# Notes

## Determination of Relative Rate Constants of Hydrolysis of Poly[(dimethylamino)ethyl methacrylate]

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In a previous paper,[1] we reported that copolymers of (dimethylamino)ethyl methacrylate (DMAEM) and methacrylic acid (MA) have different triad distributions, depending on the method of preparation: radical-initiated copolymerization, acidic hydrolysis, or basic hydrolysis of poly(DMAEM). Triad distributions for the copolymers were obtained from the ester carbonyl and ionized acid $^{13}C$ NMR resonances, as illustrated in Figure 1.

These data make possible the calculation of the relative rate constants $K_1$ and $K_2$ of poly(DMAEM) hydrolysis, which are defined as follows: Let us designate $k_0$, $k_1$, and $k_2$, respectively, as the absolute rate constants of the reaction of hydrolysis of the B-centered triads BBB, $\overline{BBA}$, and ABA, where B is the (dimethylamino)ethyl methacrylate unit and A is the methacrylic acid unit, the bar indicating that this sequence and its reverse must be taken into consideration. The absolute rate constant determination requires a knowledge of the kinetic curve and cannot be obtained from the triad data only. The relative rate constants $K_1$ and $K_2$ are $K_1 = k_1/k_0$ and $K_2 = k_2/k_0$.

The first attempt at this calculation was made by Klesper,[2] who found the hydrolysis of poly(methyl methacrylate) (poly(MMA)) by concentrated sulfuric acid to be random by simple graphical comparison of the experimental triad composition with the theoretical curves for a random distribution. However, a two-step hydrolysis of poly(MMA) in basic medium gives a copolymer with a blocklike character.[3]

The calculation of the sequence distribution can be carried out by simulation of the reaction with selected rate constants.[4-6] Then the result of the computer simulation can be used for the determination of the relative rate constants by the curve-fitting procedure[5] that was applied to the hydrolysis of poly(MMA) in a dioxane/methanol/KOH mixture at 85 °C. The copolymer was found to be predominantly alternating. However, the same method applied to copolymers obtained by hydrolysis of poly(MMA) in pyridine shows that a moderately blocklike compositional statistics prevails.[7]

A graphical method for the determination of $K_1$ and $K_2$ from triad distribution data was proposed by Klesper, Strasilla, and Barth.[8] This method applied to the hydrolysis of poly(MMA) by KOH in water at 145 °C gives for $K_1$ and $K_2$ values of 0.18 and 0.10, which indicates an alternating tendency. Another graphical method, using triangular coordinates was proposed for calculating $K_1$ and $K_2$.[9] A computer method was proposed by Bauer[10] using the predictor–corrector approximation for the integration of the differential equation of kinetics. The triad distribution is obtained from the rate constants, with a very good approximation (SEQDIST), and the relative rate constants are obtained from the triad distribution data (RATEFIND).

The purpose of this note is to calculate the relative rate constants of hydrolysis of poly(DMAEM) in acidic or basic media from our triad distribution data by three methods, (a) Bauer's method, (b) Klesper's procedure (modified), and (c) the curve-fitting procedure, and to discuss the results. We must recall the conditions of hydrolysis:[11] (i) in acidic medium, the reaction was carried out in concentrated sulfuric acid at 60 °C; (ii) in basic medium, the reaction was carried out in a 2-propanol/water/KOH mixture at 80 °C (boiling point of the mixture). The two series of copolymers have a predominantly blocklike character. The alternating character $\theta$, defined by

$$\theta = F_{\overline{AB}}/2F_AF_B = (F_{\overline{AAB}} + 2F_{BAB})/2F_AF_B$$

where $F_{XX...}$, the probability of finding the sequence XX..., is between 0.5 and 1 for all the copolymers. This means that an increase of reactivity is observed when a neighboring group is an acid unit, and so we find $K_1 > 1$.

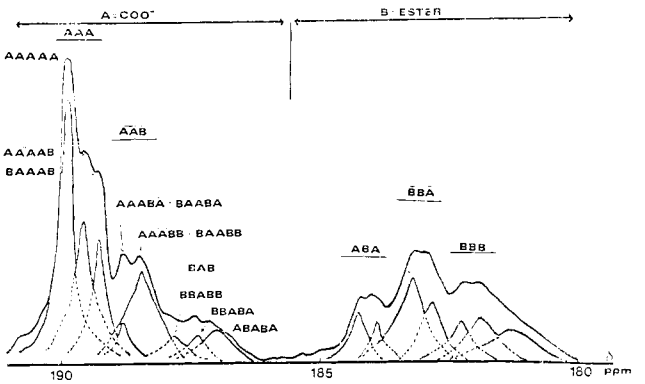


**Figure 1.** Example of resolution and interpretation of an expanded $^{13}C$ NMR spectrum: sample A4 (% A = 69). Details of deconvolution.

Table I
Relative Rate Constants of Hydrolysis

| procedure | acidic hydrolysis | | basic hydrolysis | |
|---|---|---|---|---|
| | $K_1$ | $K_2$ | $K_1$ | $K_2$ |
| a[a] | $0 < K_1 < 7.3$ | $0 < K_2 < 0.5$ | $1.3 < K_1 < 8$ | $0 < K_2 < 1.2$ |
| b[b] | 1.7 | 3.5 | 8 | 1.2 |
| c[c] | 6 | 6 | 8 | 0.2 |

[a] Bauer's single datum point procedure. [b] Klesper's procedure (modified). [c] Curve-fitting procedure.

The use of Bauer's program RATEFIND can give $K_1$ and $K_2$ from the triad distribution data, but the absolute error in the triad data, which is at least 0.01 after deconvolution of the $^{13}C$ NMR spectra, produces a relative error in $K_1$ and $K_2$ that can exceed 100%. As the values of $K_1$ and $K_2$ are obtained from a single datum point, the results are broadly dispersed. The graphical method of Klesper et al.[8] gives better results when data for several copolymers with different degrees of hydrolysis are available. A modification of this method, which leads to a simplification of the operations, was made by transformation of eq 15 of ref 8 in such way that $K_1$ and $K_2$ can be obtained by a linear regression.[12] All results are collected in Table I.

Finally, the curve-fitting procedure[5] was applied using the triads AAA, which are the most accurately measured. The theoretical curves are obtained with Bauer's program SEQDIST.[10] The best values of $K_1$ and $K_2$ that fit the triad

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Table II
Triad Molar Fractions Calculated with the Best Values of $K_1$ and $K_2$ Compared with the Experimental Data

| | | A-centered triad | | | B-centered triad | | |
|---|---|---|---|---|---|---|---|
| | | $F_{AAA}$ | $F_{\overline{AAB}}$ | $F_{BAB}$ | $F_{ABA}$ | $F_{\overline{BBA}}$ | $F_{ABA}$ |
| $F_A = 0.60, K_1 = 6, K_2 = 6$[a] | calcd | 0.353 | 0.222 | 0.025 | 0.055 | 0.162 | 0.183 |
| | exptl | 0.32 | 0.22 | 0.06 | 0.08 | 0.17 | 0.15 |
| $F_A = 0.75, K_1 = 8, K_2 = 0.2$[b] | calcd | 0.398 | 0.326 | 0.026 | 0.165 | 0.050 | 0.035 |
| | exptl | 0.42 | 0.28 | 0.05 | 0.15 | 0.07 | 0.03 |

[a] Acidic hydrolysis. [b] Basic hydrolysis.

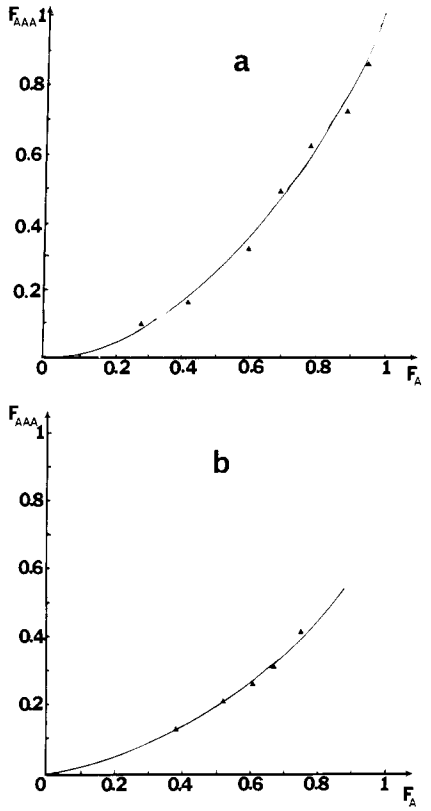



**Figure 2.** Curve-fitting procedure for determination of the relative rate constants $K_1$ and $K_2$ of hydrolysis. (a) Reaction in concentrated $H_2SO_4$: (▲) experimental points; (—) theoretical probabilities of triad AAA taking $K_1 = K_2 = 6$ (calculated with the SEQDIST program). (b) Reaction in 2-propanol/water/KOH mixture: (▲) experimental points; (—) theoretical probabilities of triad AAA taking $K_1 = 8$ and $K_2 = 0.2$ (calculated with the SEQDIST program).

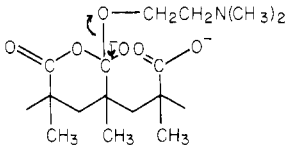
probabilities are shown in Table I (Figure 2). The theoretical values of the alternating character $\theta$ are also between 0.5 and 1.

The differences observed in the constants are due to the following:

(1) The conditions of the reactions were not chosen for a kinetic study. The purpose of these reactions was to prepare polyampholytes with different sequence distributions. In acidic medium as in basic medium, the reaction was first heterogeneous and then became homogeneous. This can modify the rate constants. The temperature was not kept absolutely constant.

(2) Klesper's procedure (modified) requires the B-centered triad data, which are less accurate due to the poorer resolution of the $^{13}C$ NMR pattern of the ester carbon. Table II gives an example for each kind of hydrolysis (acidic and basic) of the triad molar fractions calculated with the best values of $K_1$ and $K_2$ (from Table I), using the program SEQDIST, compared with the experimental data. The agreement is quite satisfactory, taking into account the errors due to the deconvolution method.

Scheme I




In conclusion, the activating effect of the neighboring carboxylic units is confirmed in acidic as well in basic media, as was determined in the past by kinetic studies of the hydrolysis of poly(MMA).[13] However, in the case of basic hydrolysis, the presence of two neighboring acid units (triad ABA) seems to slow down the hydrolysis of the ester unit, probably because the formation of the six-membered cyclic intermediate, as Morawetz et al.[14] have suggested, is more difficult due to the negative potential of the second ionized acid unit (Scheme I).

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## References and Notes

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## Preparation of Poly(styrene-*g*-phenyltrimethylenephosphine oxide) and Its Chelating Properties

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We recently reported that a five-membered deoxophostone (1) was polymerized by a cationic initiator via ring

 