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Communications to the Editor

Concerning the Paper by J. J. Gonzâles and K. W. Kehr on "Distribution of Reacted Sequences in Homopolymers"

The paper by Gonzâlez and Kehr[1] considers the derivation of kinetic equations for the probabilities of reacted-unit sequences in the products of functional-group reactions proceeding with neighboring-group effects; i.e., it concerns the theory of macromolecular reactivity. Many American, German, and Russian scientists have worked for many years in the field of the theory of macromolecular reactions. Unfortunately, Gonzâlez and Kehr have ignored many results of these studies.

For example, in the introduction to their paper, Gonzâlez and Kehr mention that it is considerably easier to describe the distribution of unreacted units than that of reacted units, as there exists the independence of finding any sequences to both sides of the diad AA. Here the authors refer only to their own papers of 1974–1977, although this fact was proved much earlier by many authors (ref 2, 3, 4, and 5).

Moreover, eq 1 of Gonzâlez and Kehr

$$q_l(t) = q_2(t)\exp\{-k(l-2)t\} \tag{1}$$

is immediately derived from the well-known equation of McQuarrie[2]

$$P(\mathrm{A}_j) = e^{-jk_0t}\exp\left\{2(k_0-k_1)\left[t-\frac{1-e^{-k_0t}}{k_0}\right]\right\} \tag{2}$$

which is valid for all $j \geq 2$, and therefore

$$P(\mathrm{A}_l) = P(\mathrm{A}_2)\exp\{-(l-2)k_0t\}$$

As $P(\mathrm{BA}_lB)$ (in the McQuarrie's denotion) is identical with q_l (in the Gonzâlez and Kehr denotion)

$$\begin{aligned} q_l = P(\mathrm{BA}_l\mathrm{B}) = P(\mathrm{A}_l) - 2P(\mathrm{A}_{l+1}) + P(\mathrm{A}_{l+2}) = \\ P(\mathrm{A}_2)e^{-(l-2)k_0t} - 2P(\mathrm{A}_2)e^{-(l-1)k_0t} + P(\mathrm{A}_2)e^{-lk_0t} = \\ e^{-(l-2)k_0t}[P(\mathrm{A}_2) - 2P(\mathrm{A}_3) + P(\mathrm{A}_4)] = P(\mathrm{BA}_2\mathrm{B})e^{-(l-2)k_0t} \end{aligned} \tag{3}$$

which is identical with eq 1 ($k = k_0$).

In part II Gonzâlez and Kehr introduce the assumption about the uniform distribution of reacted and unreacted sequences. It should be pointed out that for the first time this hypothesis was proposed by Klesper in 1971[4] (Gonzâlez and Kehr do not refer to this paper) and its validity was confirmed by Monte-Carlo calculations. On this assumption, Gonzâlez and Kehr derive the kinetic equations for the probabilities of reacted sequences. Here they exactly repeat the consideration earlier proposed and published by Platê, Litmanovich, Noah, et al.[6-9] in 1971–1974. Unfortunately, in this case Gonzâlez and Kehr again do not give the corresponding references. The final results obtained by Gonzâlez and Kehr are identical with those published earlier.[6-8] Taking into consideration the above-mentioned facts, the affirmation of the authors[1] ". . . to our knowledge nobody has yet been able to find the distribution of sequences of reacted units" seems rather surprising.

The only difference in the approach of Gonzâlez and Kehr consists in adoption of four rate constants instead of the usual three rate constants for reactions with neighboring-group effects: k_0, k_1, and k_2 (corresponding to the number of reacted neighbors). The constants of Gonzâlez and Kehr are $k = k_0$, $k(c) = k_2$, and two different constants $k(a)$ and $k(\tilde{a})$ for the substitution of functional groups with the reacted neighbors on the left and on the right of the unit under consideration. One can easily show by letting $k(a) = k(\tilde{a}) = k_1$ that eq 8 of Gonzâlez and Kehr is identical with eq 32 of ref 7. As $r_1(t) = P(\mathrm{ABA})$, $q_1(t)$

$$\mathrm{d}r_1(t)/\mathrm{d}t = -2kcr_1(t)q_1(t)/\rho(t) - k(a+\tilde{a})r_1(t)[1-q_1(t)/\rho(t)] + k\sum_{m=3}^{\infty}(m-2)q_m(t)$$

$= P(\mathrm{BAB})$, and $\rho(t) = P(\mathrm{AB})$, and with the aid of the relationships between the probabilities of j clusters and j tuplets derived by McQuarrie,[2]

$$\sum_{m=3}^{\infty}(m-2)q_m(t) = P(\mathrm{A}_3) \tag{4}$$

eq 8 of Gonzâlez and Kehr can be transformed into

$$\mathrm{d}P(\mathrm{ABA})/\mathrm{d}t = -2k_2P(\mathrm{ABA})P(\mathrm{BAB})/P(\mathrm{AB}) - 2k_1P(\mathrm{ABA})\left[1-\frac{P(\mathrm{BAB})}{P(\mathrm{AB})}\right] + k_0P(\mathrm{A}_3) \tag{5}$$

and with

$$P(\mathrm{AB}) - P(\mathrm{BAB}) = P(\mathrm{A}_2\mathrm{B}) \tag{6}$$

$$\mathrm{d}P(\mathrm{ABA})/\mathrm{d}t = k_0P(\mathrm{A}_3) - 2P(\mathrm{ABA})\frac{k_2P(\mathrm{BAB}) + k_1P(\mathrm{A}_2\mathrm{B})}{P(\mathrm{AB})} \tag{7}$$

which exactly coincides with eq 32 of ref 8.

By the same pathway, eq 9 of Gonzâlez and Kehr can be transformed into eq 36 of ref 8:

$$\begin{aligned} \mathrm{d}r_l/\mathrm{d}t = \mathrm{d}P(\mathrm{AB}_l\mathrm{A})/\mathrm{d}t = \\ -2k_2P(\mathrm{AB}_l\mathrm{A})P(\mathrm{BAB})/P(\mathrm{AB}) - 2k_1P(\mathrm{AB}_l\mathrm{A}) \times \\ [1 - P(\mathrm{BAB})/P(\mathrm{AB})] + \\ k_2P(\mathrm{BAB})\{\sum_{n=1}^{l-2}P(\mathrm{AB}_n\mathrm{A})P(\mathrm{AB}_{l-n-1}\mathrm{A})\}/P(\mathrm{AB})^2 + \\ 2k_1[1 - P(\mathrm{BAB})/P(\mathrm{AB})]P(\mathrm{AB}_{l-1}\mathrm{A}) \end{aligned} \tag{8}$$

Taking relationship 6 into account, one can obtain

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$$dP(AB_lA)/dt = 2k_1P(AB_{l-1}A)\frac{P(A_2B)}{P(AB)} - 2P(AB_lA)\frac{k_1P(A_2B) + k_2P(BAB)}{P(AB)} + \frac{k_2P(BAB)}{[P(AB)]^2}\sum_{n=1}^{l-2}P(AB_nA)P(AB_{l-n-1}A) \quad (9)$$

This equation is identical with eq 36 of ref 8 for $l \geq 2$.

It should be pointed out that not only the final equations of González and Kehr but also the approach to their derivation is identical with that proposed by Platé, Litmanovich, and Noah.[6-8] However, this approach is based on the assumption about the random distribution of the reacted and unreacted sequences and therefore its accuracy should be proved. Such proof was accomplished in ref 6–8 by comparison of the results of this approach (in ref 6–8 it is called the "B approximation") with those of the exact solution. The good agreement between these two approaches permits application of this approximation to the calculation of the distribution of reacted units for the wide range of kinetic constants.

The absence of the aforementioned references in González's article to the papers of German and Russian authors published in such widely known international journals as "Die Makromolekulare Chemie" and "Journal of Polymer Science" is deplored.

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Reply to the Criticism by N. A. Platé, A. D. Litmanovich, and O. V. Noah

It must be a common experience for many Russian scientists that their publications in Russian are overlooked by English-oriented colleagues. It must have been even more disappointing for Platé et al. that their beautiful work[1-3] which, in part, has been published in American journals was bypassed by us.[4] In fact, the basic claim by Platé and co-workers that the differential equations describing the nearest-neighbor kinetics of reacted sequences in homopolymers (our eq 8 and 9[4]) had been derived earlier by them[3] is correct. Concerning the assumption of uniform distribution of reacted and unreacted sequences along the chain, the oldest reference known to us was Felderhof.[5] But it is correct that this hypothesis was formulated earlier by Klesper et al.[6,7] We offer our regrets to Dr. Platé et al. and to Dr. Klesper et al. for our previous ignorance and oversight of their works.

Such unfortunate duplications of prior work have happened many times in the course of the history of science. Without trying to reduce our responsibility in this particular case, we would like to mention that a number of polymer scientists did hear us lecture or did read our work before publication and that our manuscript was reviewed by three referees, one of them being extremely critical of our contentions. But never did anybody mention the work by Klesper et al. and by Platé et al. in this connection. We conclude that the work by Klesper and Platé and their respective co-workers is not so widely known as it deserves. It is our hope that the present communication may compensate for the aggrievance by helping to make the important work by our German and Russian colleagues better known.

Although our claim to be the first in deriving the kinetics of reacted sequences turns out to be incorrect, it should be noted that our article contains some new results, as for example the exact formal solution of these equations and some applications. For instance, we predict the outcome of an experiment on amylose. The theoretical extent of the reaction for first and second periodate oxidation of amylose has been shown earlier to be in good agreement with experiments (ref 11 and the first part of ref 12 from our paper[4]).

There remains one point, though. Platé et al. argue that our equation

$$q_l(t) = q_2(t)\exp\{-k(l-2)t\} \quad (1)$$

follows from previous work. We agree. Indeed, at the beginning of our introduction we explicitly stated[4] that both the extent of reaction and the statistics of unreacted sequences for homopolymers were well-known and we did refer to McQuarrie et al.[8] and to Silberberg and Simha.[9] In addition, we referred to the valuable work by Boucher,[10] whose reference we miss in the papers by Platé et al.

Our point in referring to the principle of independence of unreacted neighbors, first given by one of us (J.J.G.) and Hemmer,[11-13] was to place the statistics of unreacted units and the extent of reaction for irreversible reactions with nearest-neighbor effects in the most powerful frame known to us. To help convey our point, we show briefly why this is so: It is essential to distinguish between terminal units, for example, a left-terminal unit, A—···· (the dots mean units in unspecified reaction states A or B), and nonterminal ones, such as ····—A—····. González and Hemmer's principle of independence of unreacted neighbors[11-13] states that for any time t

$$P(\mathbf{Y}\text{-A-A-}\mathbf{Z}) = P(\mathbf{Y}\text{-A})P(\text{A-}\mathbf{Z}) \quad (2)$$

Here, **Y**-A-A-**Z** is a complete chain having between the segments **Y** and **Z** two neighboring unreacted units. **Y** and **Z** are sequences of A's and B's completely describing the state of reaction of the chain to the left and right of the diad -A-A-. Notice that the probabilities on the right-hand side of eq 2 refer to half-chains. This is why Platé and co-worker's wording "there exists the independence of finding any sequences to both sides of the diad AA" is only an incomplete characterization of our principle. The introduction of half-chain probabilities $P(\mathbf{Y}\text{-A})$ and $P(\text{A-}\mathbf{Z})$ is a crucial step, as will be seen in a moment.

González and Hemmer's work[11-13] and González and Kehr's eq[4] 8–11 may be summarized as follows:

(I) *All* quantities in the irreversible kinetics of homopolymers with nearest-neighbor effects can be expressed in terms of the probabilities that the terminal units in half-chains are unreacted: $\nu(t) = P(\text{A}—\cdots\cdot)$ and $\tilde{\nu}(t) =$

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