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The application of Taft-Hancock steric constants to the free-radical initiated copolymerization of *N*-alkylmaleimides with α-methylstyrene

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Summary

The rates of free-radical initiated alternating copolymerization of α-methylstyrene with N-alkylmaleimides (RMI) decrease in the following order: Me>Et>n-Pr≈n-Bu≈n-Hex>iso-Pr>tert-Bu. A linear relationship was established in the plots of $\log(k_R/k_{Me})$ against polar substituent constants σ^*, "true steric" factors E_S and corrected steric factors $E_S{}^C$. The best fit was obtained in plots of $\log(k_R/k_{Me})$ against σ^* and $E_S{}^C$ while a large scattering of results was observed in the plot of $\log(k_R/k_{Me})$ against E_S.

Introduction

The effect of structure on the rate of hydrolysis of esters and esterification of acids has been widely and systematically investigated, and Taft-Hancock parameters are in many cases successfully applied (1a). On the other hand, in polymerization reactions it is often difficult to correlate the rates of reaction with steric parameters, since the rate represents the overall rate of polymerization and includes the initiation, propagation, termination and chain transfer reactions. An example which illustrates the difficulties in the correlation of the rate of polymerization with steric factors is the polymerization of N-butylmaleimides (RMI: R=n-Bu, iso-Bu, sec-Bu, tert-Bu) in benzene at 60°C initiated with AIBN. Otsu

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and coworkers (2) have found that tert-BuMI has the highest rate of polymerization inspite of its bulky substituent. The same authors (3) have found that in the polymerization of tert-BuMI, tert-amylMI and tert-octylMI the rate of reaction decreases as the bulkiness of substituent increases. Although it is difficult to predict the effect of steric factors on the rate of polymerization, several papers have shown that the rate of polymerization can be correlated with polar substituent and steric parameters. Heulblein and coworkers (4) have shown a good correlation between polar substituent and steric effects with the rate of cationic polymerization of alkylvinyl ethers (alkyl = tert-Bu, iso-Pr, cyclo-Hex, n-Bu, n-Pr, Et, iso-Bu, Me). Similarly a good correlation between corrected Taft--Hancock parameters and the rate of copolymerization of β-alkoxystyrenes (alkyl = Me, Et, n-Pr, iso-Pr, sec-Bu) with NPhMI was shown in our work (5). Parallelism between corrected Taft-Hancock parameters and number of C-atoms in α-olefins copolymerized with ethylene in the presence of Ziegler-Natta catalyst is described by Kissin and Beach (6). It is of interest to mention that the decomposition of copolymers of phenylvinyl alkyl ethers (alkyl = Me, Et, n-Pr, iso-Pr, sec-Bu) and phenylvinyl alkyl thioethers (alkyl = Me, n-Pr, iso-Pr, sec-Bu) respectively with maleic anhydride can also be correlated with corrected Taft-Hancock steric parameters (7). In the present paper we wish to describe the application of polar substituent constants and steric parameters to the copolymerization of N-alkylmaleimides with α-methylstyrene.

Experimental

Materials

N-Alkylmaleimides (RMI: R = Me, Et, n-Pr, iso-Pr, n-Bu, tert-Bu, n-Hex) were prepared from the corresponding RNH_2 as previously described (8). Copolymers poly(RMI-alt-α-MeSt) were prepared homogeneously by "point-by-point" method to low conversion not exceeding 15%, or continuously in differential Calvet microcalorimeter in $CHCl_3$ at 60°C. Copolymers were isolated gravimetrically. The properties of alternating copolymers are listed in the reference 8.

Results and Discussion

During the course of our studies on the copolymerization of N-alkylmaleimides (RMI) with α-MeSt it was established that regardless to the ratio of comonomers in the feed, the alternating copolymers were obtained.[8,9] It was further found that in copolymerizations, charge-transfer complexes participate, and that in the presence of homopolymerizable electron acceptor (RMI) the alternating copolymerization precedes the homopolymerization of N-alkylmaleimides. Since the concentration of CT-complex monomers in the copolymerization of RMI with α-MeSt is small in comparison with the concentration of uncomplexed monomers, it can be assumed that monomers react in pairs, so that the second-order reaction becomes pseudo-first-order, and the plot of $\ln([M_o]/[M_t])$ against time should be linear. This is exampled in Fig.1. for the copolymerization of n-PrMI, iso-PrMI and tert-BuMI with α-MeSt. Following the same procedure the rate constants of polymerizations of RMI with α-MeSt are determined and listed in Table 1.

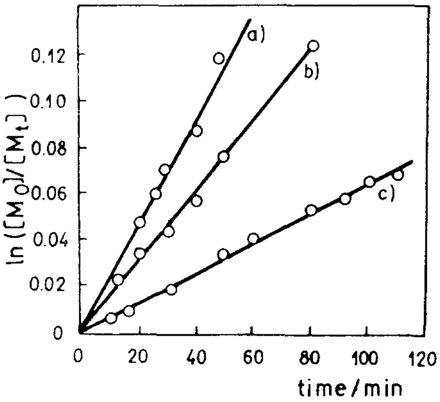

Figure 1. First order rate plots in the copolymerization of n-PrMI (a), iso-PrMI (b) and tert-BuMI (c) with α-MeSt

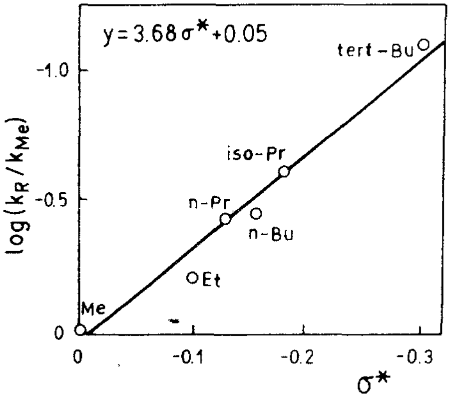

Figure 2. Plot of $\log(k_R/k_{Me})$ against polar substituent factor σ^* in the copolymerization of RMI with α-MeSt; $y=\log(k_R/K_{Me})$

Table 1. Rate constants of the copolymerization of RMI with α-MeSt determined gravimetrically by "point-by-point" method.

R	k/min^{-1}	k_R/k_{Me}	$\log(k_R/k_{Me})$
Me	0.00600	1.000	0.000
Et	0.00380	0.633	-0.198
n-Pr	0.00230	0.383	-0.416
iso-Pr	0.00150	0.250	-0.602
n-Bu	0.00220	0.367	-0.435
tert-Bu[1]	0.00049	0.082	-1.086
n-Hex	0.00224	0.373	-0.428

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[1] Determined by microcalorimetry

In Figures 2, 3 and 4 are plotted the values of $\log(k_R/k_{Me})$ against polar substituent constants σ^* (1b) (Fig 2), "true steric factors" $E_S = \log(k_R/k_{Me})_A$ (1b) (Fig 3) and steric factors corrected for the hyperconjugation $E_S^C = E_S - 0.306 \cdot (3 - n_H)$ (10) (Fig.4); n_H represents the number of α-hydrogen atoms in R. The E_S value for C_2H_5 was taken from the work of Heublein (4) (E_S = -0,34) and E_S^C value of n-Hex was taken from the work of Kissin and Beach (6) (E_S^C = -0.98).

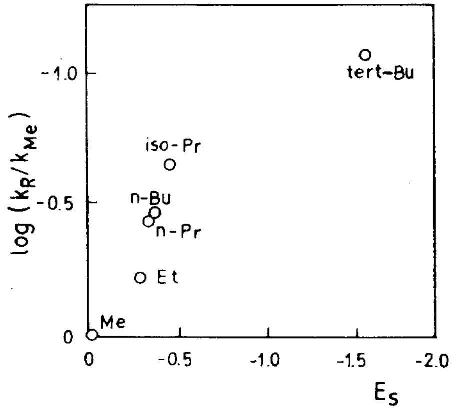

Figure 3. Plot of $\log(k_R/k_{Me})$ against "true steric factors" in the copolymerization of RMI with α-MeSt;$y=\log(k_R/k_{Me})$.

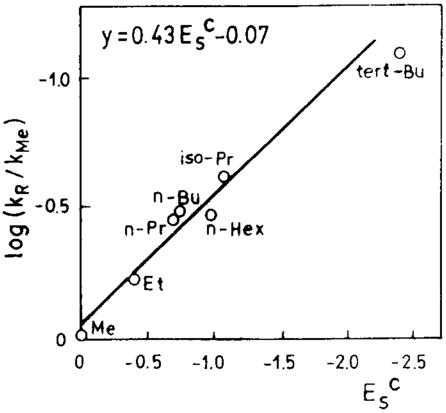

Figure 4. Plot of $\log(k_R/k_{Me})$ against corrected steric factors in the copolymerization of RMI with α-MeSt;$y=\log(k_R/k_{Me})$.

The data in Figures 2-4 indicate that a good linearity is obtained in the plot of $\log(k_R/k_{Me})$ against steric substituent factors σ^* and against corrected steric factors E_S^C respectively, while there is a large scattering of results in the plot of E_S against $\log(k_R/k_{Me})$. It is obvious that hyperconjugation has a significant effect on the rate of free-radical initiated copolymerization of RMI with α-MeSt. It is further evident that the sensitivity of rate constants against σ^* is 3.68 (Fig 2), while the sensitivity of $\log(k_R/k_{Me})$ against E_S^C is much lower, 0.43 (Fig 4).

Acknowledgements

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References

1. Taft Jr RW(1956) Separation of polar, steric, and resonance effects in reactivity. In: Newman MS(ed) Steric effects in organic chemistry. Wiley, New York NY, pp 556-675 a)p 586 b)p 591
2. Otsu T, Matsumoto A, Kubota T and Mori S (1990) Polym Bull 23:43
3. Otsu T, Matsumoto A and Tatsumi A (1990) Polym Bull 24:467
4. Heublein G, Agatha G, Dawczynski H and Zaleska B (1973) Z Chem 13(11):432
5. Vuković R, Kurešević V and Fleš D (1987) Croat Chem Acta 60(1):139
6. Kissin YV and Beach DL (1984) J Polym Sci:Polym Chem Ed 22:333
7. Vuković R, Kurešević V and Fleš D (1988) J Polym Sci: Part A Polym Chem 26:1249
8. Ranogajec F, Fleš DD, Hace D and Vuković R (1992) Polym Bull 28:319
9. Fleš DD, Vuković R, Ranogajec F, Žuanić M and Fleš D (1989) POLIMERI 10(6):143 (in English)
10. Fujita T,Takayama C,Nakajima M(1973)J Org Chem 38:1623

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