

## **Kinetic consequences of carbocationic grafting and blocking *from* and *onto*\***

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### Summary

Kinetic consequences of cationic grafting (or blocking) *onto* and *from* have been derived by assuming the operational presence of these two mechanisms. It has been found that high grafting (or blocking) efficiencies ( $f$ ) cannot be achieved by the *onto* process with polymerization systems in which termination leading to homopolymer occurs. Also,  $f$  decreases with increasing monomer conversion and rapidly so near 100% conversion in grafting or blocking *onto*. Consequently, efficient carbocationic grafting or blocking is readily explained by grafting or blocking *from* rather than by grafting or blocking *onto*.

### Introduction

Considerable progress has been made in the field of carbocationic polymerization during the last two decades and much of this progress is due to a better understanding of the elementary processes, i.e., initiation, propagation, chain transfer and termination, of such polymerizations (1,2). These developments have also led to control of elementary events, a prerequisite for macromolecular engineering. Indeed, many novel useful polymers, e.g., sequential graft and block copolymers, telechelic polymers, macromonomers, and modified polymers, have been synthesized by carbocationic techniques in recent years (for reviews see e.g. (1-5)).

Cationic grafting and blocking methods are of wide interest in research and development laboratories worldwide. Although numerous new sequential copolymers have been synthesized in the course of these studies (see e.g. (1,6)), controversial interpretations still exist in regard to the mechanism of these syntheses. Two alternative pathways have been suggested, grafting (or blocking) *from* (1,6) and grafting (or blocking) *onto* (7), and polemic articles (8,9) arguing for and against these mechanistic propositions have appeared.

This paper briefly summarizes key features of grafting (or blocking) *from* and *onto*, and derives kinetic consequences that may lead to a better understanding of these processes and stimulate further research in this area.

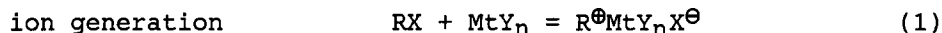
### Grafting and Blocking From

As a consequence of systematic research Kennedy and associates have found that organic halides (RX) containing

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labile halogens (tertiary, allylic, benzylic) in conjunction with suitable Friedel-Crafts acids ( $MtY_n$ ), like organoaluminums,  $BCl_3$ ,  $TiCl_4$ ,  $SnCl_4$ , etc. are excellent cationic initiators (for a comprehensive review see (1)). Initiation by these combinations is visualized to occur in two steps, ion generation followed by cationation of the monomer (1):



where M denotes a cationically polymerizable monomer. Propagation by subsequent monomer addition gives high molecular weight polymer. In the absence of protic initiation by protogenic impurities (e.g.,  $H_2O$ ) controlled initiation can be achieved leading to R head groups.

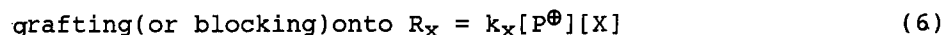
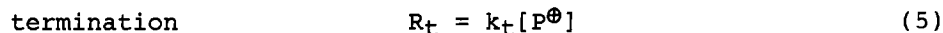
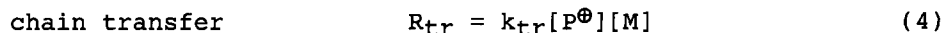
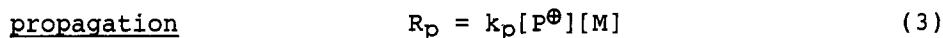
In line with this mechanism, graft copolymers can be prepared by the use of functional polymers containing labile halogens along the chain (1,6,8). Similarly, block copolymers can be synthesized by the use of polymeric initiators containing labile halogens at the chain ends (1,8). The synthesis of sequential copolymers can be visualized by equations 1 and 2, where R is a polymer chain. These processes are termed grafting from and blocking from to emphasize initiation of the second polymer sequence (graft or block) by the macrohalide precursor.

#### Grafting and Blocking Onto

An alternative proposal according to which cationic grafting and/or blocking of olefins in the presence of Friedel-Crafts acids can occur by an onto process has been suggested by Gandini and Cheradame (7,9). By this mechanism propagating chains react with added macromolecules having specific sites along the chain (grafting onto) or at the chain ends (blocking onto). These processes are regarded as electrophilic alkylation by the growing polymeric cation of specific sites (e.g., unsaturations or aromatic rings).

#### Kinetic Considerations

Assuming propagation, chain transfer to monomer, termination and grafting (or blocking) onto a growing chain ( $P^{\oplus}$ ) in solution, the rate equations are as follows:



where  $k_x$ ,  $k_p$ ,  $k_{tr}$ , and  $k_t$  are the rate constants of grafting (or blocking) onto, propagation, chain transfer to monomer, and termination, respectively, and the concentration of the specific sites capable for grafting (or blocking) onto and the monomer are denoted by  $[X]$  and  $[M]$ .

The probability of grafting (or blocking) onto (p) is given by

$$p = \frac{R_x}{R_x + R_p + R_{tr} + R_t} \quad (7)$$

Substituting equations 3-6 into equation 7

$$p = \frac{k_x[P^\oplus][X]}{k_x[P^\oplus][X] + k_p[P^\oplus][M] + k_{tr}[P^\oplus][M] + k_t[P^\oplus]} \quad (8)$$

and dividing by  $k_x[P^\oplus][X]$ ,

$$p = \frac{1}{1 + \frac{k_p}{k_x} \frac{[M]}{[X]} + \frac{k_{tr}}{k_x} \frac{[M]}{[X]} + \frac{k_t}{k_x[X]}} \quad (9)$$

Thus the probability of grafting (or blocking) onto is determined by the ratio of rate constants ( $k_p/k_x$ ,  $k_{tr}/k_x$ ,  $k_t/k_x$ ), by the ratio of  $[M]/[X]$ , and by the value of  $[X]$ .

At low conversions  $[M] \gg [X]$ . Since the sites capable for grafting (or blocking) onto are located on macromolecules, steric compression will affect the rates of these processes. Hence, the rate constant ( $k_x$ ) for a reaction between a polymer and a growing chain is expected to be low as compared to  $k_p$ , the rate constant for the reaction between the growing chain and monomer, i.e.,  $k_p \gg k_x$ . Since  $k_p$  is higher than  $k_{tr}$  and  $k_t$  by orders of magnitudes,  $k_x$  is expected to be in the range of  $k_{tr}$  and  $k_t$ . Evidently, the probability of grafting (or blocking) onto is rather low at low monomer conversions, i.e., besides propagation the growing chains will transfer or terminate rather than effect grafting (or blocking) onto. Thus at low conversions effective grafting or blocking is readily explained by grafting or blocking from.

This scenario can be illustrated by a model blocking experiment in which a 5% solution of a polymer having  $M_n = 50,000$  and containing one specific terminus capable of blocking onto is subjected to blocking. Let  $[M] = 1$  mol/liter, and since  $[X] = 10^{-3}$  mol/liter, the initial probability of blocking onto is

$$p = \frac{1}{1 + 1000 \frac{k_p}{k_x} + 1000 \frac{k_{tr}}{k_x} + 1000 \frac{k_t}{k_x}} \quad (10)$$

Let  $k_{tr}$  and  $k_t$  be in the same range, and these rate constants be relatively low as compared to  $k_p$ , i.e.,  $k_p = 1000 k_{tr} = 1000 k_t$ . Considering the probability of chain transfer ( $p_{tr}$ ) and termination ( $p_t$ ) shown by equations 11 and 12, a comparison of the elementary events can be easily made.

$$P_{tr} = \frac{1}{1 + \frac{k_p}{k_{tr}} + \frac{k_t}{k_{tr}[M]} + \frac{k_x}{k_{tr}} \frac{[X]}{[M]}} \quad (11)$$

$$P_t = \frac{1}{1 + \frac{k_p}{k_t} [M] + \frac{k_{tr}}{k_t} [M] + \frac{k_x}{k_t} [X]} \quad (12)$$

If  $k_x$  is of the same order of magnitude as  $k_{tr}$  and  $k_t$ , then the probability of blocking onto is about three orders of magnitude lower than chain transfer and termination. Since termination gives rise to homopolymer when blocking (or grafting) onto occurs, the blocking efficiency will be close to zero at low conversions. If  $k_p/k_x$  is higher, the ratio between the probabilities of blocking (or grafting) onto and termination will also be higher. However, even if  $k_p \approx k_x$ , the blocking efficiency will be only 60-70% at low conversions. Nevertheless, as already discussed,  $k_p \approx k_x$  is not a reasonable assumption. Thus efficient cationic grafting or blocking cannot be achieved by grafting or blocking onto at low monomer conversions.

According to equation 9 the probability of grafting (or blocking) onto is expected to increase at high conversions since the last term in the denominator increases as  $[X]$  decreases. However, the probability of termination (equation 12) also increases as  $[M]$  and  $[X]$  decrease. Since termination leads to homopolymer formation in grafting (or blocking) onto, low grafting (or blocking) efficiencies will be obtained even at higher conversions. Better insight into the relative importance of these processes in grafting (or blocking) onto can be obtained by comparing the concentration of polymer molecules formed by termination, chain transfer and grafting (or blocking) onto.

The rate of monomer consumption is:

$$-\frac{d[M]}{dt} = k_p[P^\oplus][M] + k_{tr}[P^\oplus][M] \quad (13)$$

The rates of polymer formation by termination, chain transfer, and grafting (or blocking) onto is given by equations 14, 15 and 16 respectively:

$$\frac{dP_t}{dt} = k_p[P^\oplus] \quad (14)$$

$$\frac{dP_{tr}}{dt} = k_{tr}[P^\oplus][M] \quad (15)$$

$$\frac{dP_x}{dt} = k_x[P^\oplus][X] \quad (16)$$

where  $P_t$ ,  $P_{tr}$ , and  $P_x$  are the concentrations of polymer molecules formed by termination, chain transfer and grafting (or blocking) onto. Dividing equation 13 by equation 14

$$\frac{d[M]}{dP_t} = \frac{k_p + k_{tr}}{k_t} [M] \quad (17)$$

Solving this differential equation with  $P_t = 0$  when  $[M] = [M_0]$  initial values gives

$$P_t = \frac{k_t}{k_p + k_{tr}} \ln \frac{1}{1-Y} \quad (18)$$

where  $Y$  is the conversion,  $([M_0] - [M])/[M_0]$ .

Similarly, dividing equation 13 with equation 15 gives

$$P_{tr} = \frac{k_{tr}}{k_p + k_{tr}} [M_0] Y \quad (19)$$

Using the same method for calculating  $P_x$ :

$$P_x = [X_0](1 - (1-Y)^a) \quad (20)$$

where

$$a = \frac{k_x}{k_p + k_{tr}} \quad (21)$$

Figure 1 shows  $P_{tr}$ ,  $P_t$ , and  $P_x$  as a function of monomer conversion ( $Y$ ). Evidently, the number of polymer molecules formed by second order chain transfer to monomer increases linearly with conversion. In contrast,  $P_t$  is a non-linear function of  $Y$ , and rapidly increases at higher conversions. Because of kinetic similarities the same kind of function is obtained for the number of polymer molecules formed by first order chain transfer to monomer:

$$P_{tr, f} = \frac{k_{tr, f}}{k_p + k_{tr}} \ln \frac{1}{1-Y} \quad (22)$$

where  $k_{tr, f}$  is the rate constant of first order chain transfer. Recent experiments by Tazi et al. (12) corroborate this finding. As exhibited by the lower portion of Figure 1,  $P_x$ , the number of polymer chains participating in grafting (or blocking) onto, markedly depends on  $k_x/(k_p + k_{tr})$ .

Since termination giving homopolymer rapidly increases at higher conversions, grafting (or blocking) efficiencies should rapidly decrease close to 100% conversion in grafting (or blocking) onto. Indeed, as shown in Figure 2, grafting (or blocking) efficiencies ( $f$ ) slowly decrease as conversion ( $Y$ ) increases, but close to 100% conversions a fast decrease of  $f$  is obtained. The data in this Figure were obtained by calculating  $f$  with

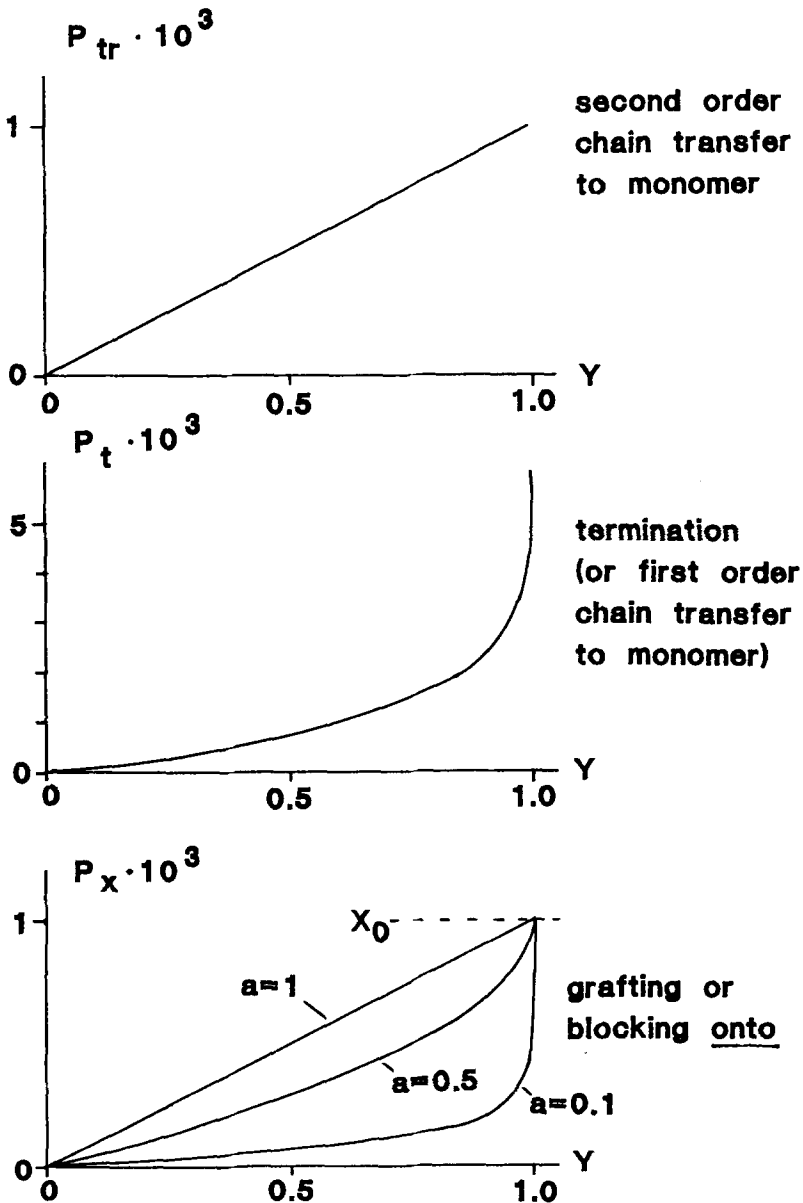


Figure 1. The concentration of polymer molecules formed by second order chain transfer ( $P_{tr}$ ), termination ( $P_t$ ) (or first order chain transfer) and grafting or blocking onto ( $P_x$ ) as a function of monomer conversion ( $Y$ ) calculated by equations 18-20;  $[M_0] = 1$ ,  $[X_0] = 0.001$  and  $k_t/(k_p + k_{tr}) = k_{tr}/(k_p + k_{tr}) = 0.001$ .

$$f = \frac{P_x}{P_x + P_t} = \frac{1}{1 + \frac{b \ln \frac{1}{1-Y}}{[X_0](1-(1-Y)^a)}} \quad (23)$$

where  $b = k_t/(k_p + k_{tr})$ ;  $b = 0.001$  in this model calculation. Equation 23 and Figure 2 indicate that 100% grafting (or blocking) efficiency can never be achieved by grafting (or

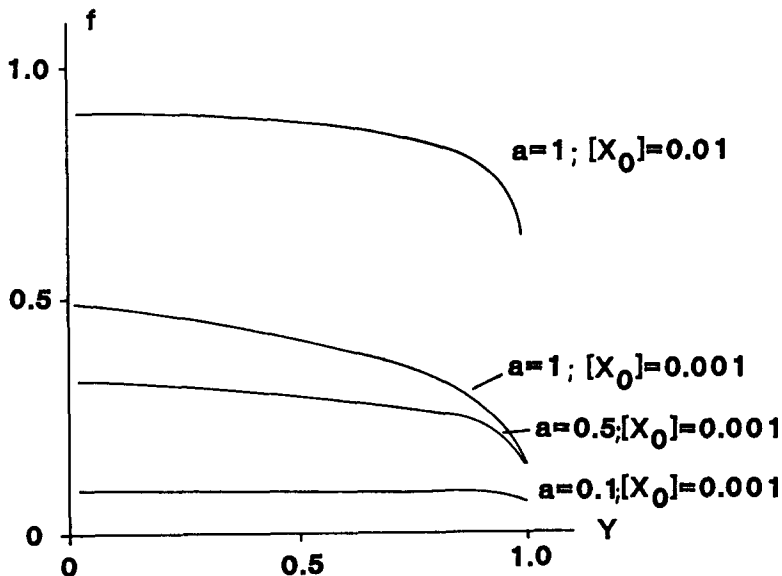


Figure 2. Grafting or blocking efficiency ( $f$ ) as a function of monomer conversion ( $Y$ ) in cationic grafting (or blocking) onto calculated by equation 23;  $b = 0.001$ .

blocking) onto if termination can occur. Even if  $k_x \approx k_p$  ( $a = 1$ ) and the concentration of the specific sites is relatively high ( $[X_0] = 0.01$ )  $f$  is  $\sim 90\%$  and will rapidly decrease at higher conversions.

In contrast to grafting (or blocking) onto, only chain transfer yields homopolymer in grafting (or blocking) from. Termination of polymer molecules initiated by macrohalide precursors yields grafts or blocks. Consequently, transferless polymerization should lead to high grafting and blocking efficiencies. Even relatively high grafting or blocking efficiencies can be reached when only second order chain transfer occurs, since  $P_{tr}$  increases only linearly with conversion. Grafting (10) and blocking (11) in the presence of proton traps, and a recent mechanistic study (15) corroborate these conclusions.

In summary, kinetic analysis indicates that efficient cationic grafting or blocking cannot be satisfactorily explained by assuming exclusively grafting or blocking onto processes. In contrast, grafting or blocking from readily explains efficient graft or block copolymer formation. Relatively high grafting efficiencies and duplication indexes have been published (13,14), however, these observations are not fully understood at the present. Further systematic experimentation is required to elucidate the reasons for these unexpected findings.

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