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GENERAL EQUATION OF MOLECULAR WEIGHT DISTRIBUTION OF TELOMERIZATION PRODUCTS

M. MODENA and P. PICCARDI

Montecatini Edison S.p.A., Centro Ricerche, Via S. Pietro, 50–20021 Bollate, Milan, Italy

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Abstract—An equation has been obtained, useful to calculate the molecular weight distribution of telomerization products in the general case when the reactivity of telomers is not negligible by comparison with that of telogen. The experimental determination of the required constants is discussed. The equation is tested using data reported by Katsobashvili *et al.* for the system ethylene–iodoethane.

THE MOLECULAR weight distribution of the products formed at any time in a telomerization reaction depends on the telogen/taxogen ratio R and on the chain transfer constants C according to the known(1) equation:

$$F_n = \frac{C_n R}{\prod\limits_{i=1}^{n} (C_i R + 1)} \tag{1}$$

where F_n represents the mole fraction of product containing n monomer units.

However when the telomers are able to react further adding more taxogen molecules (e.g. in the radical addition of ethylene to iodoalkanes or of tetrafluoroethylene to perfluoro-1-iodoalkanes), equation (1) is valid only if the concentration of telomers is negligible by comparison with that of the telogen. Hence equation (1) cannot be used to calculate the distribution of products either at finite conversion or when telomers are initially present.

The limitations of equation (1) arise from its being based on the consideration that only the following reactions govern the distribution of telomers (without taking into account initiation, termination, and eventual secondary reactions).

$$T_0 \cdot + M \xrightarrow{K_{p_0}} T_1 \cdot \tag{2a}$$

$$T_1 \cdot + T_0B \xrightarrow{K_{t_1}} T_1B + T_0 \cdot \tag{2b}$$

$$T_1 \cdot + M \xrightarrow{K_{p_1}} T_2 \cdot \tag{2c}$$

$$T_2 \cdot + T_0B \xrightarrow{K_{t_2}} T_2B + T_0 \cdot \tag{2d}$$

$$T_2 \cdot + M \xrightarrow{K_{p_2}} T_3 \cdot \tag{2e}$$

$$T_n \cdot + T_0B \xrightarrow{K_{t_n}} T_nB + T_0 \cdot \tag{2f}$$

$$T_n \cdot + M \xrightarrow{K_{p_n}} T_{n+1} \cdot \tag{2g}$$

where T_0B = telogen
T_1B, T_2B, etc. = telomers ($n = 1, 2,$ etc.)
M = taxogen
$T_0\cdot$, $T_1\cdot$ = active species (e.g. free radical) derived from T_0B, T_1B, etc.

But, when telogen and telomers have comparable reactivities, the following reactions contribute to telomer formation:

$$T_0\cdot + M \xrightarrow{K_{P_0}} T_1\cdot \tag{3}$$

$$T_1\cdot + T_0B \xrightarrow{K_{t_{1,0}}} T_1B + T_0\cdot \tag{4a}$$

$$T_1\cdot + T_1B \xrightarrow{K_{t_{1,1}}} T_1B + T_1\cdot \tag{4b}$$

$$T_1\cdot + T_2B \xrightarrow{K_{t_{1,2}}} T_1B + T_2\cdot \tag{4c}$$

$$T_1\cdot + T_nB \xrightarrow{K_{t_{1,n}}} T_1B + T_n\cdot \tag{4d}$$

$$T_1\cdot + M \xrightarrow{K_{P_1}} T_2\cdot \tag{5}$$

$$T_2\cdot + T_0B \xrightarrow{K_{t_{2,0}}} T_2B + T_0\cdot \tag{6a}$$

$$T_2\cdot + T_1B \xrightarrow{K_{t_{2,1}}} T_2B + T_1\cdot \tag{6b}$$

$$T_2\cdot + T_2B \xrightarrow{K_{t_{2,2}}} T_2B + T_2\cdot \tag{6c}$$

$$T_2\cdot + T_nB \xrightarrow{K_{t_{2,n}}} T_2B + T_n\cdot \tag{6d}$$

$$T_2\cdot + M \xrightarrow{K_{P_2}} T_3\cdot \text{ etc.} \tag{7}$$

Equations (8) and (9), giving the mole fraction of growing chains originated from T_0B that yield 1:1 product, can be obtained by the same essentially statistical procedure valid in the simpler case.

$$\frac{K_{t_{1,0}}[T_1\cdot][T_0B] + K_{t_{1,2}}[T_1\cdot][T_2B] + \cdots + K_{t_{1,n}}[T_1\cdot][T_nB]}{K_{t_{1,0}}[T_1\cdot][T_0B] + K_{t_{1,2}}[T_1\cdot][T_2B] + \cdots + K_{t_{1,n}}[T_1\cdot][T_nB] + K_{P_1}[T_1\cdot][M]} \tag{8}$$

$$= \frac{C_{1,0}R_0 + C_{1,2}R_2 + \cdots + C_{1,n}R_n}{C_{1,0}R_0 + C_{1,2}R_2 + \cdots + C_{1,n}R_n + 1} \tag{9}$$

where $C_{1,n} = K_{t_{1,n}}/K_{P_1}$; $R_n = [T_nB]/[M]$.

Reaction (4b) does not modify the distribution of products and is balanced by its reverse reaction, therefore $C_{1,1}$ can be assumed to be equal to zero. Hence the products formed from T_0B are

$$T_1B = \frac{\overset{\infty}{\underset{0}{\sum}}{}_n C_{1,n}R_n}{\overset{\infty}{\underset{0}{\sum}}{}_n C_{1,n}R_n + 1} \tag{10a}$$

where $C_{1,1} = 0$

$$T_2B = \frac{\sum_0^\infty{}_n\, C_{2,n}\, R_n}{(\sum_0^\infty{}_n\, C_{1,n}\, R_n + 1)\,(\sum_0^\infty{}_n\, C_{2,n}\, R_n + 1)} \tag{10b}$$

where $C_{2,2} = 0$; etc.

and those formed from T_1B are

$$T_2B = \frac{\sum_0^\infty{}_n\, C_{2,n}\, R_n}{\sum_0^\infty{}_n\, C_{2,n}\, R_n + 1} \tag{11a}$$

where $C_{2,2} = 0$

$$T_3B = \frac{\sum_0^\infty{}_n\, C_{3,n}\, R_n}{(\sum_0^\infty{}_n\, C_{2,n}\, R_n + 1)\,(\sum_0^\infty{}_n\, C_{3,n}\, R_n + 1)} \tag{11b}$$

where $C_{3,3} = 0$; etc.

The composition of the reaction mixture can be obtained by adding, after having taken into account the relative concentrations and reaction rates, all the terms of this kind and by subtracting the converted portions of telogen and telomers, which will be again proportional to concentration and relative reactivity.

Therefore an activity factor f_n must be defined; it is given by the ratio between converted T_nB and the molar fraction of T_0B that would react in the same conditions.

Accordingly, the composition of a mixture, initially containing T_0B, T_1B, T_2B, . . ., T_nB and M, after an infinitesimal conversion α is given by the following equations, where the summations are limited to K terms excluding the telomers present at very low concentration.

$$T_0B' = T_0B - \alpha\, T_0B \tag{12a}$$

$$T_1B' = T_1B - \alpha f_1\, T_1B + \alpha\, T_0B \frac{\sum_0^k{}_n\, C_{1,n}\, R_n}{\sum_0^k{}_n\, C_{1,n}\, R_n + 1} \tag{12b}$$

$$\begin{aligned} T_2B' = T_2B - \alpha f_2\, T_2B + \alpha\, T_0B &\frac{\sum_0^k{}_n\, C_{2,n}\, R_n}{(\sum_0^k{}_n\, C_{1,n}\, R_n + 1)\,(\sum_0^k{}_n\, C_{2,n}\, R_n + 1)} \\ + \alpha f_1 T_1B &\frac{\sum_0^k{}_n\, C_{2,n}\, R_n}{\sum_0^k{}_n\, C_{2,n}\, R_n + 1} \end{aligned} \tag{12c}$$

and in general

$$T_iB' = T_iB - a f_i T_i B + \sum_{0}^{k}{}_n C_{i,n} R_n \cdot \sum_{0}^{i-1}{}_n \frac{a f_n T_n B}{\prod\limits_{j=n+1}^{i} (\sum_{1}^{k}{}_n C_{j,n} R_n + 1)} \tag{13a}$$

$$= T_iB - a f_i T_i B + \frac{\sum_{0}^{k}{}_n C_{i,n} R_n}{\sum_{0}^{k} C_{i,n} R_n + 1} \cdot \sum_{0}^{i-1}{}_n (T_nB - T_nB') \tag{13b}$$

$$M' = M - \sum_{1}^{k}{}_i \left(\sum_{0}^{k}{}_n C_{i,n} R_n\right) \left(\sum_{0}^{i-1}{}_n \frac{(i-n)\, a f_n T_n B}{\prod\limits_{j=n+1}^{i} (\sum_{0}^{k}{}_n C_{j,n} R_n + 1)}\right) \tag{14}$$

By repeating the calculation with sufficiently small conversion increments, the relative concentrations of telomers, taxogen, and telogen are obtained for all possible final conversions and initial telogen and telomer mixtures.

If the reactivity of the telomers is negligible in comparison with that of the telogen, all f_n and $C_{i,n}$ for $n \neq 0$ will be practically zero and the preceding equations will obviously reduce to equation (1) and to other known simple expressions.

The chain transfer constants appearing in equations (13) and (14) can be determined with different series of experiments.

Constants of the family $C_{i,0}$ ($C_{1,0}$, $C_{2,0}$, . . .) are calculated by extrapolating to zero telogen conversion the values obtained in telomerization reactions of M with T_0B as suggested by Katsobashvili *et al.*⁽²⁾

However the dependence of apparent constants on conversion is rather complex, as may be seen from equation (12b), therefore sets of experiments having different initial R_0 values should not, if possible, be treated together.

Following the same procedure, constants of the families $C_{i,1}$ ($C_{2,1}$, $C_{3,1}$, . . .), $C_{i,2}$ ($C_{3,2}$, $C_{4,2}$, . . .) and in general $C_{i,n}$, where $i > n$, are obtained from telomerization reactions of T_1B, T_2B, etc.

From telomerization experiments on $T_{i-1}B$ and T_nB, data can be obtained that allow, after extrapolation to zero conversion, calculation of $C_{i,n}$ when $i < n$. For example, reactions with a mixture of T_0B and T_2B give data that can be used to calculate $C_{1,2}$ according to equation (15)

$$C_{1,2} = \frac{T_1B' - C_{1,0} R_0 (T_0B - T_0B' - T_1B')}{R_2 (T_0B - T_0B' - T_1B')} \tag{15}$$

In this case also, extrapolation to zero conversion gives the true constant.

As stated above, constants $C_{i,n}$, where $i = n$, should be taken as zero as they relate to reactions that do not interfere with product composition.

The activity factors f can be determined by measuring the relative conversions of T_0B, T_1B, T_2B, . . . in the same or parallel experiments. A reliable determination of f factors and chain transfer constants $C_{i,n}$ ($i < n$) requires very careful experiments and precise analysis; however, as reactivity in any homologous series is expected to show no significant variation after the first few terms, the parameters related to higher terms need not be determined but can be estimated by extrapolation.

Table 1. Experimental and calculated data of ethylene telomerization with iodoethane

Telogen conversion		R	(final)	$n = 1$		$n = 2$		$n = 3$		$n = 4$		$n = 5$		$n < 5$	
exptl.	calcd.	exptl.	calcd.	exptl.	calcd.	exptl.	calcd.	exptl.	calcd.	exptl.	calcd.	exptl.	calcd.	exptl.	calcd.
6·7	6·9	0·123	0·116	56·5	55·4	27·22	27·36	10·5	10·8	3·68	4·06	1·33	1·51	0·75	0·89
		0·123		55·0		28·13		10·4		3·67		1·32		0·76	
		0·125		56·16		27·7		10·4		3·66		1·32		0·76	
8·2	8·7	0·125	0·114	56·2	54·81	27·5	27·4	10·5	11·0	3·74	4·2	1·30	1·59	0·76	0·96
		0·127		56·2		27·5		10·5		3·7		1·33		0·67	
		0·127		56·1		27·5		10·6		3·7		1·35		0·75	
14·0	14·0	0·113	0·109	53·55	53·06	28·4	27·6	11·3	11·7	4·4	4·7	1·5	1·8	0·85	1·2
		0·113		53·45		28·6		11·2		4·4		1·5		0·85	
		0·121		53·65		28·3		11·3		4·4		1·5		0·85	

The values in the columns headed with various values of n are mole percentages.

A set of data suitable for testing equation (13) has been reported by Katsobashvili and co-workers.(2,3)

According to the preceding discussion, the chain transfer constants in the ethylene–iodoethane system at 100° have been evaluated again on the basis of the last nine experiments of Ref. 2, which have the same initial telogen/taxogen ratio of 0·123.

The mean squares values are:

$$C_{1,0} = 11{\cdot}0 \pm 0{\cdot}2$$
$$C_{2,0} = 14{\cdot}3 \pm 0{\cdot}3$$
$$C_{3,0} = 14{\cdot}9 \pm 0{\cdot}2$$

The chain transfer constants in the system ethylene-1-iodobutane at 100° from Table 4 of Ref. 4 are:

$$C_{2,1} = 9{\cdot}45$$
$$C_{3,1} = 11{\cdot}3$$
$$C_{4,1} = 12{\cdot}6$$

All the remaining chain transfer constants are set as a first guess equal to 15; an error in these constants is not expected to affect appreciably the final results, as the higher telomers are present at low concentration.

The activity factors are taken equal to 1 since good estimates are not available and very large variations are not expected.

The calculations have been performed on an Univac 1108 computer setting a conversion increment of 0·1 per cent per iteration.

Computed and experimental (from Ref. 2) values collected in Table 1, show a good fit.

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Résumé—On a établi une équation servant à calculer la distribution des masses moléculaires des produits de télomérisation dans le cas général où la réactivité des télomères n'est pas négligeable devant celle du corps télogène. On discute la détermination expérimentale des constantes nécessaires. La validité de l'équation a été testée en utilisant des données rapportées par Katsobashvili *et al.* pour le système éthylène–iodoéthane.

Sommario—E' stata ricavata un'equazione che permette di calcolare la distribuzione di peso molecolare dei prodotti di una reazione di telomerizzazione nel caso generale in cui i telomeri hanno reattività paragonabile a quella del telogeno. Sono discussi i metodi per determinare sperimentalmente le costanti che compaiono in tale equazione. La validità di tale equazione è controllata esemplificando un'applicazione al sistema etilene–iodoetano descritto da Katsobashvili e coll.

Zusammenfassung—Es wurde eine Gleichung aufgestellt, die anwendbar ist auf die Berechnung der Molekulargewichtsverteilung von Telomerisationsprodukten für den allgemeinen Fall, daß die Reaktivität der Telomeren nicht zu vernachlässigen ist gegenüber der des Telogens. Die experimentelle Bestimmung der erforderlichen Konstanten wird diskutiert. Die Gleichung wird getestet mit Werten, die von Katsobashvili *et al.* für das System Äthylen-Jod-äthan mitgeteilt wurden.