Determination of the transfer constant for copolymerization in the presence of a reactive substrate

Ross A. M. Thomson and C. Kee Ong
Department of Chemical Sciences, The Polytechnic, Queensgate, Huddersfield HD1 3DH, UK

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Important equations recently presented by Bamford *et al.*[1], for chain transfer with reactive substrates in copolymerizing systems are analogous to the well-known relationship:

$$\ln[S]/[S]_o = C_s \ln[M]/[M]_o$$

which is applicable to homopolymerization. This paper reports the first direct experimental testing of the validity of these equations. Gas/liquid chromatographic measurement of residual substrate concentration as a function of monomer removal, measured dilatometrically for the systems methyl acrylate/styrene/bromotrichloromethane and methyl methacrylate/styrene/bromotrichloromethane has been carried out. Results indicate that the equations accurately describe the course of the reaction and permit evaluation of the appropriate transfer constant.

INTRODUCTION

In order to measure the transfer constant of a reactive radical, $B^{\cdot}$, with a reactive substrate, S, Bamford[1–4] suggested the concept of moderated copolymerization. Monomer B was copolymerized with a large excess of monomer A, chosen because its transfer constant with S is much smaller.

In the development of Bamford's kinetic analysis, the following equation[1] was obtained:

$$\frac{-r_A C_A}{r_A - 1}\ln\frac{U_o}{U} + \left(\frac{r_A C_A}{r_A - 1} + \frac{r_B C_B}{r_B - 1}\right)\ln\left\{\frac{(r_B - 1)U + 1 - r_A}{(r_B - 1)U_o + 1 - r_A}\right\} = \ln\frac{[S]}{[S]_o} \qquad (1)$$

where r_A and r_B are the monomer reactivity ratios for monomers A and B; C_A and C_B are the transfer constants for radicals with terminal $A^{\cdot}$ and $B^{\cdot}$ units respectively. $[S]$ is the substrate concentration when the residual concentration ratio of monomers, $[B]/[A]$ is U. The subscript o refers to zero time.

Bamford also deduced the relationship[1]:

$$\frac{-r_A}{r_A - 1}\ln\frac{U}{U_o} + \frac{r_A r_B - 1}{(r_A - 1)(r_B - 1)}\ln\left\{\frac{(r_B - 1)U + 1 - r_A}{(r_B - 1)Uo + 1 - r_A}\right\} + \ln(1 + U) = \ln\left\{1 + U_o - \frac{\Delta([A] + [B])}{[A]_o}\right\} \qquad (2)$$

where $\Delta([A] + [B])$ is the total drop in monomer concentration when the monomer ratio has changed from U_o to U.

These equations are important because when combined, they relate substrate and monomer removal as a function of transfer constant, etc. As Bamford has pointed out[1], the equivalent expression for homopolymerization is:

$$\ln\frac{[S]}{[S]_o} = C_s \ln\frac{[M]}{[M]_o} \qquad (3)$$

Equation (1) had not been previously reported, and is of obvious importance in copolymerization transfer kinetics. Bamford made use of the equation[1] by replacing terms in $[S]$ by an appropriate expression in $\bar{Pn}$, the number average degree of polymerization of the polymer obtained in the presence of substrate at concentration $[S]$. He was unable to test its validity directly however.

In the present study, $[S]$ was measured as a function of extent of reaction. This eliminated uncertainty introduced in the relationship between $\bar{Pn}$ and $[S]$ and in the effect of precipitation of the copolymers on their molecular weight. The data thus obtained permitted validation of the equation as follows.

Re-arrangement of equation (1) gives:

$$\left\{\left(\frac{r_A C_A}{r_A - 1}\right)\frac{U_o}{U} + \frac{r_B C_B}{r_B - 1}\right\}\ln\gamma = \ln[S]/[S]_o \qquad (4)$$

where

$$\gamma = \frac{(r_B - 1)U + 1 - r_A}{(r_B - 1)U_o + 1 - r_A} \qquad (5)$$

Making the reasonable assumption that:

$$\left(\frac{r_A C_A}{(r_A - 1)}\right)\frac{U_o}{U} \ll \frac{r_B C_B}{r_B - 1} \qquad (6)$$

equation (4) simplifies to:

$$\ln\gamma = \frac{r_B - 1}{r_B C_B}\ln[S]/[S]_o \qquad (7)$$

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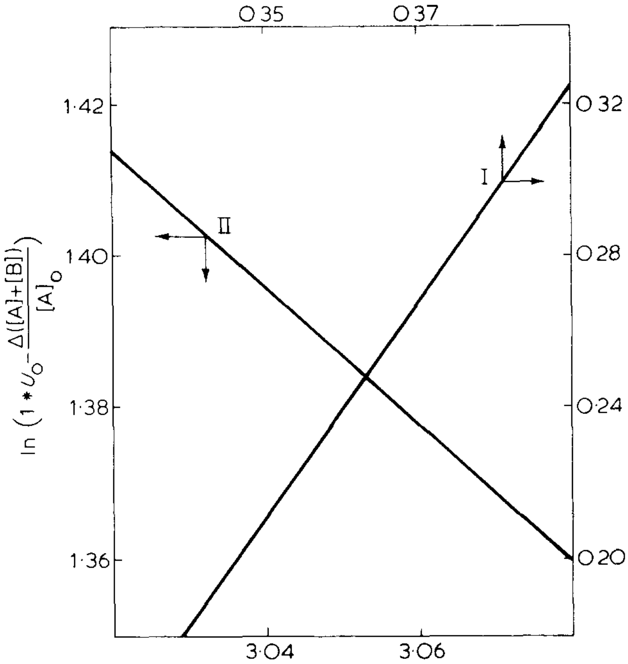

Figure 1 Plot of equation (2) for graph I — methyl acrylate/styrene system. $U_o = 0.393$, $r_A = 0.18$, $r_B = 0.75$. Graph II — methyl methacrylate/styrene system. $U_o = 3.04$, $r_A = 0.47$, $r_B = 0.50$

in which form the equation is easily tested experimentally, provided the range of values of U is sufficiently small to ensure C_B remains effectively constant.

The value of U may be obtained as a function of $\Delta([A] + [B])$ using the graphical method described by Bamford[1]. The latter is easily calculated from dilatometric measurements using the expression:

$$\Delta([A] + [B]) = \frac{10Q}{\Delta V} \text{ mol dm}^{-3} \qquad (8)$$

where Q is the percentage contraction and ΔV the volume contraction which would take place on the formation of 1 mole of copolymer whose mole ratio of A to B is n, given by the copolymer composition equation:

$$n = \frac{[A]}{[B]} \left\{ \frac{r_A + [B]/[A]}{r_B[B]/[A] + 1} \right\} \qquad (9)$$

It is easily shown that ΔV is given by:

$$\Delta V = \frac{n}{n+1} \left\{ M_A \left(\frac{1}{\rho_{\text{cop}}} - \frac{1}{\rho_A} \right) + \frac{M_B}{n} \left(\frac{1}{\rho_{\text{cop}}} - \frac{1}{\rho_B} \right) \right\} \qquad (10)$$

where M_A, M_B, ρ_A and ρ_B refer to the molecular weights and densities of the co-monomers A and B respectively; ρ_{cop} is the density of the copolymer, which has been estimated in the present study by assuming that it is a function of n and the densities of the appropriate homopolymers $\rho_{P(A)}$ and $\rho_{P(B)}$ according to

$$\rho_{\text{cop}} = \frac{nM_A + M_B}{\dfrac{nM_A}{\rho_{P(A)}} + \dfrac{M_B}{\rho_{P(B)}}} \qquad (11)$$

EXPERIMENTAL

Materials

Azo-bis-isobutyronitrile (AIBN), bromotrichloromethane (BTCM), styrene (St), methyl methacrylate (MM) and methyl acrylate (MA) were purified as in a previous paper[5], with the added precaution that the monomers were prepolymerized before use.

Procedure

A suitable mixture of AIBN, BTCM, and the appropriate monomers was prepared by conventional means. This mixture was distributed among a calibrated dilatometer and a series of glass tubes. After degassing and sealing, the vessels were simultaneously placed in a thermostat at 60 ± 0.01°C. Tubes were removed at known extents of monomer removal (measured dilatometrically). A measured volume of products was diluted by a factor of 50 using toluene doped with a trace of chloroform to permit checking of sample size. Analysis was performed on a Pye 204 gas/liquid chromatograph using a 1.5 m column at 80°C packed with 4% Apiezon M/Chromosorb G-AW-DMCS with an electron-capture detector connected to a Pye DP88 computing integrator. The detector response had previously been calibrated with solutions of BTCM under identical conditions.

RESULTS AND DISCUSSION

Excellent chromatographic separation was obtained with a high level of reproducibility. Graphical solution of equation (2) is depicted in *Figure 1* for two experiments: I – MA/St/BTCM and II – MM/St/BTCM. The strict linearity of these graphs permitted accurate estimation of U for given values of U_o and $\Delta([A] + [B])$.

Table 1 presents data for two quite different systems which have been treated as outlined above to yield *Figure 2*. The linearity of both graphs demonstrates quite clearly the validity of Bamford's equation[1] under very different circumstances. The equation would therefore appear to describe the results very satisfactorily and will be used to evaluate transfer constants for systems currently under study by the present workers, which will be reported shortly.

The values obtained for C_B in both cases indicate that the error involved in the simplification by expression (6) is negligible. Calculation shows that

$$\frac{(r_A C_A)}{r_A - 1} \frac{U_o}{U}$$

is generally about 0.1% of the magnitude of

$$\frac{r_B C_B}{r_B - 1}$$

in these systems.

Another source of error is the method of estimating copolymer density. It was considered however, that the experimental isolation of copolymers, particularly those involving methyl acrylate and determination of their densities would be subject to possibly greater experimental error.

Similarly, the use of the non-integrated form of the copolymer composition equation is not thought to be a serious

Table 1 Copolymerization with styrene (monomer B) in the presence of BTCM at 60°C [AIBN] = 1.3×10^{-3} mol dm^{-3}

System	Comonomer (A)	$[A]_0$ mol dm^{-3}	ρ_{cco} g cm^{-3}	ΔV cm^3 mol^{-1}	Percentage contraction (Q)	$\Delta([A]+[B])$ mol dm^{-3}	U	$-\ln[S]$	10^3 $\ln\gamma$	C_B
I	Methyl[1,6,7] acrylate $r_A = 0.18$ $r_B = 0.75$ $\rho_A = 0.905$ g cm^{-3} $\rho P(A) = 1.91$ g cm^{-3} $C_A = 0.1$	7.032	1.1123	21.70	0	0	0.394	4.556	0	38.5
					0.505	0.233	0.384	5.000	3.5	
					1.013	0.467	0.376	5.347	6.2	
					1.519	0.700	0.367	5.693	9.3	
					2.027	0.934	0.357	6.032	12.7	
					2.469	1.138	0.349	6.362	15.5	
II	Methyl[8,9] methacrylate $r_A = 0.47$ $r_B = 0.5$ $\rho_A = 0.897$ g cm^{-3} $\rho P(A) = 1.176$ g cm^{-3} $C_A = 0.06$	2.104	1.0841	22.35	0	0	3.040	4.60	0	44.0
					0.152	0.068	3.049	4.793	4.5	
					0.454	0.203	3.066	5.189	13.4	
					0.679	0.304	3.080	5.520	20.1	
					0.907	0.406	3.094	5.798	26.9	

Values of ρ_B and $\rho_{P(B)}$ were taken to be 0.869 and 1.048 respectively at 60°C[10]

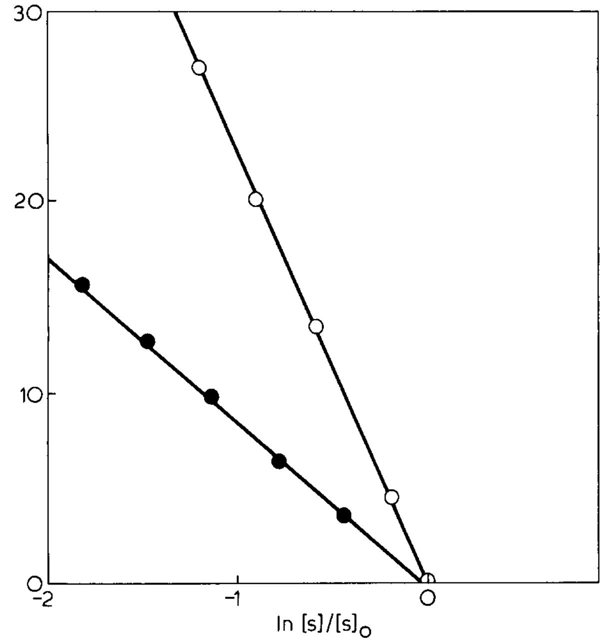

Figure 2 Plot of equation (7). System 1 (●): methyl acrylate/styrene/bromotrichloromethane. System II (○): methyl methacrylate/styrene bromotrichloromethane

source of error. Since a knowledge of U would be required for the integrated form, a laborious process of successive approximations would be necessary. The small effect on the final result would not warrant such a lengthy and time-consuming procedure.

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