dependence of the structural units 1, 2, 4, 5, 6 and 8: SCVP at situation a); the curves for the ideal statistical situation (all k's are equal) are given in dotted lines.

Figure 21: Simulation of conversion dependence of the structural units 1, 2, 4, 5, 6 and 8: SCVP at situation a); the curves for the ideal statistical situation (all k's are equal) are given in dotted lines.

Figure 22: Simulation of conversion dependence of the structural units 1, 2, 4, 5, 6 and 8: SCVP at situation b); the curves for the ideal statistical situation (all k's are equal) are given in dotted lines.

Figure 23: Simulation of conversion dependence of the structural units 1, 2, 4, 5, 6 and 8: SCVP at situation b); the curves for the ideal statistical situation (all k's are equal) are given in dotted lines.

Figures

Figure 1:

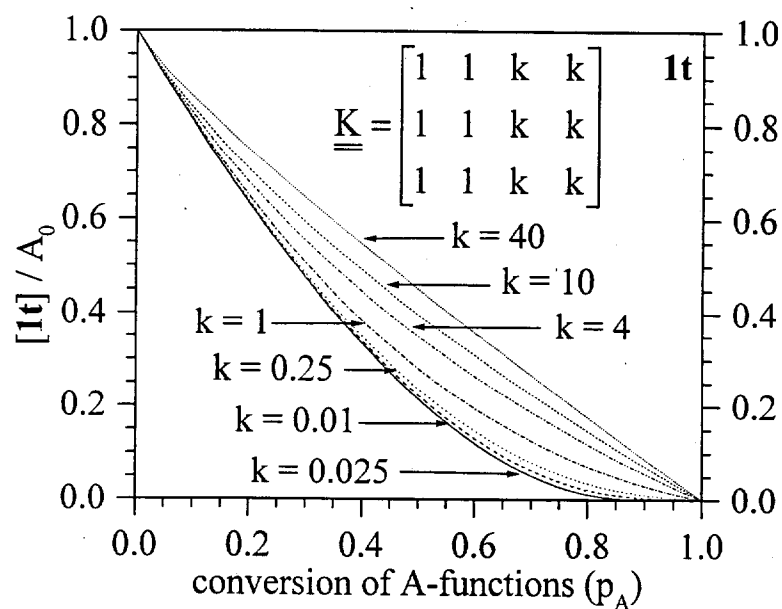


Figure 2:

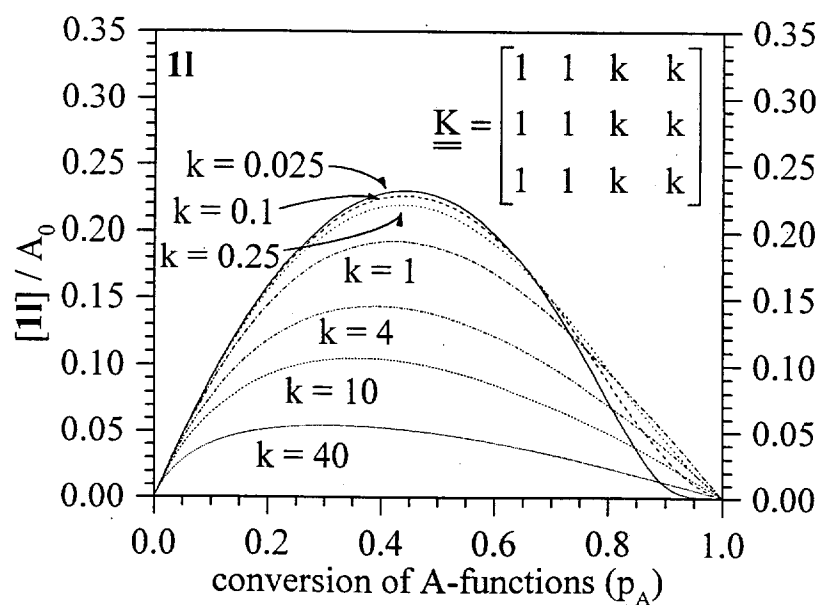


Figure 3:

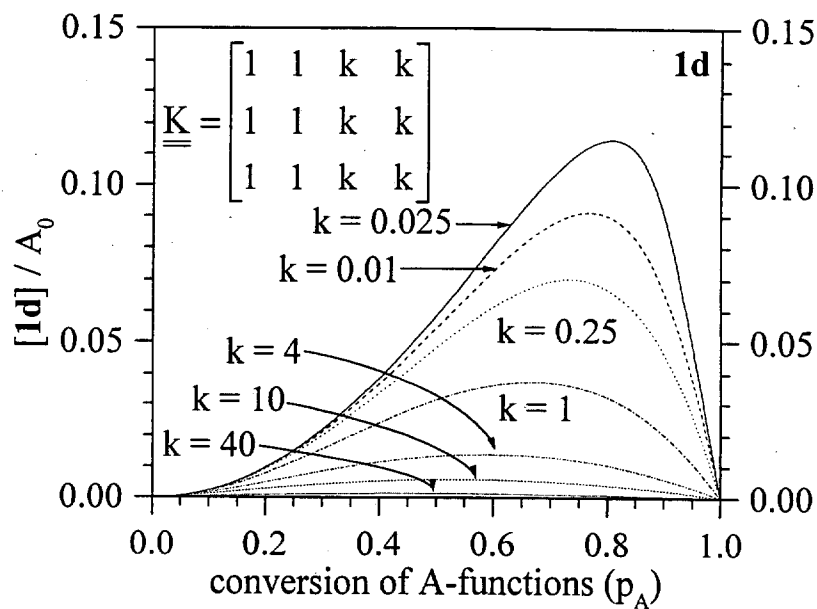


Figure 4:

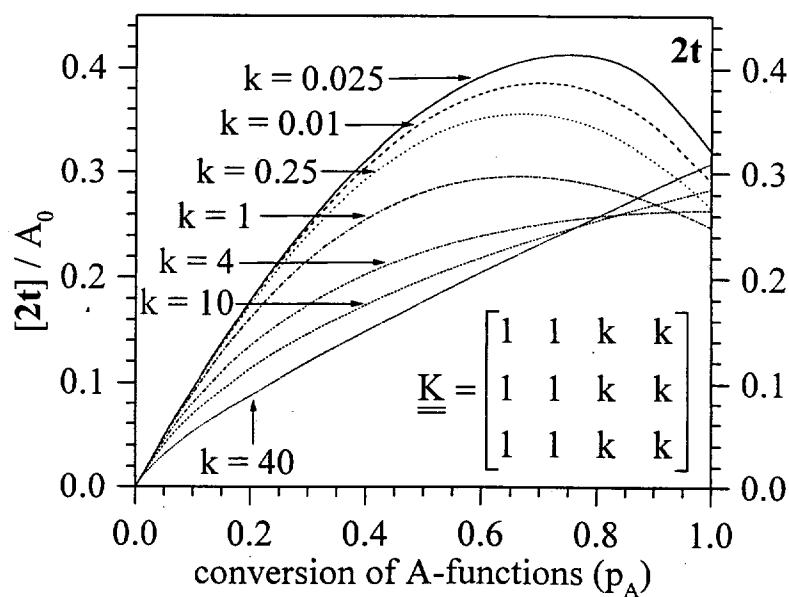


Figure 5:

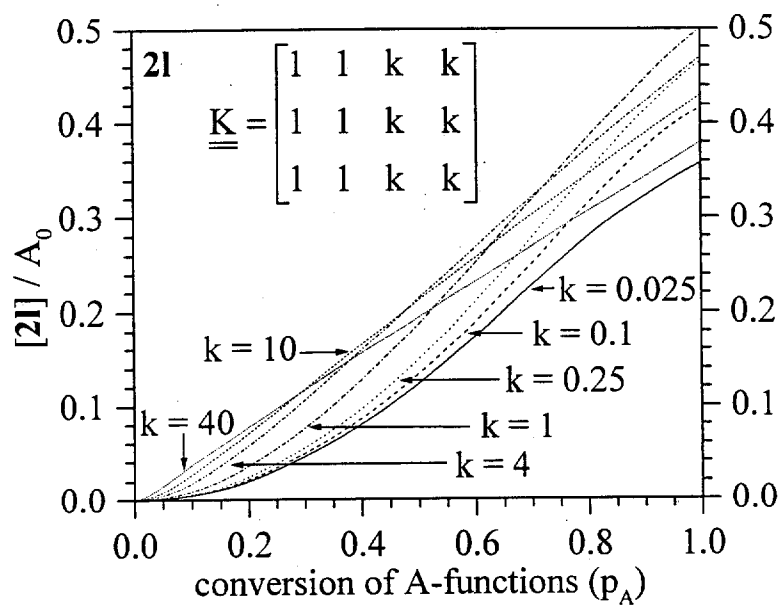


Figure 6:

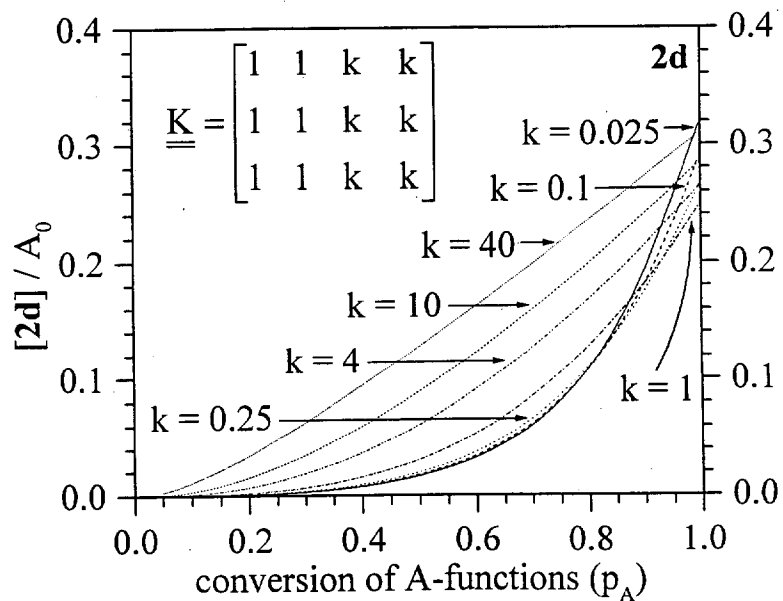


Figure 7:

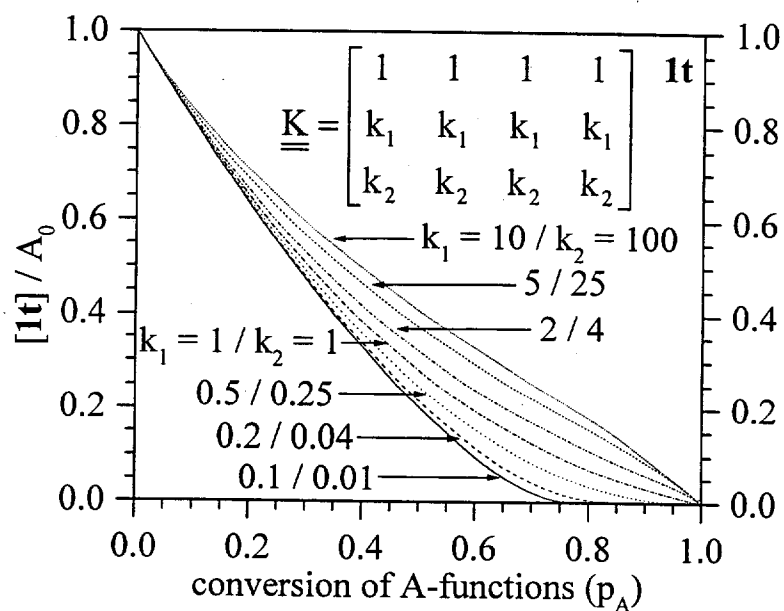


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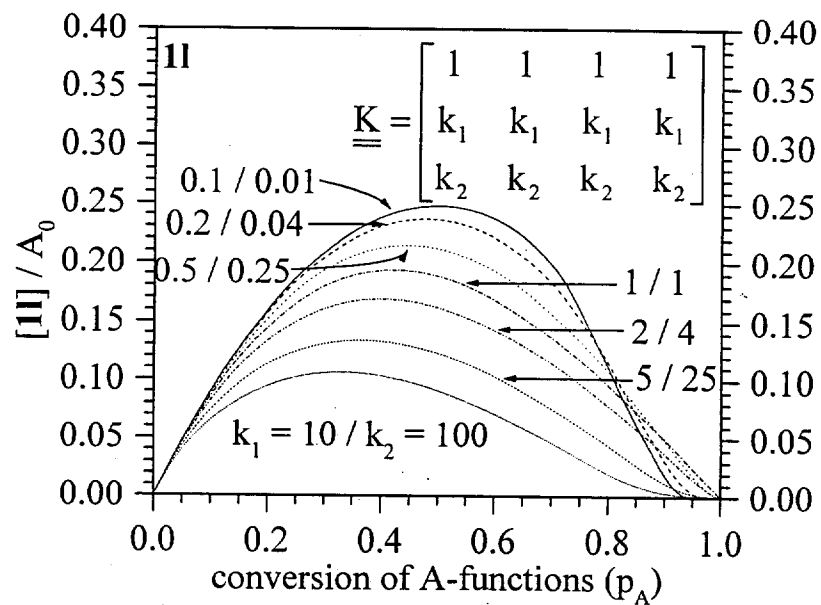


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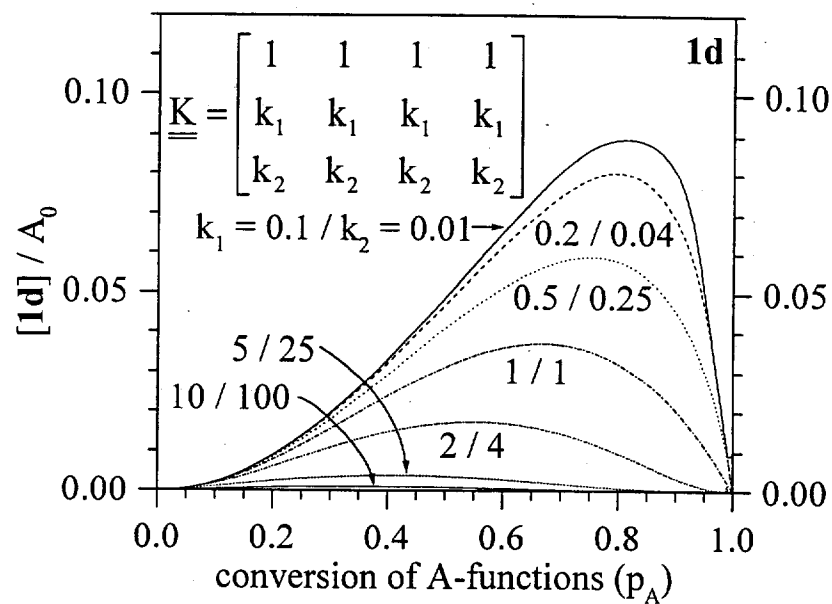


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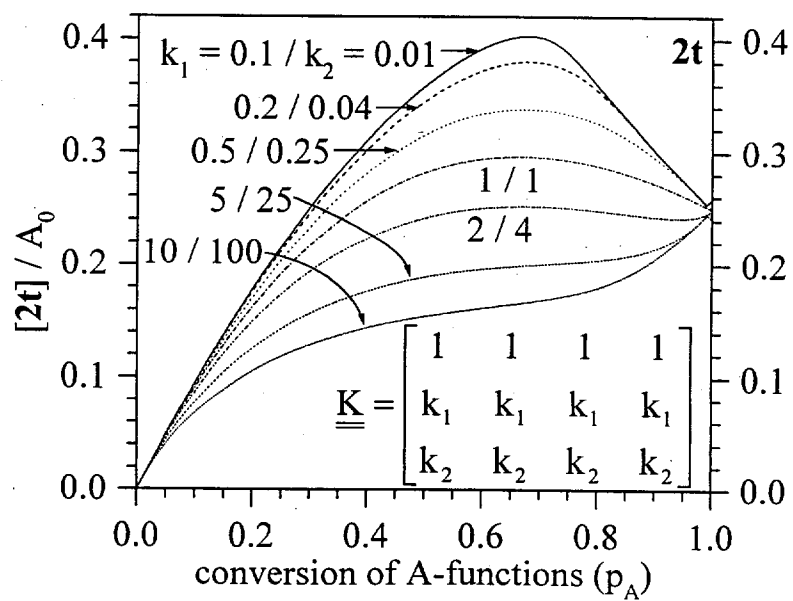


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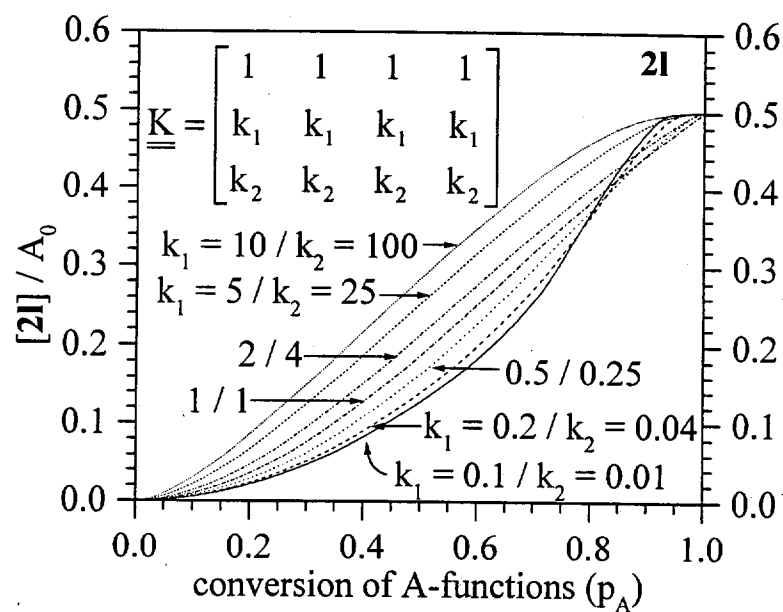


Figure 12:

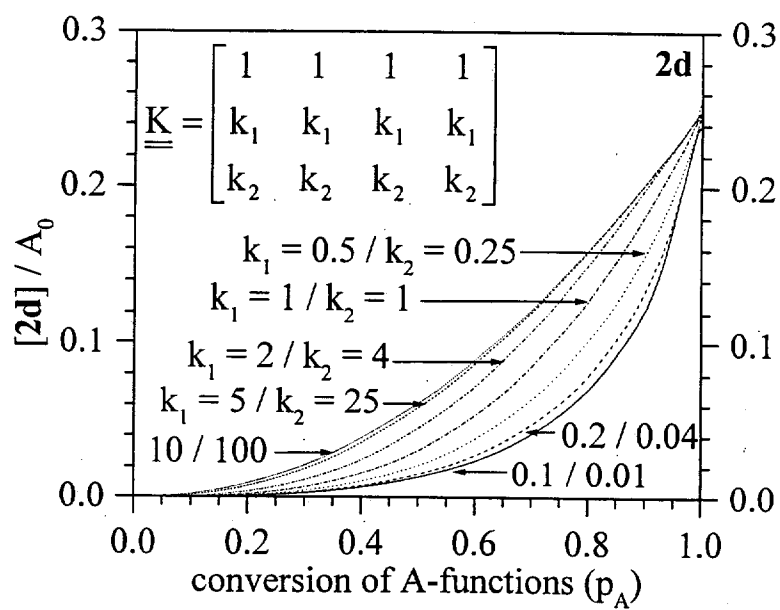


Figure 13:

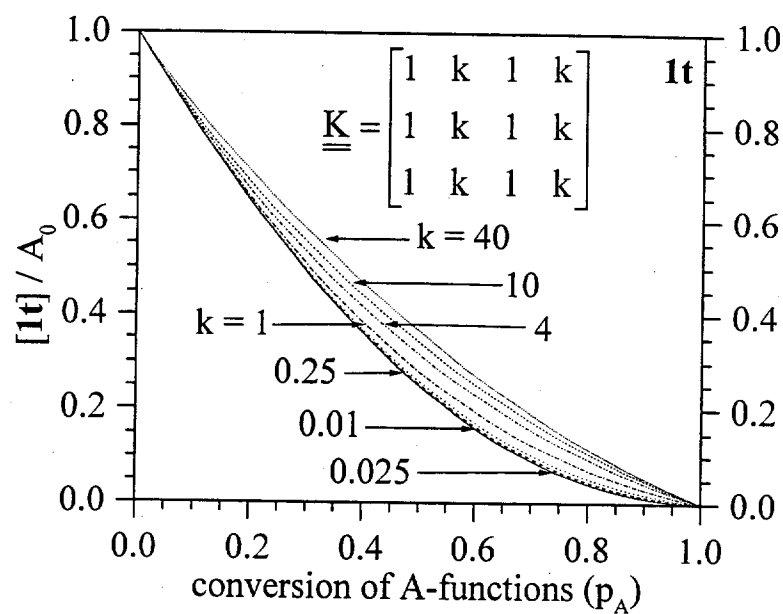


Figure 14:

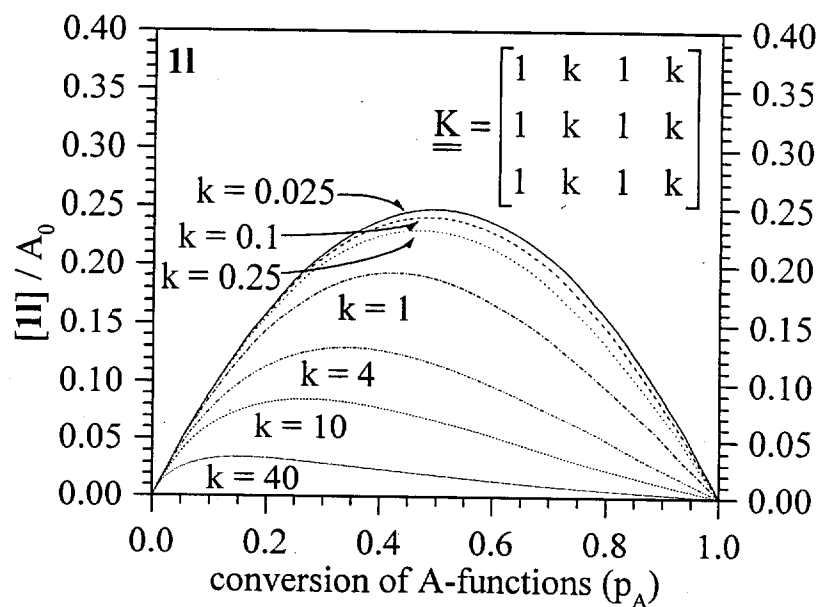


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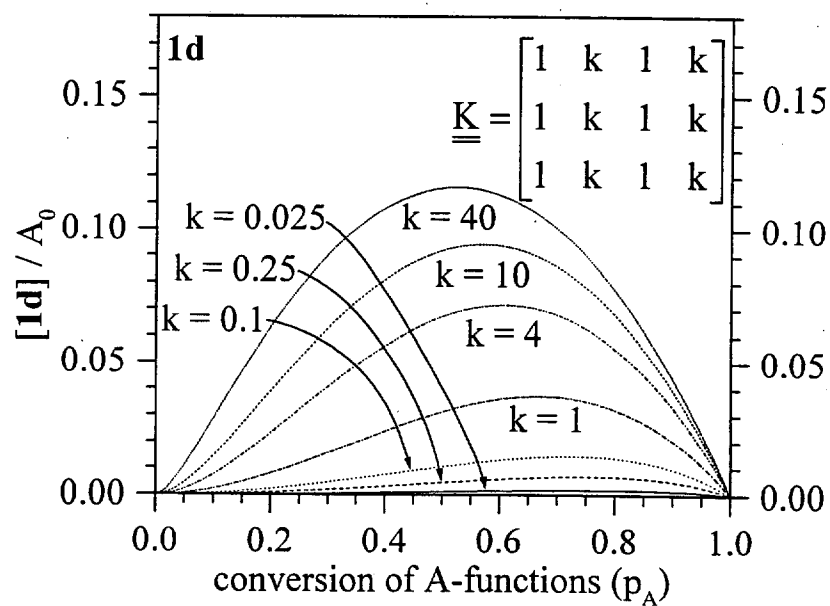


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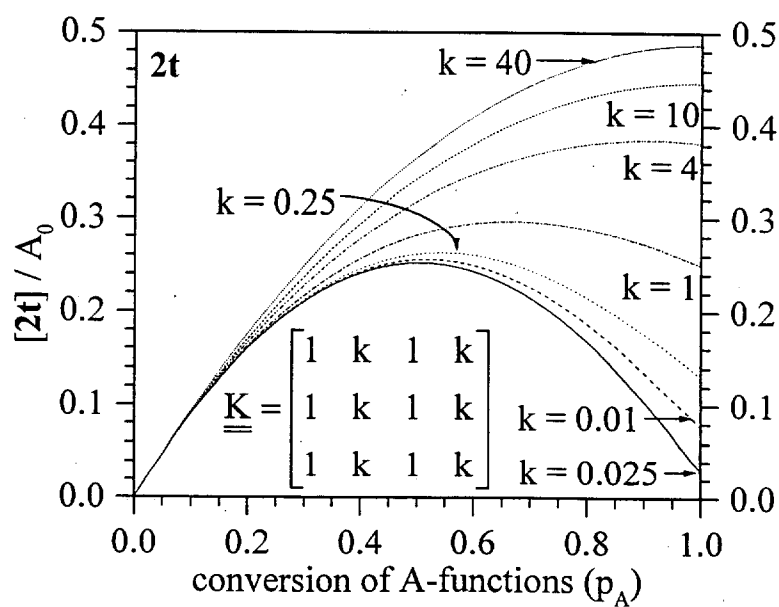


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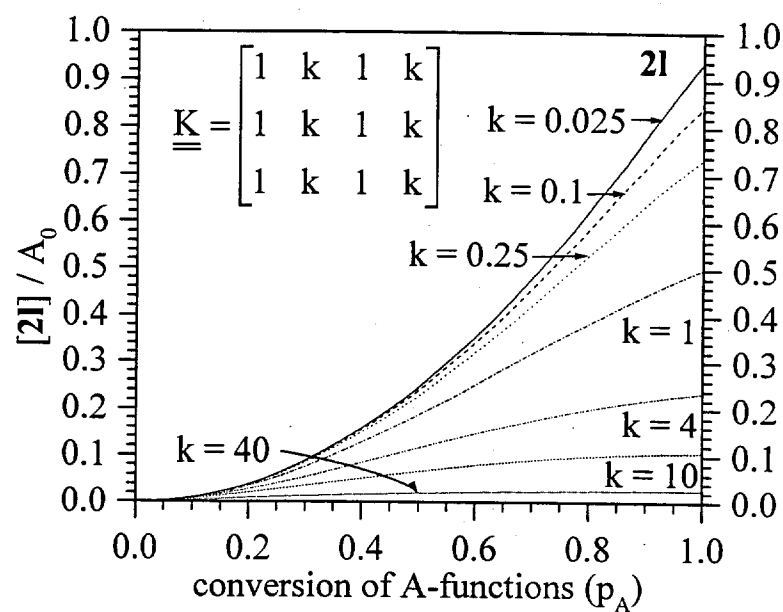


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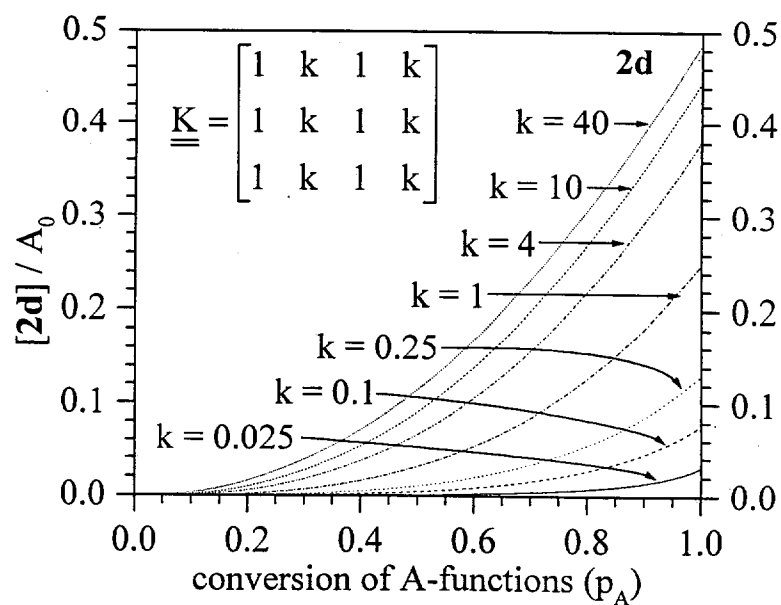


Figure 19:

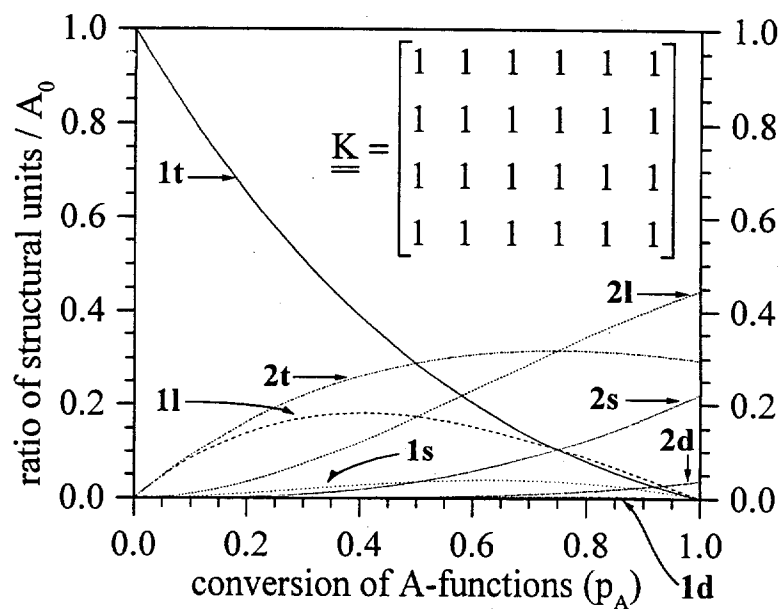


Figure 20:

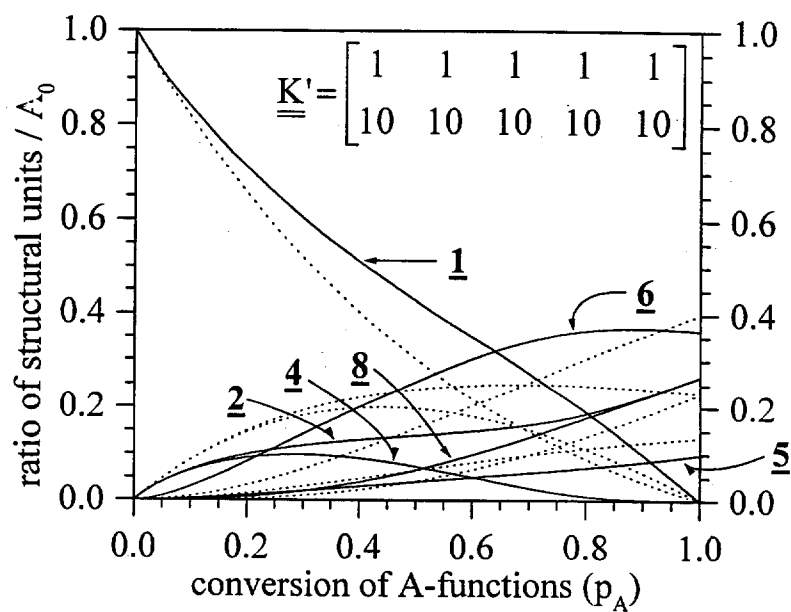


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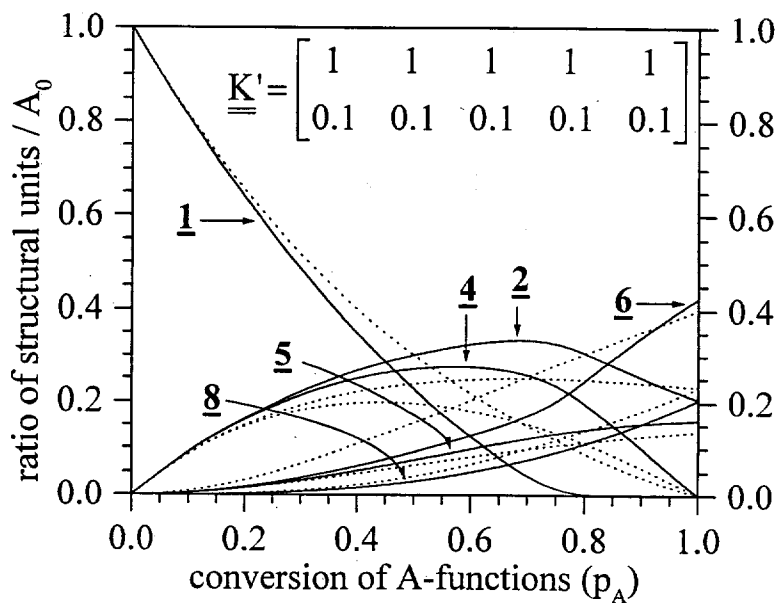


Figure 22:

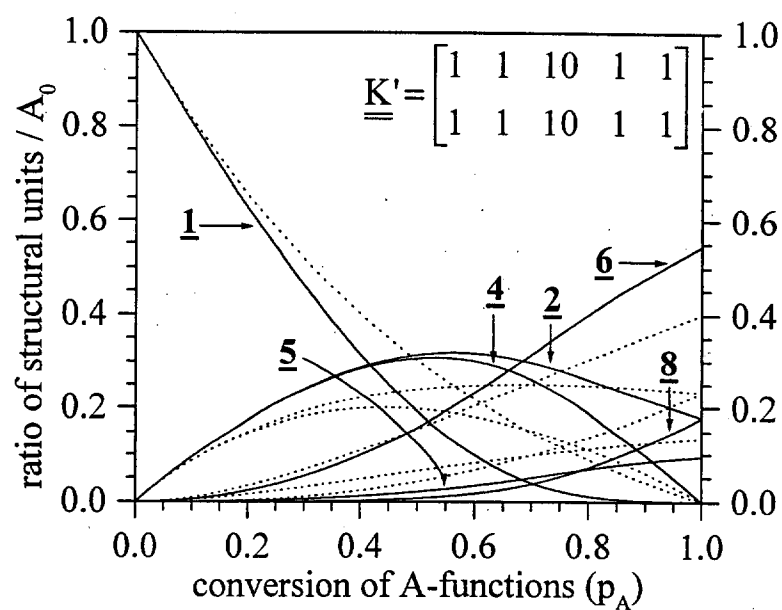


Figure 23:

