$$\mathrm{d}P(\mathrm{AB}_l\mathrm{A})/\mathrm{d}t = 2k_1P(\mathrm{AB}_{l-1}\mathrm{A})\frac{P(\mathrm{A_2B})}{P(\mathrm{AB})} - 2P(\mathrm{AB}_l\mathrm{A})\frac{k_1P(\mathrm{A_2B}) + k_2P(\mathrm{BAB})}{P(\mathrm{AB})} + \frac{k_2P(\mathrm{BAB})}{[P(\mathrm{AB})]^2}\sum_{n=1}^{l-2}P(\mathrm{AB}_n\mathrm{A})P(\mathrm{AB}_{l-n-1}\mathrm{A}) \quad (9)$$

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: $\nu(t) = P(\mathrm{A}{-}\cdots)$ and $\tilde{\nu}(t) =$

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$P(\cdots\text{–A})$. These probabilities are given by simple expressions satisfying an elementary differential equation. For instance, for infinitely long chains and with $\tau = kt$:

$$d\nu(\tau)/d\tau = -e^{-\tau}\nu(\tau) - a(1 - e^{-\tau})\nu(\tau) \tag{3}$$

with the unique solution with $\nu(0) = 1$:

$$\nu(\tau) = \exp\{-a\tau - (1 - a)(1 - e^{-\tau})\} \tag{4a}$$

Similarly:

$$\tilde{\nu}(\tau) = \exp\{-\tilde{a}\tau - (1 - \tilde{a})(1 - e^{-\tau})\} \tag{4b}$$

While the kinetics of irreversible reactions with nearest-neighbor effects on *homopolymers* has been extensively studied by many authors since 1962, the more general and important problem of such reactions on *copolymers* is a more difficult mathematical problem, which, to our knowledge, was first solved by González and Hemmer.[11,12]

(II) The methods mentioned in statement I can be easily generalized to solve the kinetics of irreversible reactions with nearest-neighbor effects on copolymers.

Actually, González and Hemmer only applied their method to the general case of reactions of (second order Markovian) copolymers[11,12] and to the case of repeated reactions on homopolymers.[13] The case at issue, the first reaction of a homopolymer, is a special case of the two more general problems just mentioned.

A method which both explains and solves what other approaches do (first reaction on homopolymers) and also explains and solves problems where those other approaches fail is clearly superior. This is why we chose to word the introduction of our paper[4] as we did. The new references supplied by Dr. Platé and co-workers do not appear to change the situation in this respect.

Finally, we list the results announced in statement I. The reader can either derive them by straightforward application of eq 2 or he may specialize our results[11-13] to the case in question. For $l \geq 2$:

$$q_l(\tau) = (1 - e^{-\tau})^2\nu(\tau)\tilde{\nu}(\tau)\exp[-(l - 2)\tau] \tag{5}$$

For $l = 1$

$$q_1(\tau) = 1 - y(\tau) - (2 - e^{-\tau})\nu(\tau)\tilde{\nu}(\tau) \tag{6}$$

where the extent of reaction is given by

$$y(\tau) = 1 - e^{-c\tau}\left\{1 - (1 - a - \tilde{a} + c)\int_0^\tau ds\, e^{(c-1)s}\nu(s)\tilde{\nu}(s) - (a + \tilde{a} - 2c)\int_0^\tau ds\, e^{cs}\nu(s)\tilde{\nu}(s)\right\} \tag{7}$$

By consulting our solution of the differential equations for the densities of reacted sequences,[4] the reader may convince himself that the r_l's can all be expressed in terms of the q_l's and, hence, in terms of ν and $\tilde{\nu}$.

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Annealing-Induced Changes in Orientation and Mobility in the Noncrystalline Region of Drawn Linear Polyethylene: A ^{13}C NMR Study

Solid state ^{13}C NMR in organic systems[1,2] holds out the promise of simultaneously studying molecular mobility and orientation. Molecular mobility influences relaxation behavior[3] which, in turn, can be studied as a function of resonance position. The resonance frequency, ν_{res}, of a given carbon is related to molecular orientation through the equation

$$\nu_{\text{res}} = (2\pi)^{-1}\gamma_C B_0(1 - \lambda_{xx}{}^2\sigma_{xx} - \lambda_{yy}{}^2\sigma_{yy} - \lambda_{zz}{}^2\sigma_{zz}) \tag{1}$$

where γ_C is the gyromagnetic ratio, B_0 is the applied magnetic field, and the λ_{ii} are the direction cosines of the angle between B_0 and the direction corresponding to the ith principal value, σ_{ii}, of the chemical shift tensor of the carbon considered. Equation 1 is valid when the ^{13}C signal is obtained in the presence of high-power proton decoupling[1] and in the absence of magic angle sample spinning.[4]

Preliminary results on the changes in orientation and mobility in the *noncrystalline* component (NCC) of drawn linear polyethylene (LPE) are presented here as a function of annealing temperature for a single cold drawn sample having a nominal draw ratio of 15. The characterization of the noncrystalline region of drawn LPE is interesting from an engineering point of view because this region connects the strong, oriented crystalline domains, thereby playing a key role in determining the modulus.

For LPE the methylene chemical shift tensor components and their assignments have been determined.[5-7] With respect to external tetramethylsilane (Me_4Si) as a reference, σ_{xx} is 51.4 ± 1.3 ppm and is assigned to the direction parallel to the intramethylene H–H vector, σ_{yy} is 38.9 ± 1.3 ppm with a direction parallel to the H–C–H angle bisector, and σ_{zz} is 12.9 ± 1.3 ppm and is parallel to the chain axis. Figure 1 shows two ^{13}C spectra obtained by spin-lock cross-polarization (SLCP).[1] These spectra contain contributions from both the NCC and the crystalline component (CC). The top spectrum is that of polycrystalline LPE, while the lower spectrum is the drawn LPE with B_0 parallel to the drawing direction. The polycrystalline line shape agrees qualitatively with the shape expected from theory[8] for a purely crystalline substance. The spectrum of the drawn LPE is centered at 12.9 ppm, indicating that most of the chain segments are aligned in the drawing direction; however, an amplification (×8) of this spectrum shows that some of the chain segments have not been well oriented by drawing and that the time averaged segment orientation seen locally at these