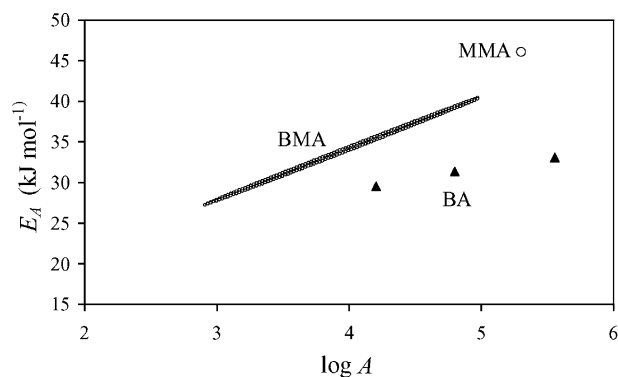


# Measurement of Transfer Coefficients to Monomer for *n*-Butyl Methacrylate by Molecular Weight Distributions from Emulsion Polymerization

David F. Sangster, Jesper Feldthusen, Jelica Strauch, Christopher M. Fellows\*

The average kinetic coefficient for chain transfer to monomer ( $\langle k_{tr,M} \rangle$ ) in the free-radical polymerization of *n*-butyl methacrylate (BMA) has been determined by the analysis of molecular weight distributions obtained by seeded emulsion polymerization under conditions such that chain transfer to monomer is the dominant chain-stopping event. Measurements between 40 and 70 °C gave data fitting an Arrhenius-type relationship with exponential factor  $E_A = 30\,900 \pm 4\,500 \text{ J} \cdot \text{mol}^{-1}$  and pre-exponential factor  $\log A = 3.45 \pm 0.15$ . The value for  $E_A$  is comparable with published data for chain transfer to monomer from methyl methacrylate (MMA) and *n*-butyl acrylate (BA). The  $A$  value, however, is 1–3 orders of magnitude smaller, suggesting that there is more hindrance for chain transfer to monomer for BMA than for either MMA or BA.



## Introduction

While the number of chain transfer events in a typical free-radical polymerization is miniscule in proportion to the number of propagation events, chain transfer is of great importance to the overall kinetics and mechanism of these reactions in emulsion polymerization. Literature data for the chain transfer to monomer coefficient  $C_M$  for methacrylates with relatively short side chains lie in the range of  $1.4\text{--}5.4 \times 10^{-5}$  and cannot be readily correlated

with monomer structure.<sup>[1]</sup> Nor can data for a single methacrylate species be fitted with any degree of confidence to an Arrhenius relation, with the single exception of methyl methacrylate (MMA).<sup>[2]</sup> The aim of this work is to evaluate values of  $C_M$  for *n*-butyl methacrylate (BMA) in order to determine values for the average chain transfer coefficient ( $\langle k_{tr,M} \rangle$ ) for comparison with literature values for MMA<sup>[2–4]</sup> and for *n*-butyl acrylate (BA).<sup>[5]</sup>

The standard technique for determining  $C_M$  (the Mayo Method) involves plotting for the number-average molecular weight ( $\bar{M}_n$ ) as a function of  $[I]/R_p$  (where  $[I]$  is the concentration of initiator and  $R_p$  is the polymerization rate).<sup>[6]</sup> Problems may arise in this method from uncertainties in the determination of  $\bar{M}_n$  under conditions where transfer to monomer dominates chain termination.<sup>[7,8]</sup> An alternative formulation,<sup>[9]</sup> which has been shown to be of equivalent reliability by Heuts and Davis,<sup>[10]</sup> makes use of the information provided by the complete

D. F. Sangster, J. Feldthusen, J. Strauch  
Key Centre for Polymer Colloids, School of Chemistry F11,  
University of Sydney, New South Wales 2006, Australia  
C. M. Fellows  
Chemistry, School of Science and Technology, The University of  
New England, New South Wales 2351, Australia  
Fax: (+61) 2 6773 3268; E-mail: cfellows@une.edu.au

molecular weight distribution (MWD) ( $P(M)$ ) to obtain consistent values for chain transfer coefficients.<sup>[7,8,11–16]</sup> In the portion of this distribution where chain termination is dominated by chain transfer to monomer, the relationship  $\ln(P(M)) \propto -C_M \times M/M_0$  applies, where  $M_0$  is the molecular weight of the monomer.

While it is theoretically always possible to reach the transfer-dominated limit by reducing the radical flux, it may be impractical to obtain suitable samples for size exclusion chromatography (SEC) under these conditions. This difficulty can be overcome by making use of free-radical emulsion polymerization, where compartmentalization of the growing polymer radicals allows any amount of polymer to be grown to high conversions under conditions of low radical flux. A seeded emulsion polymerization system is used and conditions are selected such that the entry of a radical into a growing polymer particle causes very rapid termination (i.e., zero-one kinetics<sup>[9]</sup>). These conditions may usually be obtained by using sufficiently small seed polymer particles and avoiding the formation of additional particles during the polymerization.

The MWD of interest is obtained by subtracting the MWD of the seed particles from the cumulative MWD. The seed particles need not necessarily be of the same polymer as the polymer of interest, and it is often easier to use a well-characterized seed latex of a different polymer species rather than prepare a suitably sized low-dispersity latex of the polymer whose  $\langle k_{tr,M} \rangle$  is to be determined.<sup>[17]</sup>

The conditions required to carry out determination of  $\langle k_{tr,M} \rangle$  by emulsion polymerization in this manner have been described by Tobita and Shiozaki.<sup>[13]</sup> An overview of this background theory to the method and its application to the BMA system is given in the Appendix. In this work, a number of poly(BMA) and polystyrene seeds of different sizes were employed over a range of temperatures (40–70 °C) to estimate empirical Arrhenius parameters  $A$  and  $E_A$  for  $\langle k_{tr,M} \rangle$ . Higher temperatures were avoided because at such temperatures depropagation becomes a significant complicating factor.<sup>[18]</sup>

The parameters derived from the Arrhenius plot for  $\langle k_{tr,M} \rangle$  for BMA can be used to estimate its values at temperatures over the range of 40–70 °C for the prediction of reaction rates and product distributions in academic studies of reactions involving BMA or in industrial optimization. It will also provide a base for work on copolymers involving BMA. Beyond this limited goal, the comparison of estimated  $E_A$  values with values obtained for chain-transfer to monomer reactions for similar monomers can shed light on the relative importance of various labile hydrogen environments in giving rise to this chain-transfer to monomer, a topic of practical and theoretical interest for many acrylate and methacrylate polymerizations. Because of the ten-fold extrapolation combined with the scatter of the data in the Arrhenius plot, the value of  $A$

is not accurate enough to give more than an estimate of the frequency factor for comparison with other reactions.

## Experimental Part

### Reagents

BMA (Merck, 99%) was purified by washing repeatedly with aliquots of 0.1 mol · L<sup>-1</sup> sodium hydroxide to facilitate removal of the inhibitor, then with Milli-Q water (×3), and 0.1 mol · L<sup>-1</sup> sodium chloride solution. The monomer was dried overnight over anhydrous calcium chloride, filtered through basic alumina and distilled under reduced pressure at approximately 40 °C. In a second series of experiments, BMA (Aldrich) was purified by passing through a column of inhibitor remover (Aldrich) and stored at 4 °C.

Sodium dodecyl sulfate (SDS, Aldrich, 98%), Disponil FES77 [sodium poly(ethylene glycol) sulfonate monodecyl ether, 30% w/w, BASF-AG], Texapon NSO (sodium dodecylether sulfonate, BASF-AG), Dowfax 2A1 (an alkyl diphenyloxide disulfonate, Dow Chemical), Emulphor NPS 25 (sodium nonylphenyl polyglycoether sulfate, BASF-AG), sodium hydrogencarbonate buffer (Aldrich), sodium persulfate (NaPS, Fluka), potassium persulfate (KPS, Ajax, 99%), methyl ethyl hydroquinone (MEHQ, Aldrich) and tetrahydrofuran (THF, Unilab) were used as received. Deionized water was provided by a Millipore Milli-Q ultrafiltration system. A number of previously prepared polystyrene and poly(BMA) seed latices were used to seed the polymerization, which will be referred to as Styrene 1 (unswollen radius  $r_u = 36$  nm), Styrene 2 ( $r_u = 15$  nm), BMA 1 ( $r_u = 53$  nm) and BMA 2 ( $r_u = 37 \pm 7$  nm). All seeds were prepared in the Key Centre for Polymer Colloids, University of Sydney, except Styrene 2, which was provided by BASF-AG.

### Characterization and Purification of Seeds

Poly(BMA) seed latices were prepared as follows: BMA (200 g) was added to an aqueous solution (660 mL) containing Aerosol MA 80 (10 g) and NaHCO<sub>3</sub> (1.0 g) previously heated to 85 °C and deoxygenated by bubbling with nitrogen for 30 min. The mixture was homogenized and the polymerization was initiated by adding a preheated solution of KPS in water (1.0 g in 10 mL) to the reaction. The polymerization was carried out for 3 h at 85 °C. The seed was purified by dialysis for 3 d with three water changes at 20 °C (>5 water changes led to coagulation of the BMA seed). The unswollen radii  $r_u$  of the seed latices were determined by Capillary Hydrodynamic Fractionation (CHDF, Matec Applied Sciences) and Transmission Electron Microscopy. Polystyrene seed latex provided by BASF-AG was diluted with an SDS solution to give 10<sup>17</sup> particles per liter in 8 mmol · L<sup>-1</sup> SDS and filtered through a microfilter. The particle radius of this latex was measured using a photon correlation spectrometer (Brookhaven Instruments).

### Measurement of Reaction Rate

During the seeded emulsion polymerization of BMA the rate of reaction was determined by dilatometry<sup>[19]</sup> in order to determine conditions where chain transfer to monomer was the predominant chain termination mechanism. The reaction vessel (60 mL

jacketed dilatometer) was first cleaned by washing with distilled water ( $\times 3$ ), acetone ( $\times 3$ ) and THF ( $\times 3$ ) and then filled with tetrahydrofuran until use. Immediately before use it was rinsed with acetone and dried. Throughout the polymerization, the dilatometer was linked to a water bath enabling the jacket temperature to be maintained within  $\pm 0.1^\circ\text{C}$ . In a typical dilatometry experiment, deionized water was degassed by heating and stirring under reduced pressure and then putting argon above the water surface. A solution of SDS in water was added to the dilatometer, then BMA, and the mixture emulsified by stirring for 30 min. Seed latex was added to the dilatometer

while mixing. The mixture was stirred overnight and then heated to the appropriate reaction temperature. A solution of KPS or NaPS in water was preheated to the same temperature and 1 mL of this solution was added. At this time the dilatometer was filled with a small additional amount of deionized water and connected to a capillary tube of known internal radius, which was filled with decane to an appropriate height for the automatic tracking instrument. The change of the meniscus height was recorded automatically by an optical tracking device connected to a computer. A summary of the conditions under which the rates of polymerization were measured is given in Table 1.

Table 1. Determination of the average number of radicals per particle,  $\bar{n}$ .

| $T$<br>$^\circ\text{C}$ | $N_c$                | Surfactant | [Surfactant]                              | [Initiator]                               | $\bar{n}$       |      |                 |                 |
|-------------------------|----------------------|------------|-------------------------------------------|-------------------------------------------|-----------------|------|-----------------|-----------------|
|                         |                      |            | $10^{-3} \text{ mol} \cdot \text{L}^{-1}$ | $10^{-3} \text{ mol} \cdot \text{L}^{-1}$ |                 |      |                 |                 |
| Styrene 1               |                      |            |                                           |                                           |                 |      |                 |                 |
| 70                      | $1.0 \times 10^{17}$ | SDS        | 3.0                                       | KPS, 1.0                                  | $0.21 \pm 0.02$ |      |                 |                 |
|                         |                      |            | 5.5                                       |                                           | 0.30            |      |                 |                 |
| Styrene 2               |                      |            |                                           |                                           |                 |      |                 |                 |
| 70                      | $1.0 \times 10^{17}$ | SDS        | 14.2                                      | KPS, 1.0                                  | $0.20 \pm 0.02$ |      |                 |                 |
|                         |                      |            | 13.8                                      |                                           | $0.21 \pm 0.02$ |      |                 |                 |
|                         |                      |            | 13.4                                      |                                           | $0.23 \pm 0.02$ |      |                 |                 |
|                         |                      |            | 2.1                                       |                                           | $0.12 \pm 0.03$ |      |                 |                 |
|                         |                      |            | 0.5                                       |                                           | $0.12 \pm 0.03$ |      |                 |                 |
|                         |                      |            | 1.6                                       |                                           | $0.10 \pm 0.04$ |      |                 |                 |
|                         |                      |            | –                                         |                                           | NaPS, 0.27      | 0.28 |                 |                 |
|                         |                      |            | –                                         |                                           | NaPS, 0.22      | 0.43 |                 |                 |
|                         |                      |            | $1.0 \times 10^{17}$                      |                                           | FES77           | 1.6  | KPS, 1.0        | $0.11 \pm 0.02$ |
|                         |                      |            | $1.0 \times 10^{17}$                      |                                           | NSO             | 1.6  |                 | $0.09 \pm 0.02$ |
|                         |                      |            | $3.0 \times 10^{16}$                      |                                           | SDS             | 1.6  |                 | $0.20 \pm 0.03$ |
|                         |                      |            |                                           |                                           |                 | 1.6  | $0.35 \pm 0.05$ |                 |
|                         |                      |            | $3.0 \times 10^{16}$                      |                                           | FES77           | 3.2  |                 | $0.18 \pm 0.02$ |
|                         |                      |            |                                           |                                           |                 | 1.6  | $0.22 \pm 0.06$ |                 |
|                         |                      |            | $3.0 \times 10^{16}$                      |                                           | NSO             | 1.6  |                 | $0.24 \pm 0.03$ |
|                         |                      |            | $3.0 \times 10^{16}$                      |                                           | NPS25           | 1.6  |                 | $0.27 \pm 0.04$ |
| $3.0 \times 10^{16}$    | 2A1                  | 1.6        |                                           | $0.24 \pm 0.04$                           |                 |      |                 |                 |
| $1.0 \times 10^{17}$    | SDS                  | 13.4       | KPS, 0.10                                 | $0.30 \pm 0.02$                           |                 |      |                 |                 |
| 65                      | $1.0 \times 10^{17}$ | SDS        | –                                         | NaPS, 0.27                                | 0.31            |      |                 |                 |
| 60                      | $1.0 \times 10^{17}$ | SDS        | –                                         | NaPS, 0.41                                | 0.33            |      |                 |                 |
|                         |                      |            | –                                         | NaPS, 0.63                                | 0.33            |      |                 |                 |
|                         |                      |            | –                                         | NaPS, 0.07                                | 0.21            |      |                 |                 |
|                         |                      |            | –                                         | NaPS, 0.81                                | 0.15            |      |                 |                 |
| 50                      | $1.0 \times 10^{17}$ | SDS        | –                                         | NaPS, 0.75                                | 0.16            |      |                 |                 |
|                         |                      |            | –                                         | NaPS, 0.08                                | 0.12            |      |                 |                 |
|                         |                      |            | –                                         | NaPS, 2.97                                | 0.07            |      |                 |                 |
| 40                      | $1.0 \times 10^{17}$ | SDS        | –                                         |                                           |                 |      |                 |                 |

These  $\bar{n}$  values are typically lower than those found by Halnan et al.<sup>[20]</sup> at 50 °C under conditions where it was ascertained that termination was transfer-dominated.

### Preparation of Polymer for Size Exclusion Chromatography

Series One: Polymer samples for SEC were prepared in a 90 mL side arm jacketed dilatometer, which was cleaned as for the dilatometry experiments. A solution of SDS in water was combined with degassed deionized water in the dilatometer. BMA was then added and the mixture was stirred for 30 min. Seed latex was added to the dilatometer with continuous stirring. The reaction mixture was then heated under argon to the appropriate temperature for 1 h. A solution of KPS was preheated to this temperature and 1.0 mL of this solution was injected through the side arm to give the desired initiator concentration. Preheated water was injected similarly in order to fill the capillary tube to an appropriate height. After the meniscus fell to the level of the reaction vessel (equivalent to about 2% conversion), samples of approximately 2 mL volume were removed by syringe and transferred into 10 mL glass vials which were cooled in ice. To each of these samples, a saturated solution of sodium chloride in water (1 mL) and then methanol (4 mL) was added to precipitate the polymers. After settling overnight, each sample was decanted and the precipitated polymers were washed with deionized water. The samples were then dried in an oven at 45 °C.

Series Two: The seed/surfactant solution was degassed by evacuation and about 24 mL was transferred to the dilatometer vessel (volume 27 mL), a weighed quantity (about 1 g) of monomer was added and the vessel was stoppered. The gas in the space above the contents was removed by a 30 mL syringe and the vessel was stirred by a magnetic stirrer overnight. Additional monomer (if required), initiator (to make  $0.3\text{--}3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$  NaPS) and seed/surfactant (to fill vessel to 27 g) were added and the vessel was connected to an automatic tracker. Samples for molecular weight measurement were collected when the polymer concentration was in the range of 1–3%, as indicated by the fall in the capillary, by adding the contents of the vessel to a beaker containing 1 g of  $10 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$  MEHQ. Polymer content was determined by evaporating a weighed amount to dryness, weighing and subtracting the weight of surfactant, seed and initiator.

Both Series: A summary of the conditions under which polymers were prepared for SEC is given in Table 2. The tabulated dissociation rate coefficient of KPS,  $k_d$ , is calculated from the Arrhenius expression of Behrman and Edwards.<sup>[21]</sup>

### Size Exclusion Chromatography

Solutions for GPC were made up at 0.2 wt.-% poly(BMA) in THF and filtered through a microfilter. A Waters Chromatograph system with a 510 HPLC Pump was used at a flow rate of  $0.8 \text{ mL} \cdot \text{min}^{-1}$ . 100  $\mu\text{L}$  was injected into a Waters Size Exclusion Chromatographic train at 30 °C comprised of degasser, filter and guard columns, three Dow Styragel/HT6E columns (Series One) or two HT6E columns and one HT7E column (Series Two) and a Waters R401 differential refractometer (Series One) or Shimadzu differential refractometer (Series Two).

For both series, the system was calibrated using eight Polymer Laboratories narrow MWD polystyrene standards covering the molecular weight range  $5.0 \times 10^3\text{--}10.2 \times 10^6$ . The output was processed by Polymer Laboratories 'Cirrus' software and the raw data were transferred to a Microsoft Excel worksheet for analysis. In order to determine the MWD from the  $G(V_{el})$  curves, universal calibration was carried out using polystyrene standards by applying the following Mark-Houwink parameters for polystyrene and poly(BMA):  $K_{PS} = 1.14 \times 10^{-4} \text{ dL} \cdot \text{g}^{-1}$ ,  $\alpha_{PS} = 0.716$  and  $K_{PBMA} = 1.48 \times 10^{-4} \text{ dL} \cdot \text{g}^{-1}$ ,  $\alpha_{PBMA} = 0.664$ .<sup>[22]</sup>

## Results

### Rate Data

A typical plot showing the change in rate of conversion as a function of time is shown in Figure 1. At initiator concentrations between  $0.2 \times 10^{-4}$  and  $4.3 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ , periods of constant  $dx/dt$  were observed in the rate curves, suggesting that the polymerization under these conditions can be described by zero-one kinetics.

The rate of conversion  $dx/dt$  is directly related to  $\bar{n}$ , the number of polymer radicals per latex particle (Equation A1). The values obtained at a number of monomer feed concentrations, initiator concentrations and seed types are given in Table 1.

### MWD Data

A typical SEC distribution obtained in this work is shown in Figure 2. The distributions of the seed polystyrene and the poly(BMA) formed during the polymerization are quite different. The bulk of the poly(BMA) is seen at  $M > 10^6$ , while the seed is found primarily at  $M < 10^6$ . The quality of the seed signal subtraction may be gauged from the relatively flat character of the low molecular weight region of the subtracted curve.<sup>[23]</sup> It is important to note that this SEC distribution will not be an instantaneous picture of the population of polymer generated at a particular degree of conversion, but will contain the history of polymer growth at earlier stages in the reaction. Accordingly, experiments were restricted to as low a conversion as practicable. Some typical  $\ln(P(M))$  plots obtained for the polystyrene seed are given in Figure 3. It is apparent that the plots are generally linear in  $M$ . Apparent  $C_M$  was estimated from the slope at the maximum molecular weight by fitting a straight line to the  $\ln(P(M))$  plot obtained from the section of the SEC trace corresponding to a signal intensity within 90% of the peak intensity, as band-broadening artifacts should be minimized at the peak molecular weight.<sup>[24]</sup> The variation in slope over this range was used to estimate an error in  $C_M$ , and curves giving a markedly nonlinear  $\ln(P(M))$  plot in this region were discarded.

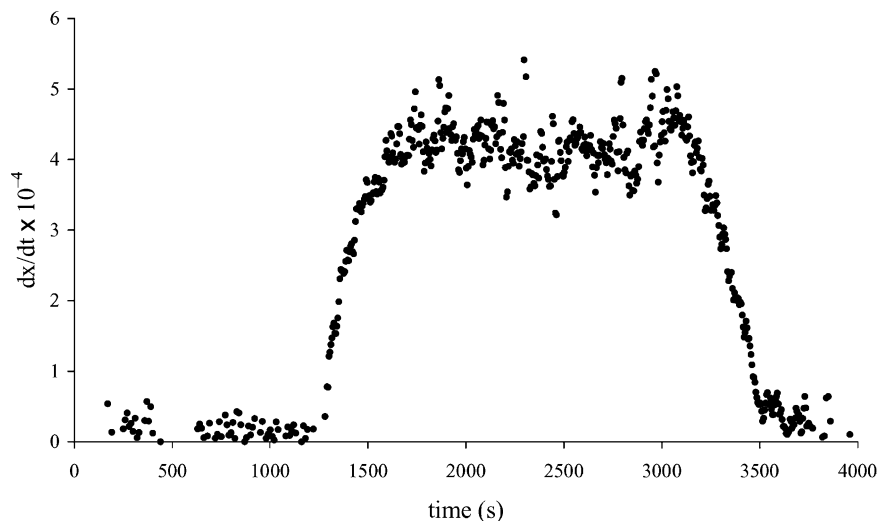
Table 2. SEC experiments. The particle concentration  $N_C$  is measured in  $L^{-1}$ .

| Seed                                               | $T$                   | $k_a$                 | $[I]$                              | Conversion | Apparent $C_M \times 10^{-5}$ |      |
|----------------------------------------------------|-----------------------|-----------------------|------------------------------------|------------|-------------------------------|------|
|                                                    | $^{\circ}C$           | $s^{-1}$              | $10^{-4} \text{ mol} \cdot L^{-1}$ | %          |                               |      |
| BMA $2N_C = 1.0 \times 10^{17}$                    | 40                    | $2.42 \times 10^{-7}$ | 30                                 | $20 \pm 4$ | 4.02                          |      |
|                                                    | 45                    | $5.47 \times 10^{-7}$ | 30                                 | $32 \pm 3$ | 3.88                          |      |
|                                                    | 55                    | $2.59 \times 10^{-6}$ | 10                                 | $33 \pm 4$ | 3.76                          |      |
|                                                    |                       |                       |                                    | $21 \pm 4$ | 3.72                          |      |
|                                                    | 60                    | $5.44 \times 10^{-6}$ | 10                                 | $29 \pm 7$ | 3.74                          |      |
| BMA $1N_C = 3.0 \times 10^{16}$                    | 70                    | $2.25 \times 10^{-5}$ | 1.0                                | 23         | 6.61                          |      |
|                                                    |                       |                       |                                    | 22         | 5.93                          |      |
|                                                    |                       |                       |                                    | 20         | 6.22                          |      |
|                                                    |                       |                       |                                    | 20         | 5.49                          |      |
|                                                    |                       |                       |                                    | 21         | 6.21                          |      |
|                                                    |                       |                       |                                    | 21         | 5.87                          |      |
| Styrene 2<br>(Series 1) $N_C = 1.0 \times 10^{17}$ | 70                    | $2.25 \times 10^{-5}$ | 1.0                                | 21         | 4.06                          |      |
|                                                    |                       |                       |                                    | 20         | 4.37                          |      |
|                                                    |                       |                       |                                    | 19         | 3.96                          |      |
|                                                    |                       |                       |                                    | 16         | 3.83                          |      |
|                                                    |                       |                       |                                    | 23         | 3.90                          |      |
| Styrene 2<br>(Series 2) $N_C = 1.0 \times 10^{17}$ | 40                    | $2.42 \times 10^{-7}$ | 1.6                                | 33         | 3.85                          |      |
|                                                    |                       |                       |                                    | 14.2       | –                             | 3.01 |
|                                                    |                       |                       |                                    | 48         | –                             | 3.64 |
|                                                    | 45                    | $5.47 \times 10^{-7}$ | 17.4                               | 25         | 3.66                          |      |
|                                                    |                       |                       |                                    | 34         | 3.77                          |      |
|                                                    |                       |                       |                                    | 32         | 3.42                          |      |
|                                                    | 50                    | $1.20 \times 10^{-6}$ | 0.8                                | 36         | 4.08                          |      |
|                                                    |                       |                       |                                    | 36         | 4.08                          |      |
|                                                    |                       |                       |                                    | 25         | 3.49                          |      |
|                                                    |                       |                       |                                    | 15.7       | 25                            | 3.49 |
|                                                    | 60                    | $5.44 \times 10^{-6}$ | 4.1                                | 62         | 3.93                          |      |
|                                                    |                       |                       |                                    | 6.3        | 35                            | 3.57 |
|                                                    |                       |                       |                                    | 7.3        | 47                            | 3.85 |
| 8.0                                                |                       |                       |                                    | 54         | 3.76                          |      |
| 2.7                                                |                       |                       |                                    | –          | 3.50                          |      |
| 65                                                 | $1.12 \times 10^{-5}$ | 2.7                   | –                                  | 3.50       |                               |      |
|                                                    |                       |                       | 34                                 | 3.79       |                               |      |
| 68                                                 | $1.71 \times 10^{-5}$ | 2.8                   | 34                                 | 3.79       |                               |      |
|                                                    |                       |                       | 34                                 | 3.79       |                               |      |
|                                                    |                       |                       | 37                                 | 3.98       |                               |      |
| 70                                                 | $2.25 \times 10^{-5}$ | 2.2                   | 37                                 | 3.98       |                               |      |
|                                                    |                       |                       | 2.3                                | 34         | 4.56                          |      |
|                                                    |                       |                       | 3.3                                | 5          | 3.58                          |      |

From the slopes  $\Lambda$  of the  $\ln(P(M))$  plots, values of apparent  $C_M$  uncorrected for termination by entering radicals could be determined.

Average propagation rate coefficients  $\langle k_p \rangle$  for BMA have been found<sup>[33]</sup> by pulsed-initiation polymerization (PLP) at temperatures between  $-20$  and  $90$   $^{\circ}C$  and fit the Arrhenius

relation with pre-exponential factor  $\log A = 6.58$  and activation energy  $E_A = 22880 \text{ J} \cdot \text{mol}^{-1}$ . Values of  $\langle k_p \rangle$  determined from this expression were combined with apparent  $C_M$  values to give apparent  $\langle k_{tr,M} \rangle$  values for BMA (Table 2). Over the temperature range investigated a sufficiently good fit is found (Figure 4) to allow calculation



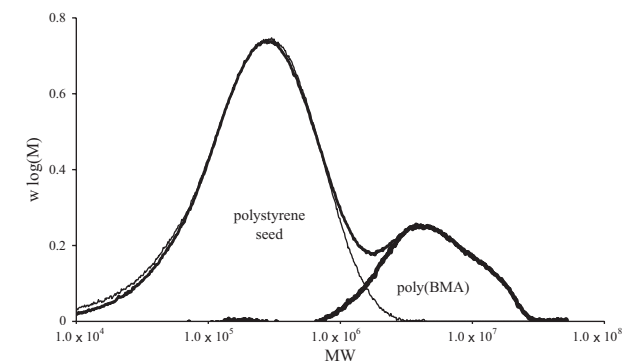
**Figure 1.** Rate of conversion of BMA to poly(BMA) as a function of time for  $[KPS] = 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ , initial  $[BMA] = 7.6 \text{ mol} \cdot \text{L}^{-1}$ ,  $T = 70^\circ \text{C}$ .

of empirical Arrhenius parameters for the apparent chain transfer reaction of poly(BMA) radical to BMA monomer.

In addition to termination by chain transfer to monomer in this system, there is a contribution from radical-radical termination by the entry of small radicals. This can be evaluated from Equation (A5). Values of the rate coefficient for entry,  $\rho$ , were calculated<sup>[25]</sup> and used to estimate  $\rho/k_p C_p$ .

$$-\Lambda M_0 = -C_M + \frac{\rho}{k_p C_p} \quad (1)$$

where  $M_0$  is the molecular weight of BMA. The value of  $3.8 \text{ mol} \cdot \text{L}^{-1}$  for  $C_p$ , the saturated concentration of BMA in poly(BMA) reported by Halnan et al.<sup>[20]</sup> at  $50^\circ \text{C}$ , was used in all calculations. This was confirmed by measuring the value at  $70^\circ \text{C}$  as  $4.0 \text{ mol} \cdot \text{L}^{-1}$  in the presence of monomer

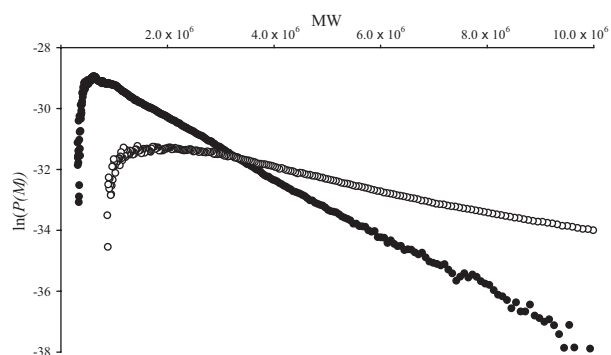


**Figure 2.** SEC distributions  $G(V_{el})$  for poly(BMA) obtained with  $[KPS] = 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ,  $T = 70^\circ \text{C}$ , at 12.7% conversion. Light line is MWD of polystyrene seed; heavy lines are MWD after second-stage growth and MWD of poly(BMA) formed by second-stage growth, obtained by subtraction of seed distribution.

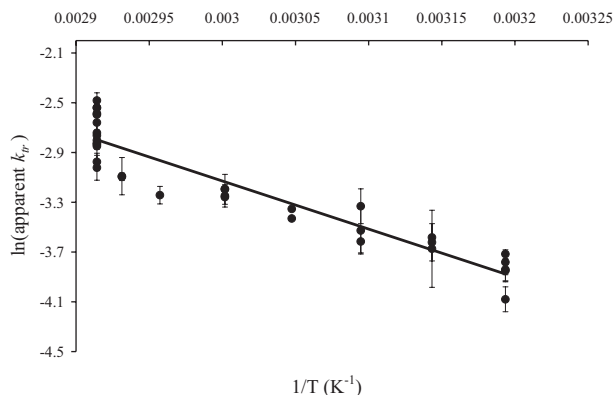
droplets. Parameters necessary for the estimation of  $\rho$  were the initiator concentration  $[I]$ , the dissociation coefficient of the initiator ( $k_d$ ), the termination rate coefficient of small radicals in the aqueous phase ( $k_t^{il} \approx 10^9 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ), the concentration of BMA in the aqueous phase ( $C_w$ ,  $2.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$  at  $50^\circ \text{C}$ <sup>[20]</sup>) and the particle number concentration,  $N_C$ . The limits where  $z$ , the critical degree of polymerization for a radical to enter a particle, is 2 and 4 were considered, on the basis of the relationship between  $z$  and the saturated concentration of monomer in water proposed by Maxwell et al.<sup>[25]</sup> Values of  $\langle k_{tr,M} \rangle$  obtained incorporating the correction may be summarized in an Arrhenius plot fitting the equation  $\log A = 3.45 \pm$

$0.15$  and activation energy  $E_A = 30\,900 \pm 4\,500 \text{ J} \cdot \text{mol}^{-1}$  (Figure 5). The set of data points obtained with the larger poly(BMA) seed BMA 1 at  $70^\circ \text{C}$  could not be brought into line with the other data points by the  $\rho/k_p C_p$  correction and may be affected by other termination mechanisms.

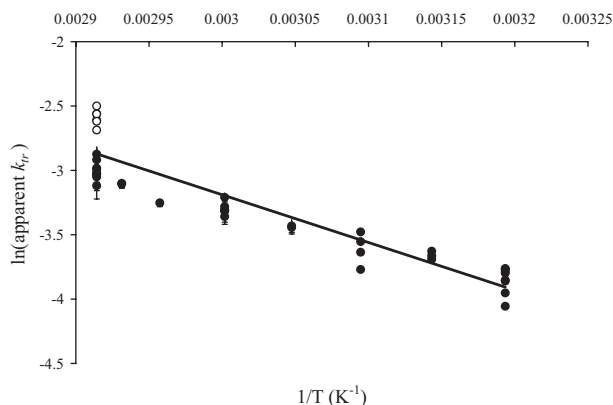
The error limits quoted for Figure 5 do not give a true picture of the uncertainty in the data, which is better expressed as a  $\chi^2$  plot (Figure 6) showing highly correlated values for  $E_A$  and  $A$ . The Arrhenius parameters quoted were determined by using the lowest  $\chi^2$  obtained on the grid as an initial guess and searching for a local minimum using the function 'Solver' in Microsoft Excel by weighted linear least-squares curve fitting, with 95% confidence intervals determined from the standard error in  $E_A$  and tabulated values for the T-distribution. However, it is easy to converge on almost equally good local minima within the mid-range of the confidence interval shown in Figure 6.



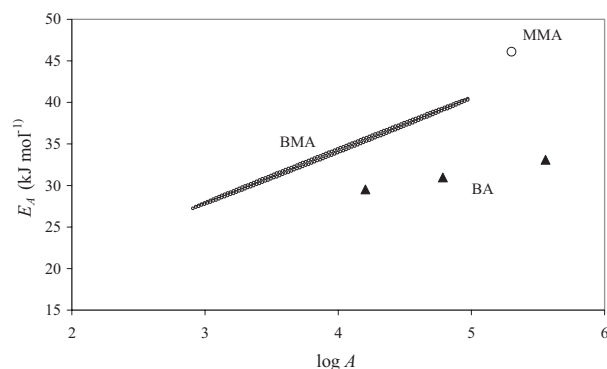
**Figure 3.** MWD for poly(BMA) displayed as  $\ln(P(M))$ , for samples obtained at  $T = 70^\circ \text{C}$  with (i)  $\circ$   $[KPS] = 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ , 12.7% conversion; (ii)  $\bullet$   $[KPS] = 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ , 10.6% conversion.



**Figure 4.** Plot of Arrhenius relationship for apparent  $\langle k_{tr,M} \rangle$  values in chain transfer to BMA monomer. Error bars are based on the uncertainty in the slopes of the  $\ln(P(M))$  plots.



**Figure 5.** Arrhenius plot for  $\langle k_{tr,M} \rangle$  values in chain transfer to BMA monomer adjusted to account for the effects of radical-radical termination. Open circles indicate the results of experiments obtained at 70 °C with the large poly(BMA) seed, BMA1. Error bars are based on the degree of variation induced by consideration of the  $z = 2$  and  $z = 4$  cases for entry.



**Figure 6.** 95% joint confidence interval for  $E_A$  and  $\log A$  for BMA  $\langle k_{tr,M} \rangle$  calculated, following the method of van Herk, [26] compared with literature values for BA ( $\blacktriangle$ ) and MMA ( $\circ$ ).

In considering the mechanistic implications of this data, it is therefore most appropriate to consider the overlap between this confidence interval and the Arrhenius parameters reported for similar systems. The Arrhenius parameters derived from the literature for BA<sup>[5]</sup> lie entirely within an ellipse which is not collinear with the confidence ellipse for BMA, suggesting strongly that chain transfer to monomer in BA polymerization and BMA polymerization proceed by different mechanisms. The sole data point for MMA<sup>[2]</sup> lies off the major axis of the BMA confidence ellipse, but not significantly enough to support mechanistic hypotheses.

## Discussion

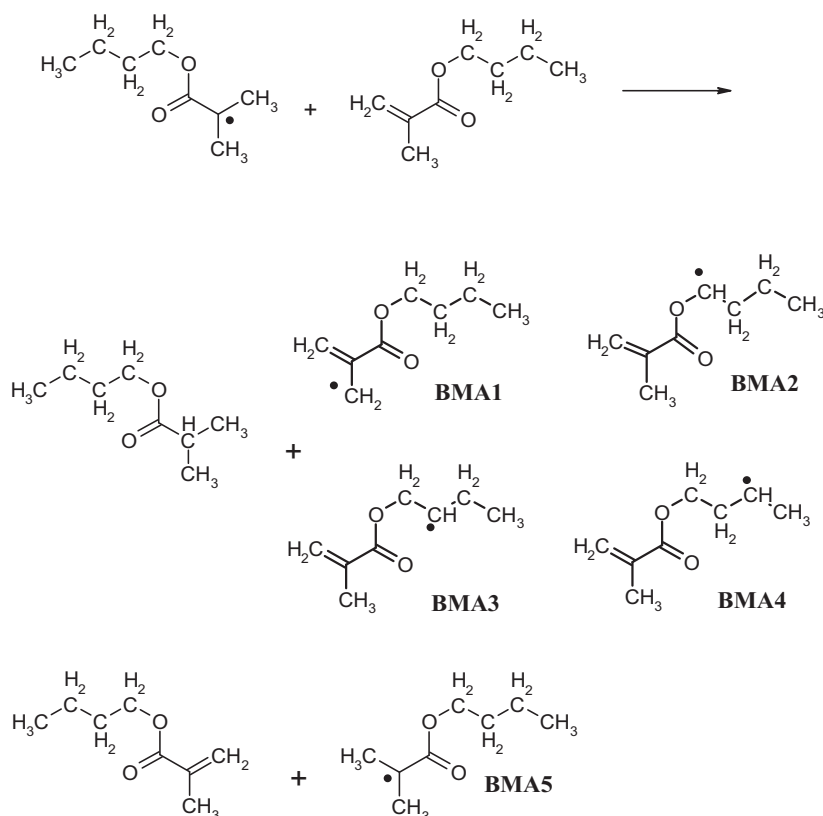
Possible end-chain transfer to monomer reactions for BMA are shown below (Scheme 1).

Abstraction of vinylic hydrogens, or methyl hydrogens from the terminus of the *n*-butyl group, is not considered because of the high C–H bond strength and limited capacity for stabilization of unpaired spin density at these positions. If chain transfer is by abstraction from the  $\alpha$ -methyl group (**BMA1**), it might be expected that the  $E_A$  would be similar to that seen for poly(MMA), as  $E_A$  in chain transfer reactions is correlated with the lability of the abstracted hydrogen atom.<sup>[27,28]</sup> If chain transfer is primarily by abstraction of the relatively labile hydrogen atoms on the carbon adjacent to the  $sp^3$  ester oxygen (**BMA2**), giving a product stabilized by interactions with the oxygen lone pairs,  $E_A$  should be expected to be similar to  $E_A$  for poly(BA).

## Comparison with Literature

Table 3 summarizes the reported results for propagation and for chain transfer to monomer for BMA and for the two possibly analogous monomers, MMA and BA. The values are listed as quoted, although the accuracy is not greater than two to three significant figures.

In Table 3, other evaluations of  $\langle k_p \rangle$  for MMA<sup>[38,39]</sup> are not included, since they give almost the same result as the benchmark set by the IUPAC working group on propagation rate coefficients.<sup>[29]</sup> Similarly, a number of other evaluations of  $\langle k_p \rangle$  for BA<sup>[40,41]</sup> and BMA<sup>[42]</sup> are not included as they also approach the IUPAC benchmark.<sup>[31]</sup> The data of Buback and Degener for BA<sup>[30]</sup> are included as it is the only dataset covering the same temperature range as that of Maeder and Gilbert for  $C_M$ .<sup>[5]</sup> However, it should be noted that this dataset is highly dependent on literature values for initiator  $k_d$  and photoinitiator quantum efficiency which have relatively high uncertainties.



■ Scheme 1. Chain transfer to monomer reactions in BMA polymerization.

Furthermore, it contained only one PLP experiment (predating the current best practice laid down by the IUPAC working party) with most data derived from single-pulse PLP and steady-state polymerization experiments. The values of effective  $\langle k_p \rangle$  reported by Nikitin et al.<sup>[32]</sup> gave a straight line in an Arrhenius plot, which has been extrapolated to the temperatures used by Maeder and Gilbert. Other evaluations of  $\langle k_p \rangle$  for BMA<sup>[42–44]</sup> are in general agreement with the benchmark.<sup>[33]</sup>

The  $C_M$  data previously reported for MMA,<sup>[3,4,34]</sup> BA<sup>[35]</sup> and BMA<sup>[36,37]</sup> show that the values of  $\langle k_{tr,M} \rangle$  obtained in this work and emerging from previously reported Arrhenius expressions for  $\langle k_p \rangle$  are consistent with other determinations over the appropriate temperature range. For MMA, the Arrhenius expression for  $C_M$  determined by Stickler and Meyerhoff<sup>[2]</sup> over the temperature range of 0–140 °C was combined with benchmark  $\langle k_p \rangle$  values calculated over the temperature range of –1–90 °C by the IUPAC working group on propagation rate coefficients.<sup>[29]</sup> This gives  $\log A = 5.30$  and  $E_A = 46\,100 \text{ J} \cdot \text{mol}^{-1}$  for MMA. For BA, an Arrhenius expression for  $C_M$  has been determined

<sup>a</sup> Because of the competition between unimolecular intramolecular chain transfer and bimolecular propagation,  $\langle k_p \rangle$  will be dependent on monomer concentration.<sup>[32]</sup>

over the range of 50–72 °C by Maeder and Gilbert.<sup>[5]</sup> For acrylates but not methacrylates, interpretation of  $C_M$  is complicated significantly by the contribution of 1,5 intramolecular hydrogen transfer (also referred to as backbiting or mid-chain transfer). In the polymerization of BA, this leads to the formation of a tertiary radical significantly less reactive in propagation than is the secondary poly(BA) radical and Asua et al.<sup>[31]</sup> point out that this will tend to induce curvature in any Arrhenius expression. The poly(BA)  $\langle k_p \rangle$  Arrhenius expression of the IUPAC working group on propagation rate coefficients has been based on selected data obtained over the range of –65–20 °C to minimize the effect of backbiting.<sup>[31]</sup> A more appropriate expression for  $\langle k_p \rangle$  to use in determining  $\langle k_{tr,M} \rangle$  for BA should therefore be an expression for ‘effective’  $\langle k_p \rangle$  over the appropriate temperature, monomer concentration,<sup>a</sup> and molecular weight range at which  $C_M$  data were collected. The only published values for BA over this temperature range were obtained over the temperature range of 25–80 °C by Buback and Degener,<sup>[30]</sup> but are not in accordance with current IUPAC guidelines: the data for effective  $\langle k_p \rangle$  reported by Nikitin et al.<sup>[32]</sup> (viz. as listed as  $k_p^{av}$  in their Table 2) between –10 and 30 °C are in accordance with the IUPAC guidelines for PLP. Accordingly, the  $C_M$  Arrhenius expression determined by Maeder and Gilbert<sup>[5]</sup> over the temperature range of 50–70 °C was combined with an extrapolation of the Arrhenius expression for effective  $\langle k_p \rangle$  from the data of Nikitin et al.,<sup>[32]</sup> which incorporate the effects of backbiting. This treatment gives  $\log A = 4.8$  and  $E_A = 30\,970 \text{ J} \cdot \text{mol}^{-1}$ . By comparison, the  $\langle k_p \rangle$  expression of Buback and Degener<sup>[30]</sup> gives  $\log A = 4.2$ ,  $E_A = 29\,530 \text{ J} \cdot \text{mol}^{-1}$  and using the IUPAC working party values for  $\langle k_p \rangle$  of the secondary radical of Asua et al.<sup>[31]</sup> gives  $\log A = 5.6$ ,  $E_A = 33\,100 \text{ J} \cdot \text{mol}^{-1}$ .

The chain transfer to monomer reaction of poly(BA) appears to have a similar activation energy to the chain transfer to monomer reaction of poly(BMA), while both have an activation energy less than that of MMA. The pre-exponential factor declines by approximately one order of magnitude on proceeding from poly(MMA) to poly(BA) and a further one to two orders of magnitude on proceeding to poly(BMA). The  $C_M$  data of Maeder and Gilbert was obtained over a molecular weight range significantly above the peak molecular weight, where band broadening effects may be important<sup>[24]</sup> and where long-chain branching has been reported in the emulsion

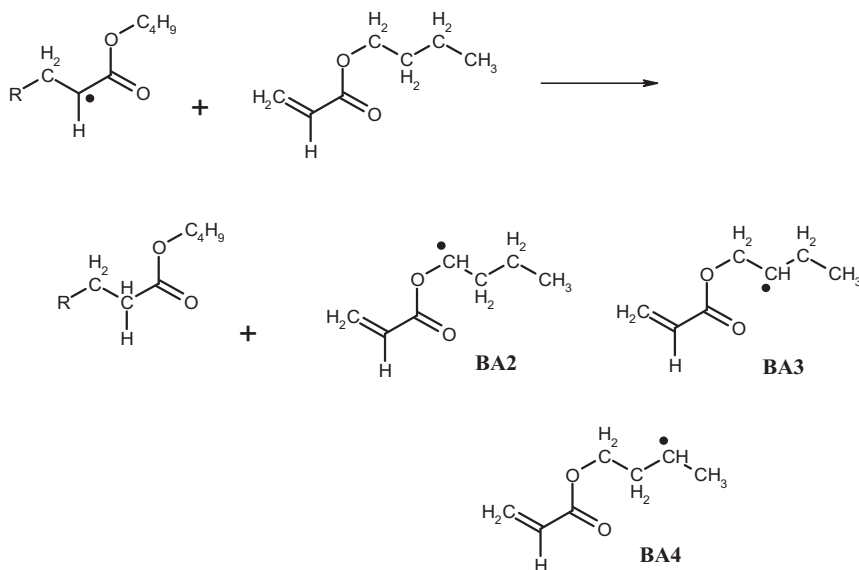
**Table 3.** Comparison of values for MMA, BA and BMA of  $A$ ,  $E_A$  and  $\langle k_p \rangle$ ,  $C_M$  and  $\langle k_{tr,M} \rangle$ , and of  $\langle k_p \rangle$ ,  $C_M$  and  $\langle k_{tr,M} \rangle$  at representative temperatures. For  $k_{tr,M}$ , the  $T$  range given is the range over which the experiments to determine  $C_M$  and  $k_p$  overlap.

| Monomer | $A$                                                  | $E_A$                            | $\langle k_p \rangle (50^\circ\text{C})$               | Reference                                                                   | $T$ ( $^\circ\text{C}$ ) |
|---------|------------------------------------------------------|----------------------------------|--------------------------------------------------------|-----------------------------------------------------------------------------|--------------------------|
|         | $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ | $\text{J} \cdot \text{mol}^{-1}$ | $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$   |                                                                             |                          |
| MMA     | $2.69 \times 10^6$                                   | 22 360                           | 651                                                    | Beuermann et al. <sup>[29] a)</sup>                                         | −1/90                    |
| BA      | $1.03 \times 10^6$                                   | 14 330                           | 4 576                                                  | Buback and Degener <sup>[30]</sup>                                          | 25/80                    |
|         | $2.24 \times 10^7$                                   | 17 900                           | 28 536                                                 | Asua et al. <sup>[31] a)</sup>                                              | −65/20                   |
|         | $3.79 \times 10^6$                                   | 15 770                           | 10 690                                                 | Nikitin et al. <sup>[32] b)</sup>                                           | −10/30                   |
|         | $3.91 \times 10^6$                                   | 16 170                           | 9 490                                                  | Nikitin et al. <sup>[32] c)</sup>                                           | −10/30                   |
|         | $3.78 \times 10^6$                                   | 22 880                           | 754                                                    | Beuermann et al. <sup>[33] a)</sup>                                         | −20/90                   |
| Monomer | $A$                                                  | $E_A$                            | $C_M (50^\circ\text{C})$                               | Reference                                                                   | $T$ ( $^\circ\text{C}$ ) |
|         |                                                      |                                  |                                                        |                                                                             |                          |
| MMA     | $7.4 \times 10^{-2}$                                 | 23 740                           | $1.07 \times 10^{-5}$                                  | Stickler and Meyerhoff <sup>[2]</sup>                                       | 0/140                    |
|         |                                                      |                                  | $4\text{--}5 \times 10^{-5}$                           | Whang et al. <sup>[34]</sup>                                                | 50                       |
|         |                                                      |                                  | $5.15 \times 10^{-5}$                                  | Kukulj et al. <sup>[3]</sup>                                                | 50                       |
|         |                                                      |                                  | $2.3 \times 10^{-5}$                                   | Van Berkel et al. <sup>[4]</sup>                                            | 50                       |
| BA      | $1.6 \times 10^{-2}$                                 | 15 200                           | $5.57 \times 10^{-5}$                                  | Maeder and Gilbert <sup>[5]</sup>                                           | 50/72                    |
|         |                                                      |                                  | $1.05 \times 10^{-4}$                                  | Capek <sup>[35]</sup>                                                       | 70                       |
| BMA     | $7.5 \times 10^{-4}$                                 | 7 980                            | $5.4 \times 10^{-5}$                                   | Matyska et al. <sup>[36]</sup>                                              | 50                       |
|         |                                                      |                                  | $1.4 \times 10^{-5}$                                   | Nair et al. <sup>[37]</sup>                                                 | 60                       |
|         |                                                      |                                  | $3.8 \times 10^{-5}$                                   | This work                                                                   | 40/70                    |
| Monomer | $A$                                                  | $E_A$                            | $\langle k_{tr,M} \rangle (50^\circ\text{C})$          | Reference                                                                   | $T$ ( $^\circ\text{C}$ ) |
|         |                                                      |                                  | $(\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$ |                                                                             |                          |
| MMA     | $2.0 \times 10^5$                                    | 46 100                           | $6.8 \times 10^{-3}$                                   | Stickler and Meyerhoff <sup>[2]</sup><br>× Beuermann et al. <sup>[29]</sup> | 0/90                     |
| BA      | $1.6 \times 10^4$                                    | 29 530                           | 0.26                                                   | Maeder and Gilbert <sup>[5]</sup><br>× Buback and Degener <sup>[30]</sup>   | 50/72                    |
|         |                                                      |                                  | 0.60                                                   | Maeder and Gilbert <sup>[5]</sup><br>× Nikitin et al. <sup>[32] b)</sup>    | No overlap               |
|         |                                                      |                                  | 0.53                                                   | Maeder and Gilbert <sup>[5]</sup><br>× Nikitin et al. <sup>[32] c)</sup>    | No overlap               |
|         |                                                      |                                  | 1.59                                                   | Maeder and Gilbert <sup>[5]</sup><br>× Asua et al. <sup>[31]</sup>          | No overlap               |
| BMA     | $2.8 \times 10^3$                                    | 30 860                           | 0.029                                                  | This work<br>× Beuermann et al. <sup>[33]</sup>                             | 40/70                    |

<sup>a)</sup>Benchmark recommendation of IUPAC working party on propagation rate coefficients; <sup>b)</sup>from data reported by Nikitin et al.<sup>[32]</sup> at  $[\text{BA}] = 7.02$ ; <sup>c)</sup>extrapolation from data reported by Nikitin et al.<sup>[32]</sup> at  $[\text{BA}] = 7.02$  using the monomer concentration employed by Maeder and Gilbert<sup>[5]</sup>  $[\text{BA}] = 5.7$  and the expression for dependence of  $k_p^{\text{av}}$  on  $[\text{M}]$  given by Nikitin et al.

polymerization of BA.<sup>[45]</sup> Long-chain branching could lead to an apparent reduction in the termination rate.<sup>[46]</sup> At 60 and 70  $^\circ\text{C}$  where long-chain branching would be expected to be more significant, it does appear that the slope at the

peak molecular weight is appreciably greater than that at the high molecular weight tail used.<sup>[5]</sup> Thus, it is possible that both  $A$  and  $E_A$  for  $\langle k_{tr,M} \rangle$  in BA may be significantly higher than reported here.



■ Scheme 2. Chain transfer to monomer reactions in BA polymerization.

This value of  $\log A$  found in this work for end-chain transfer to monomer in poly(BMA) corresponds to a pre-exponential factor of approximately  $2800 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ,  $-1.25$  times less than the pre-exponential factor calculated for poly(BA) chain transfer to BA<sup>[5,30,32]</sup> and considerably less than the calculated pre-exponential factor for poly(MMA) chain transfer to MMA.<sup>[2,29]</sup> This low pre-exponential factor may be credible, considering the more restricted environment about the forming and breaking bonds in BMA cf. MMA and BA. For several series of similar hydrogen abstraction reactions where steric

hindrance increases, reductions in  $A$  of two or three orders of magnitude have been reported in both experimental and computational studies.<sup>[47–50]</sup> Within the range of experimental error, there is little difference in  $E_A$  between BA and BMA, suggesting that there is little difference in the structure of the transition states of the two chain transfer reactions.

An isodesmic energy calculation of the form  $R^\bullet + MH \rightarrow M^\bullet + RH$ , where  $R$  is the unsaturated analogue to a monomer  $M$ , was carried out for each of the possible chain transfer reactions in Scheme 2 and the analogous chain transfer reactions for MMA and BA (Table 4). The unrestricted Hartree-Fock 6–31G\* and B3 LYP 6–31G\* levels of theory were applied using Spartan 04. The similar values of  $\Delta G_{\text{rxn}}^0$  obtained for chain transfer reactions from the butyl

group of BA and BMA imply that similar  $E_A$  values should apply, which is consistent with experimental results. Products **BMA3** and **BMA4** appear to be thermodynamically favored at both levels of theory, in contradiction to the assumption that the carbon adjacent to the oxygen lone pairs would bear the most labile hydrogens. The energy differences between products and reactants are very small in all cases, suggesting that it is inappropriate to assume from the Hammond postulate that the transition state is more 'product-like' or 'reactant-like'; instead, the pattern of substitution on both the hydrogen-donating and hydrogen-accepting species must be considered. Where other factors are equal, the most stable transition state can be expected to be the one where the reactant radical and the product radical have the greatest number of  $\alpha$ -carbon hydrogens capable of participation in hyperconjugation. For the reaction giving rise to product **BMA3**, there are seven such hydrogens, cf. four for the analogous reaction of BA, while for the reaction giving rise to product **BMA1** there are the same number of  $\alpha$ -hydrogens. The  $\Delta G_{\text{rxn}}^0$  differences between different hydrogen-abstraction reactions are not large, suggesting that the experimental  $E_A$  and  $A$  values arise from some combination of all chain transfer reactions. In the polymerization of BA, the observed  $\langle k_{\text{tr},M} \rangle$  will also include a possibly significant contribution arising from hydrogen abstraction by the tertiary mid-chain poly(BA) radical formed by backbiting.<sup>[31]</sup> To a first approximation, the mid-chain poly(BA) radical can be expected to behave similarly to a poly(BMA) radical, giving an even greater number of possible H-abstraction reactions contributing to the observed  $\langle k_{\text{tr},M} \rangle$ . ESR studies have demonstrated that

Table 4. Gibbs free energies of reaction and activation energies for chain transfer to monomer, calculated for 70 °C.

| M•                    | $\Delta G_{\text{rxn}}^0$                    |              |
|-----------------------|----------------------------------------------|--------------|
|                       | $\text{kJ} \cdot \text{mol}^{-1}$            |              |
|                       | UHF-6-31G*                                   | B3LYP-6-31G* |
| $\alpha$ -MMA radical | 2.6                                          | 17.2         |
| BA2                   | 7.7                                          | 10.2         |
| BA3                   | −5.8                                         | −8.9         |
| BA4                   | −6.4                                         | −8.4         |
| BMA1                  | 2.3                                          | 15.5         |
| BMA2                  | 5.8                                          | 12.7         |
| BMA3                  | −1.7                                         | −8.3         |
| BMA4                  | −0.1                                         | −10.8        |
| BMA5                  | 0 by inspection for monomeric model compound |              |

at equilibrium the overwhelming majority of radicals present in poly(BA) are mid-chain radicals,<sup>[51]</sup> and in the presence of  $0.4 \text{ mol} \cdot \text{L}^{-1}$  of a thiol chain-transfer agent it has been reported that essentially all of these radicals undergo transfer rather than propagation,<sup>[52]</sup> so the mid-chain poly(BA) radical may well contribute disproportionately to the observed  $\langle k_{\text{tr},M} \rangle$  for BA.

The Arrhenius parameters which have been derived for these three systems are most useful for evaluating transfer coefficients at temperatures within the ranges spanned by the experimental measurements, where values derived by interpolation or limited extrapolation are valid. They are the mathematical values which represent a line of best fit to the data when expressed as an Arrhenius-type relationship. Due to the scatter occasioned by experimental uncertainties, extrapolation beyond those ranges must be treated with caution. In particular, extrapolation to  $1/T=0$  to determine the pre-exponential factor involves projection for  $\langle k_{\text{tr},M} \rangle$  of the MMA, BA and BMA data by factors of 3, 15 and 10 times, respectively. In addition, the effective  $\langle k_{\text{tr},M} \rangle$  observed is likely to be the sum of several separate hydrogen transfer reactions. The  $E_A$  and  $A$  values obtained thus far for  $\langle k_{\text{tr},M} \rangle$  should be considered insufficient for drawing mechanistic conclusions. However, until better methods are devised, they could be useful for semi-quantitative comparison between systems.

## Conclusion

Over a range of accessible temperatures below the onset of significant depropagation, consistent values for the average rate coefficient for chain transfer to monomer,  $\langle k_{\text{tr},M} \rangle$ , in polymerization of poly(BMA) have been calculated by the analysis of MWDs generated by seeded emulsion polymerization experiments using seeds of different sizes and composition. The results found could be fitted by an Arrhenius relation to give  $E_A = 30\,900 \pm 4\,500 \text{ J} \cdot \text{mol}^{-1}$  and  $\log A = 3.45 \pm 0.15$  for the chain transfer to monomer reaction. These values are comparable to literature values in the analogous chain transfer to monomer reactions of poly(BA) and poly(MMA), although  $A$  is significantly smaller than reported for these systems. It should be stressed that due to the extent of extrapolation back to  $1/T=0$ , it is not possible to draw firm mechanistic conclusions from this data, but the results obtained are consistent with a chain transfer process dominated by abstraction of methylene hydrogens in the *n*-butyl side chain. This reaction would require a more hindered transition state than plausible chain-transfer reactions in BA or MMA polymerization, leading to a lower  $A$ .

## Appendix: Background Theory and Application to Butyl Methacrylate<sup>[9]</sup>

### Zero-One Kinetics

In Interval II of an emulsion polymerization of a monomer such as BMA, monomer droplets maintain a constant concentration of monomer ( $C_P$ ) in the growing particles. During this interval, the rate of polymerization ( $dx/dt$ ) remains constant and is given by the following expression:

$$\frac{dx}{dt} = \frac{k_p C_P \bar{n} N_C}{n_M^0 N_A} \quad (\text{A1})$$

Here,  $k_p$  is the rate coefficient for propagation,  $\bar{n}$  the average number of radicals per polymer particle,  $N_C$  the number of latex particles per unit volume of aqueous phase,  $n_M^0$  the molar concentration of monomer per unit volume of water and  $N_A$  Avogadro's constant. If the system follows zero-one kinetics, the value of  $\bar{n}$  should be less than or equal to 0.5. The two conditions  $dx^2/dt^2 = 0$  (i.e.  $dx/dt = \text{constant}$  and  $\bar{n} \leq 0.5$ ) are necessary but not sufficient for 'zero-one' kinetics to be applicable. An experimental test to verify the applicability of zero-one kinetics is the convergence of  $\bar{n}$  to 0.5 as  $[I]$  increases.

### Molecular Weight Distribution in a Zero-One System

The SEC distribution  $G(V_{\text{el}})$  of polymer formed in the polymerization may be obtained by subtracting the  $G(V_{\text{el}})$  of the seed from the  $G(V_{\text{el}})$  of the sample. The SEC MWD,  $X(M)$ , can be obtained from this  $G(V_{\text{el}})$  in turn using the relationship

$$X(M) = G(V_{\text{el}}) \frac{dV_{\text{cal}}}{d(\log M)} \quad (\text{A2})$$

where  $V_{\text{cal}}(M)$  is the SEC calibration curve. If the calibration curve can be expressed as a linear relation in  $\log M$  [i.e.  $V_{\text{cal}}(M) = a + b \log(M)$ ],  $X(M)$  may be transformed into the cumulative MWD,  $\bar{P}(M)$ , by the relation

$$\bar{P}(M) = \frac{X(M)}{M^2} \quad (\text{A3})$$

If necessary, the instantaneous MWD  $P(M)$  may then be approximated from  $\bar{P}(M)$  by subtracting appropriately normalized cumulative distributions obtained at different conversions.<sup>[23]</sup>

In a zero-one system the only chain-stopping events are chain transfer and entry of another radical species,

and the rate of termination of a given growing chain is given by the sum of these chain-stopping events:

$$C_P k_{tr,M} + [A] k_{tr,A} + wp(M_0/d_p) k_{tr,P} + \rho \quad (A4)$$

where  $\rho$  is the rate coefficient for radical entry;  $k_{tr,M}$ ,  $k_{tr,A}$  and  $k_{tr,P}$  are respectively the rate coefficients for transfer to monomer, to chain transfer agent and to polymer;  $[A]$  is the concentration of chain-transfer agent;  $wp$  is the total weight fraction of polymer in the latex particles and  $d_p$  is the mean density of polymer in the particles. In the case of acrylate and some other systems at other than quite low temperatures, it is necessary to consider the effects of backbiting and mid-chain transfer.

$P(M)$  will show an exponential dependence on  $M$  with a coefficient given by the total of the first-order loss processes.<sup>[12,53]</sup>

$$P(M) = \exp\left\{\frac{C_P k_{tr,M} + [A] k_{tr,A} + \rho}{k_p C_P}\right\} \frac{M}{M_0} \quad (A5)$$

In the absence of a chain-transfer agent or chain transfer to polymer, this expression simplifies to

$$\ln(P(M)) = \left\{C_M + \frac{\rho}{k_p C_P}\right\} \frac{M}{M_0} \quad (A6)$$

in the limit  $M \rightarrow \infty$  and radical flux  $\rightarrow 0$ , where  $C_M = k_{tr,M}/k_p$ .

In a zero-one emulsion polymerization system where the dominant chain-stopping event is transfer to monomer, the entry term in expression (A6) may be neglected. It is clear that under these conditions  $C_M$  can be determined by plotting  $\ln(P(M))$  as a function of  $M$ . The slope of the linear region of this plot should be approximately  $-C_M/M_0$ .

The entry rate coefficient  $\rho$  can be approximated analytically by the following expression<sup>[25]</sup>:

$$\rho = \frac{2k_d[I]N_A}{N_C} \left(\frac{\sqrt{k_d[I]k_t}}{k_p C_W} + 1\right)^{z-1} \quad (A7)$$

where  $[I]$  is the concentration of the initiating species,  $k_d$  the rate of decomposition of this species,  $k_{t,aq}$  and  $k_{p,aq}$  are respectively the termination and propagation rate coefficients of the monomer in the aqueous phase,  $C_W$  the aqueous phase concentration of the monomer and  $z$  the critical degree of polymerization required for a radical in the aqueous phase to enter a particle (a semi-empirical thermodynamic model has been suggested relating  $z$  directly to  $C_{W,sat}$ , the saturation value of  $C_W$ ).<sup>[25]</sup>

## Design of a Zero-One Butyl Methacrylate System

Specifications for selecting conditions such that zero-one kinetics are obeyed have been presented previously.<sup>[5,9]</sup> A sufficient condition for zero-one kinetics is that termination is rapid when a radical enters a particle containing a polymer radical. In this context, 'rapid' is defined as follows:

$$c^{iL} \gg k_p^1 C_P \quad (A8)$$

$$c^{iL} \gg k_{dM} \quad (A9)$$

where  $c^{iL}$  is the pseudo-first order rate coefficient for termination between an entering radical of length  $i$  and a long polymer radical,  $k_p^1$  is the propagation rate coefficient of a monomeric radical, and  $k_{dM}$  is the rate coefficient for escape by diffusion in the aqueous phase of a monomeric radical from the particle, which is given by the following expression:

$$k_{dM} = \frac{3D_W C_W}{r_s^2 C_P} \quad (A10)$$

where  $D_W$  is the diffusion coefficient of the desorbing species in the aqueous phase,  $r_s$  the swollen radius of a polymer particle and  $C_W/C_P$  the coefficient for partitioning of the monomer between the aqueous and organic phases. While it is possible to ignore transfer to monomer when looking at the probability of the new radical propagating to a significant length before termination, due to the relatively short mutual growth times of the two chains, desorption of monomeric radicals can have an important effect on the termination mechanism. Under some circumstances, rapid exit followed by re-entry and re-escape can effectively eliminate the compartmentalization of the system, leading to 'pseudo-bulk' behavior even though  $\bar{n}$  may be well below 0.5. This behavior is seen in the emulsion polymerization of MMA<sup>[54]</sup> but is unlikely in the polymerization of BMA, as its  $k_{dM}$  should be  $\sim 150$  times less than the value of MMA.

The relative probability  $P_j$  of an entering radical of length  $z$  propagating to a length  $j$  without undergoing termination is given by<sup>[5]</sup>

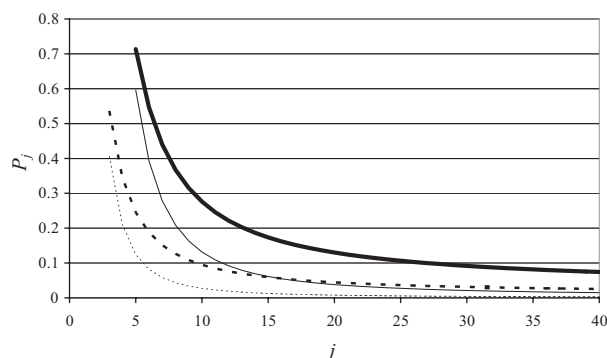
$$P_j = \prod_j^{i=z} \frac{k_p^i C_P}{k_p^i C_P + \frac{k^{iL}}{N_A V_s}} \quad (A11)$$

**Table A1.** Parameters used in determining zero-one conditions for butyl methacrylate polymerization at 70 and 50 °C.

| Parameter            | Value at 70 °C/50 °C                                                                                                                             |
|----------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|
| $k_p$                | $1.2 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} /$<br>$7.5 \times 10^2 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ |
| $k_p^1$              | $3.6 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} /$<br>$2.2 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ |
| $C_p$                | $3.8 \text{ mol} \cdot \text{L}^{-1}$                                                                                                            |
| $C_w$                | $2.5 \times 10^{-3}$                                                                                                                             |
| $D_i^{\text{com}}$   | $4.2 \times 10^{-5}$                                                                                                                             |
| $w_p$                | 0.42                                                                                                                                             |
| $M_0$                | 142                                                                                                                                              |
| $d_p$                | $1.041 \text{ kg} \cdot \text{L}^{-1}$                                                                                                           |
| $d_M$                | $0.855 \text{ kg} \cdot \text{L}^{-1}$                                                                                                           |
| $r_u$                | 53 nm                                                                                                                                            |
| $\sigma$             | 0.7 nm                                                                                                                                           |
| $p^{il}$             | 0.25                                                                                                                                             |
| $k_{tr}$ (estimated) | $2 \times 10^{-2} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$                                                                      |
| $k_d$                | $2.3 \times 10^{-5} \cdot \text{s}^{-1} / 7.0 \times 10^{-7} \cdot \text{s}^{-1}$                                                                |
| $z$                  | 2 and 4                                                                                                                                          |
| $N_C$                | $1 \times 10^{17} \text{ L}^{-1}$                                                                                                                |

where  $k_p^i$  is the propagation rate coefficient for a radical of length  $i$ ,  $V_s$  the swollen particle volume and  $k_t^{il}$  the diffusion-controlled termination rate coefficient of a long radical with a radical of length  $i$ . The value of  $k_t^{il}$  can be estimated using the following expression.<sup>[9]</sup>

$$k_t^{il} = 4\pi D^{il} p^{il} \sigma N_A \quad (\text{A12})$$



**Figure A1.** Cumulative probability of propagation  $P_j$  of an oligomeric radical to length  $j$  without termination on entering a poly(BMA) particle. Heavy curves are for 70 °C, light curves for 50 °C; broken curves  $z = 2$  and unbroken curves  $z = 4$ .

where  $D^{il}$  is the relative diffusion coefficient of a long radical and a radical of length  $i$  and  $p^{il}$  is the probability that they will terminate on encounter (defined as approaching within a distance  $\sigma$ , typically of the order of an atomic diameter). The factor  $p^{il}$  arises from the requirement that approaching radicals must have opposite spins in order to combine; there are three possible repulsive triplet states for interacting radicals of identical spin, and only one singlet state for radicals of opposite spin, giving  $p^{il} = 0.25$ . This prediction has been verified experimentally for a number of small radical species.<sup>[55]</sup>

$D^{il}$  is the sum of diffusion coefficients for centre-of-mass ( $D_i^{\text{com}}$ ) and reactive diffusion ( $D^{rd}$ ) terms. Previous work has shown that the reaction-diffusion component is unimportant in low-conversion systems such as those considered in this paper, giving  $D^{il} \approx D_i^{\text{com}}$ .<sup>[40,41]</sup>

The probability of an entering radical of length  $z$  propagating to length  $j$  without undergoing termination (Equation A10–A13) was evaluated. The calculation was performed for different initiator concentrations and for  $z = 2$  and 4 at temperatures of 50 and 70 °C. The parameters for this simulation are tabulated in Table A1, and the results obtained are displayed in Figure A1.

The propagation coefficient for a monomeric BMA radical,  $k_p^i$ , was estimated to be three times the value given by this relation, in line with the experimentally observed reactivity of similar monomeric species.<sup>[56,57]</sup> An initial estimate of  $k_{tr,M}$  was provided by using  $k_{tr,M}$  determined for MMA by Stickler and Meyerhoff.<sup>[2]</sup> The saturated concentration of BMA in the seed,  $C_p$ , was set at the value of  $3.8 \text{ mol} \cdot \text{L}^{-1}$  determined by Halnan et al.<sup>[20]</sup> This saturation value of  $C_p$  can normally be assumed to be dependent on the nature of the monomer only, and not the polymer matrix.<sup>[58]</sup>

The centre-of-mass component of the polymer diffusion coefficient  $D_i$ , a function of the weight fraction of polymer in the growing polymer particles, was estimated using a scaling relationship experimentally determined for BMA oligomers at 40 °C.<sup>[59]</sup>

$$D_i^{\text{com}}(wp) = \frac{1.69 \times 10^{-5} wp + 3.72 \times 10^{-5} wp^2}{j^{0.7+1.77wp}} \quad (\text{A13})$$

## Nomenclature

|     |                                              |
|-----|----------------------------------------------|
| A   | Pre-exponential factor of Arrhenius equation |
| A   | Chain-transfer agent                         |
| BMA | <i>n</i> -Butyl methacrylate                 |

|                       |                                                                                                                                       |                              |                                                                                                                                         |
|-----------------------|---------------------------------------------------------------------------------------------------------------------------------------|------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------|
| $c^{iL}$              | Pseudo-first order rate coefficient for termination between an entering radical of length $i$ and a long polymer radical ( $s^{-1}$ ) | $k_{tr,M}$                   | Rate coefficient for chain-transfer to monomer ( $L \cdot mol^{-1} \cdot s^{-1}$ )                                                      |
| $C_M$                 | Transfer constant to monomer, defined as $k_{tr,M}/k_p$                                                                               | $\langle k_{tr,M} \rangle$   | Average rate coefficient for chain-transfer to monomer ( $L \cdot mol^{-1} \cdot s^{-1}$ )                                              |
| $C_P$                 | Concentration of monomer in the latex particles ( $mol \cdot L^{-1}$ )                                                                | $M$                          | Molecular weight of polymer                                                                                                             |
| $C_W$                 | Concentration of monomer in the aqueous phase ( $mol \cdot L^{-1}$ )                                                                  | $M_0$                        | Molecular weight of monomer                                                                                                             |
| $C_{Wsat}$            | Saturation value of $C_W$ ( $mol \cdot L^{-1}$ )                                                                                      | MMA                          | Methyl methacrylate                                                                                                                     |
| $d_M$                 | Mean density of monomer ( $kg \cdot L^{-1}$ )                                                                                         | $\bar{M}_n$                  | Number-average molecular weight                                                                                                         |
| $d_P$                 | Mean density of polymer in latex particles ( $kg \cdot L^{-1}$ )                                                                      | $\bar{M}_w$                  | Weight-average molecular weight                                                                                                         |
| $D_i^{com}$           | Centre-of-mass diffusion coefficient of a radical of length $i$                                                                       | MWD                          | Molecular weight distribution                                                                                                           |
| $D^{iL}$              | Relative diffusion coefficient of a long radical and a radical of length $i$                                                          | $\bar{n}$                    | Average number of polymer radicals per latex particle                                                                                   |
| $D_W$                 | Diffusion coefficient of a monomeric radical in the aqueous phase ( $m^2 \cdot s^{-1}$ )                                              | $N_A$                        | Avogadro's number, $6.022 \times 10^{23}$                                                                                               |
| $dx/dt$               | Rate of change in mole fraction of polymer ( $s^{-1}$ )                                                                               | $N_C$                        | Number of latex particles per litre of aqueous phase ( $L^{-1}$ )                                                                       |
| $E_A$                 | Exponential factor of Arrhenius equation ( $J \cdot mol^{-1}$ )                                                                       | $P(M)$                       | Molecular weight distribution giving the probability of a particular polymer chain being of molecular weight $M$                        |
| $G(V_{el})$           | Size exclusion chromatography distribution of signal intensity as a function of volume                                                | $\bar{P}(M)$                 | Cumulative molecular weight distribution; the sum of all $P(M)$ s formed as experimental conditions vary within a single polymerization |
| $I$                   | Initiator                                                                                                                             | $p^{iL}$                     | Probability that two radicals will terminate on encounter (defined as approaching within a distance $\sigma$ )                          |
| $k_d$                 | Rate coefficient for decomposition of initiator ( $s^{-1}$ )                                                                          | $P_j$                        | Relative probability of an entering radical of length $z$ propagating to a length $j$ without undergoing termination                    |
| $k_{dM}$              | Rate coefficient for escape by diffusion in the aqueous phase of a monomeric radical from a latex particle ( $s^{-1}$ )               | $R_p$                        | Rate of polymerization ( $mol \cdot L^{-1} \cdot s^{-1}$ )                                                                              |
| $k_p$                 | Rate coefficient for propagation ( $L \cdot mol^{-1} \cdot s^{-1}$ )                                                                  | $r_s$                        | Radius of a monomer-swollen latex particle (m)                                                                                          |
| $\langle k_p \rangle$ | Average rate coefficient for propagation ( $L \cdot mol^{-1} \cdot s^{-1}$ )                                                          | $r_u$                        | Radius of an unswollen latex particle (m)                                                                                               |
| $k_p^1$               | Rate coefficient for propagation of a monomeric radical ( $L \cdot mol^{-1} \cdot s^{-1}$ )                                           | SEC                          | Size-exclusion chromatography                                                                                                           |
| $k_p^i$               | Rate coefficient for propagation of a radical of length $i$ ( $L \cdot mol^{-1} \cdot s^{-1}$ )                                       | $V_{cal}(M)$                 | SEC calibration function of volume of eluant as a function of molecular weight                                                          |
| $k_{p,aq}$            | Rate coefficient for propagation in the aqueous phase ( $L \cdot mol^{-1} \cdot s^{-1}$ )                                             | $w_p$                        | Weight fraction of polymer in latex particles                                                                                           |
| $K_{PBMA}, K_{PS}$    | Pre-exponential Mark-Houwink parameters for poly(butyl methacrylate) and polystyrene                                                  | $X(M)$                       | Molecular weight distribution given by SEC                                                                                              |
| KPS                   | Potassium persulfate                                                                                                                  | $z$                          | Degree of polymerization required for significant surface-activity of an aqueous phase oligomeric radical                               |
| $k_{t,aq}$            | Rate coefficient for radical termination in the aqueous phase ( $s^{-1}$ )                                                            | $\alpha_{PBMA}, \alpha_{PS}$ | Exponential Mark-Houwink parameters for poly(butyl methacrylate) and polystyrene                                                        |
| $k_{t,ij}$            | Diffusion controlled termination rate coefficient of a long radical with a radical of length $i$                                      | $\Lambda$                    | Absolute value of the slope of a plot of $\ln P(M)$ as a function of $M$                                                                |
| $k_{tr,A}$            | Rate coefficient for chain-transfer to chain-transfer agent ( $L \cdot mol^{-1} \cdot s^{-1}$ )                                       | $\rho$                       | Rate coefficient for radical entry per particle ( $s^{-1}$ )                                                                            |
|                       |                                                                                                                                       | $\sigma$                     | Distance of approach of two radicals at which probability of termination may be considered 1 (nm)                                       |

Acknowledgements: The vital contribution of Prof. Robert Gilbert (The University of Queensland) in initiating this line of research is gratefully acknowledged. Fruitful discussions with Prof. Leo Radom (The University of Sydney), Dr. Graeme Moad (CSIRO Chemical and Polymers) and Dr. Patrice Castignolles (The University of Queensland), and the assistance of Michaela Steng in carrying out preliminary experimental investigations, are greatly appreciated. The donation of the polystyrene seed latex Styrene 2 by BASF-AG is also gratefully acknowledged. The Key Centre was established and supported by the Australian Research Council's Key Centres program.

Received: January 30, 2008; Revised: April 24, 2008; Accepted: April 24, 2008; DOI: 10.1002/macp.200800059

Keywords: activation energy; chain transfer; emulsion polymerization; kinetics; molecular weight distribution; *n*-butyl methacrylate; radical polymerization

- [1] A. Ueda, S. Nagai, "Transfer Constants to Monomer", in: *Polymer Handbook*, 5<sup>th</sup> edition, J. Brandrup, E. H. Immergut, E. A. Grulke, Eds., John Wiley & Sons, New York 1999, p. II/98.
- [2] M. Stickler, G. Meyerhoff, *Makromol. Chem.* **1978**, *179*, 2729.
- [3] D. Kukulj, T. P. Davis, R. G. Gilbert, *Macromolecules* **1998**, *31*, 994.
- [4] K. Y. van Berkel, G. T. Russell, R. G. Gilbert, *Macromolecules* **2005**, *38*, 3214.
- [5] S. Maeder, R. G. Gilbert, *Macromolecules* **1998**, *31*, 4410.
- [6] R. A. Gregg, D. M. Alderman, F. R. Mayo, *J. Am. Chem. Soc.* **1948**, *70*, 3740.
- [7] R. A. Hutchinson, D. A. Paquet, J. H. McMinn, *Macromolecules* **1995**, *28*, 5655.
- [8] G. Moad, C. L. Moad, *Macromolecules* **1996**, *29*, 7727.
- [9] R. G. Gilbert, "Emulsion Polymerization: A Mechanistic Approach", 1<sup>st</sup> edition, Academic Press, London 1995.
- [10] J. P. A. Heuts, T. P. Davis, *Macromolecules* **1999**, *32*, 6019.
- [11] D. I. Christie, R. G. Gilbert, *Macromol. Chem. Phys.* **1996**, *197*, 403.
- [12] P. A. Clay, R. G. Gilbert, *Macromolecules* **1995**, *28*, 552.
- [13] H. Tobita, H. Shiozaki, *Macromol. Theory Simul.* **2001**, *10*, 676.
- [14] K. G. Suddaby, D. R. Maloney, D. M. Haddleton, *Macromolecules* **1997**, *30*, 702.
- [15] H. A. Schoonbrood, S. C. J. Pierik, B. van den Reijen, J. P. A. Heuts, A. L. German, *Macromolecules* **1996**, *29*, 6717.
- [16] J. L. De la Fuente, E. Lopez Madruga, *Macromol. Chem. Phys.* **2001**, *202*, 375.
- [17] H. A. S. Schoonbrood, A. L. German, R. G. Gilbert, *Macromolecules* **1995**, *28*, 34.
- [18] M. C. Grady, W. J. Simonsick, R. A. Hutchinson, *Macromol. Symp.* **2002**, *182*, 149.
- [19] R. Sack-Kouloumbri, G. Meyerhoff, *Makromol. Chem.* **1989**, *190*, 1133.
- [20] L. F. Halnan, D. H. Napper, R. G. Gilbert, *J. Chem. Soc. Faraday Trans. 1*, **1984**, *80*, 2851.
- [21] E. J. Behrman, J. O. Edwards, *Rev. Inorg. Chem.* **1980**, *2*, 179.
- [22] R. A. Hutchinson, D. A. Paquet, J. H. McMinn, S. Beuermann, R. E. Fuller, C. Jackson, *DEHEMA Monographs* **1995**, *131*, 467.
- [23] P. A. Clay, R. G. Gilbert, G. T. Russell, *Macromolecules* **1997**, *30*, 1935.
- [24] J. V. Castro, K. Y. van Berkel, G. T. Russell, R. G. Gilbert, *Aust. J. Chem.* **2005**, *58*, 178.
- [25] I. A. Maxwell, B. R. Morrison, D. H. Napper, R. G. Gilbert, *Macromolecules* **1991**, *24*, 1629.
- [26] A. M. van Herk, *J. Chem. Ed.* **1995**, *72*, 138.
- [27] J. P. A. Heuts, Sudarko, R. G. Gilbert, *Macromol. Symp.* **1996**, *111*, 147.
- [28] J. A. Kerr, Ed., "Rate Processes in the Gas Phase", Vol. 1, Wiley Interscience, New York 1973.
- [29] S. Beuermann, M. Buback, R. G. Gilbert, R. A. Hutchinson, B. Klumpermann, F. O. Olaj, G. T. Russell, J. Schweer, *Macromol. Chem. Phys.* **1997**, *198*, 1545.
- [30] M. Buback, B. Degener, *Makromol. Chem.* **1993**, *194*, 2875.
- [31] J. M. Asua, S. Beuermann, M. Buback, P. Castignolles, B. Charleux, R. G. Gilbert, R. A. Hutchinson, J. R. Leiza, A. N. Nikitin, J.-P. Vairon, A. M. van Herk, *Macromol. Chem. Phys.* **2004**, *205*, 2151.
- [32] A. N. Nikitin, R. A. Hutchinson, M. Buback, P. Hesse, *Macromolecules* **2007**, *40*, 8631.
- [33] S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, A. Kajiwara, B. Klumperman, G. T. Russell, *Macromol. Chem. Phys.* **2000**, *201*, 1355.
- [34] B. C. Y. Whang, M. J. Ballard, D. H. Napper, R. G. Gilbert, *Aust. J. Chem.* **1991**, *44*, 1133.
- [35] I. Capek, *Collect. Czech. Chem. Commun.* **1986**, *51*, 2546.
- [36] B. Matyska, I. Kössler, V. Šrajer, *Collect. Czech. Chem. Commun.* **1958**, *23*, 1456.
- [37] A. S. Nair, M. S. Muthana, *Makromol. Chem.* **1961**, *47*, 128.
- [38] R. A. Hutchinson, M. T. Aronson, J. R. Richards, *Macromolecules* **1993**, *26*, 6410.
- [39] U. Bergert, M. Buback, J. Heyne, *Macromol. Rapid Commun.* **1995**, *16*, 275.
- [40] R. A. Lyons, J. Hutovic, M. C. Piton, D. I. Christie, P. A. Clay, B. G. Manders, S. H. Kable, R. G. Gilbert, *Macromolecules* **1996**, *29*, 1918.
- [41] S. Beuermann, D. A. Paquet, J. H. McMinn, R. A. Hutchinson, *Macromolecules* **1996**, *29*, 4206.
- [42] M. Buback, U. Geers, C. H. Kurz, J. Heyne, *Macromol. Chem. Phys.* **1997**, *198*, 3451.
- [43] T. P. Davis, K. F. O'Driscoll, M. C. Piton, M. A. Winnik, *Macromolecules* **1990**, *23*, 2113.
- [44] R. A. Hutchinson, D. A. Paquet, J. H. McMinn, R. E. Fuller, *Macromolecules* **1995**, *28*, 4023.
- [45] C. Former, J. Castro, C. M. Fellows, R. I. Tanner, R. G. Gilbert, *J. Polym. Sci. Polym. Chem.* **2002**, *40*, 3335.
- [46] R. Balic, C. M. Fellows, A. M. van Herk, *Macromol. Res.* **2004**, *12*, 323.
- [47] K. Hemelsoet, V. Van Speybroeck, D. Moran, G. B. Marin, L. Radom, M. Waroquier, *J. Phys. Chem. A* **2006**, *110*, 13624.
- [48] P. Brandi, C. Galli, P. Gentili, *J. Org. Chem.* **2005**, *70*, 9521.
- [49] D. L. Reid, G. V. Shustov, D. A. Armstrong, A. Rauk, M. N. Schuchmann, M. S. Akhlaq, C. von Sonntag, *Phys. Chem. Chem. Phys.* **2002**, *4*, 2965.
- [50] M. Finn, R. Friedline, N. K. Suleman, C. J. Wohl, J. M. Tanko, *J. Am. Chem. Soc.* **2004**, *126*, 7578.
- [51] R. X. E. Willemsse, A. M. van Herk, E. Panchenko, T. Junkers, M. Buback, *Macromolecules* **2005**, *38*, 5098.
- [52] T. Junkers, S. P. S. Koo, T. P. Davis, M. H. Stenzel, C. Barner-Kowollik, *Macromolecules* **2007**, *40*, 8906.
- [53] G. Lichti, R. G. Gilbert, D. H. Napper, *J. Polym. Sci. A* **1980**, *18*, 1297.

- [54] M. J. Ballard, D. H. Napper, R. G. Gilbert, *J. Polym. Sci., Polym. Chem. Edn.* **1984**, *22*, 3225.
- [55] H. Fischer, P. Henning, *Acc. Chem. Res.* **1987**, *20*, 200.
- [56] M. Deady, A. W. H. Mau, G. Moad, T. H. Spurling, *Makromol. Chem.* **1993**, *194*, 1691.
- [57] B. R. Morrison, I. A. Maxwell, R. G. Gilbert, D. H. Napper, *ACS Symp. Series-Polymer Latexes-Preparation, Characterization and Applications*, Vol. 492, E. S. Daniels, E. D. Sudol, M. El-Aasser, Eds., American Chemical Society, Washington D.C 1992, p. 28.
- [58] H. A. Schoonbrood, PhD Thesis, Eindhoven University of Technology, Netherlands 1994.
- [59] M. C. Griffiths, J. Strauch, M. J. Monteiro, R. G. Gilbert, *Macromolecules* **1998**, *31*, 7835.