CHAIN TRANSFER CONSTANTS IN THE EMULSION COPOLYMERIZATION OF ACRYLONITRILE AND BUTYL ACRYLATE
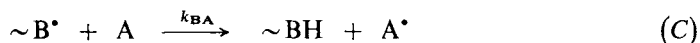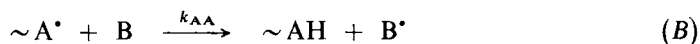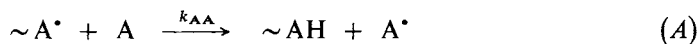
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Chain transfer constants to monomer have been measured by an emulsion copolymerization technique at 70°C. The effects of ammonium persulfate (I) and sodium dodecylphenoxybenzene-disulphonate (E) on the chain transfer mechanism in the emulsion copolymerization of acrylonitrile and butyl acrylate have been investigated. For the system with the emulsifier concentration ([E] $7.32 \cdot 10^{-2}$ mol dm^{-3} and the initiator concentration ([I]) $2.28 \cdot 10^{-2}$ mol dm^{-3} (the concentrations related to water volume) the relative transfer constant to monomer is $5.7 \cdot 10^{-5}$ for acrylonitrile polymerization and $1.05 \cdot 10^{-4}$ for the polymerization of butyl acrylate. In the system with lower [E] $0.63 \cdot 10^{-2}$ mol dm^{-3} and the same [I] as given above the relative transfer constant to monomer is $3.33 \cdot 10^{-5}$ for both acrylonitrile and butyl acrylate polymerizations. In the system with [E] $7.32 \cdot 10^{-2}$ mol dm^{-3} and [I] $1.4 \cdot 10^{-2}$ mol dm^{-3} the relative transfer constant to monomer is $1.02 \cdot 10^{-4}$ for acrylonitrile and $1.25 \cdot 10^{-4}$ for butyl acrylate polymerizations.

We show in this paper that a classical theory permits estimation of chain transfer constants between each monomer and macroradical in an emulsion copolymerization system. In emulsion systems the normal termination is suppressed and chain transfer processes are thought to be the most significant in determining the number-average degree of polymerization. The chain transfer to initiator, solvent or polymer need not be considered; the chain transfer to initiator[1] is unlikely, there is no solvent, and transfer to polymer does not affect the number-average molecular weight of the copolymer. Thus the chain transfer to monomer within polymer particles are most significant and it involves the following steps

$$\sim A^\bullet \;+\; A \;\xrightarrow{\;k_{AA}\;}\; \sim AH \;+\; A^\bullet \tag{A}$$

$$\sim A^\bullet \;+\; B \;\xrightarrow{\;k_{AA}\;}\; \sim AH \;+\; B^\bullet \tag{B}$$

$$\sim B^\bullet \;+\; A \;\xrightarrow{\;k_{BA}\;}\; \sim BH \;+\; A^\bullet \tag{C}$$

$$\sim B^\bullet \;+\; B \;\xrightarrow{\;k_{BB}\;}\; \sim BH \;+\; B^\bullet \tag{D}$$

Here $\sim A^{\bullet}$ and $\sim B^{\bullet}$ represent growing radicals with terminal units in monomers A and B, respectively. $A^{\bullet}$ and $B^{\bullet}$ are radicals derived by transfer into monomers and they are capable of reinitiating the polymerization without any change in the rates of polymerization, and k_{AA}, k_{AB}, k_{BA}, and k_{BB} are transfer rate constants.

The rate of chain transfer to monomer for this emulsion copolymerization system is given by

$$R_{tr} = k_{AA}[A^{\bullet}][A] + k_{AB}[A^{\bullet}][B] + k_{BA}[B^{\bullet}][A] + k_{BB}[B^{\bullet}][B], \qquad (1)$$

where the square brackets denote concentrations. The number-average degree of polymerization, $\bar{P}_n$, can be expressed as

$$\bar{P}_n = \frac{R_p}{R_i/n + R_{tr}}, \qquad (2)$$

where R_i is the rate of initiation, R_p is the overall polymerization rate and n is 2 (for emulsion systems). Rudin and coworkers[2,3] showed that a straightforward application of the simple copolymer theory permits estimation of chain transfer constants to monomer in the emulsion copolymerization system. The assumptions are here standart and include the steady-state radical concentration and the independence of the rate constants on macroradical size, and authors neglect other transfer reactions. Thus the number-average degree of polymerization is related to kinetic parameters by following Eqs (3) and (4):

$$\frac{1}{\bar{P}_n} = \frac{R_i}{n}\frac{1}{R_p} + k_{AA}\frac{\varrho}{\beta} + k_{BB}\frac{\sigma L^2}{\beta} + (k_{AB}\varrho + k_{BA}\sigma)\frac{L}{\beta}, \qquad (3)$$

where L is the monomer ratio $[B]/[A]$, β is $r_1 + 2L + r_2 L^2$, ϱ is r_1/k_{pAA}, σ is r_2/k_{pAA}, r_1 and r_2 are the reactivity ratios, and k_{pAA} and k_{pBB} are the propagation constants for monomer A and B, respectively. Substitution of the expressions for C ($C_{jj} = k_{jj}/k_{pjj}$), ϱ, σ, and $r_1 = k_{pAA}/k_{pAB}$, $r_2 = k_{pBB}/k_{pBA}$ into Eq. (3) gives

$$\frac{1}{\bar{P}_n} = \frac{R_i}{n}\frac{1}{R_p} + \frac{C_{AA}r_1}{\beta} + \frac{C_{BB}r_2 L^2}{\beta} + (C_{AB} + C_{BA})\frac{L}{\beta}. \qquad (4)$$

The homopolymerization rate consants and reactivity ratios must be known for these calculations. Values for R_i, transfer rate constants k_{AA} and k_{BB} and term ($k_{AB}\varrho + k_{BA}\sigma$) can be determined from Eq. (3). These four unknowns can be generated from $\bar{P}_n$ and R_p data obtained in the emulsion copolymerization from four different monomer concentrations using Eq. (3). The cross-transfer rate constants k_{AB} and k_{BA} cannot be determined independently of each other because they dependent on the same parameter L. Rudin and coworkers[2,3] succesfully applied the method for de-

termination of the transfer constants to monomer in styrene/α-methylstyrene and styrene/methyl methacrylate emulsion systems.

Here it has been applied this method determining homo- and cross-transfer constants for acrylonitrile and butyl acrylate in the emulsion copolymerization.

It should be emphasized that the values of relative transfer constants to monomer calculated by Eq. (3) (which is derived under some assumptions) may give only rough information about chain transfer processes in the emulsion polymerization. Advantages of this method are ascribed to convenience of the technique and its applicability for copolymerization.

It is important to verify the polymerization technique used for determining the relative transfer constants to monomer for a system with high rate of initiation in which one of the comonomers has high water solubility. Acrylonitrile and butyl acrylate can be considered as model monomers for such investigation. Although the relative transfer constants to monomer for acrylonitrile and butyl acrylate in homogeneous polymerizations are well known, the homo- and cross-transfer rate constants to monomer in dispersion polymerizations have so far not been reported.

EXPERIMENTAL

Material

The acrylonitrile (A) and butyl acrylate (B) monomers were purified by conventional methods[4]. Analytical grade ammonium persulfate (I) was used as polymerization initiator. The anionic emulsifier sodium dodecylphenoxybenzenedisulphonate (E) was used as supplied. Twice distilled water was used as polymerization medium.

Polymerization Procedure

Emulsion copolymerizations of acrylonitrile and butyl acrylate were carried out at 70°C. The recipe in all runs comprised 140 g of water, 96·6 g of monomers, and 0·772 g or 0·474 g of ammonium persulfate. The conventional batch technique was used for following the polymerization history[4]. The swelling of the final latexes and determination of $\omega_{m/p}$ (the ratio of the weight of monomer and polymer in the particles) were done as described previously[5]. The number-average molecular weights were measured on a Membrane osmometer (Knauer Co.) in acetone at 30°C.

RESULTS AND DISCUSSION

The measured rates of copolymerization of acrylonitrile and butyl acrylate in the interval 2 and the number-average degrees of polymerization for copolymers obtained at 100% conversion are listed in Table I. It is evident that the rates of copolymerization are strongly influenced by the emulsifier concentration in the feed. It has been found that the polymerization rate is proportional approximately to the 0·5 power of the emulsifier concentrations ($[E]$) (cf. systems 1 and 3) and to the 0·3 power of the initiator concentration ($[I]$) (cf. systems 1 and 2). In the light of the Smith–

–Ewart–Gardon theory the rate of the emulsion polymerization is[6,7]

$$R_p \sim [I]^{0.4} \cdot [E]^{0.6} . \tag{5}$$

It is seen that the experimental values of the reaction orders for the initiator and the emulsifier are somewhat lower than those given in Eq. (5). However, as it was shown in literature[7] the relation between the rate of polymerization and concentrations of initiator and emulsifier (Eq. 5) is held only for latexes of very small particle sizes $(d \leqq 100 \text{ nm})$ prepared at low initiation rate. In the emulsion copolymerization of butyl acrylate and acrylonitrile middle size particles $(d \geqq 100 \text{ nm})$ were generated and copolymerizations proceeded at high initiation rate[4]. Due to these factors and high water-solubility of acrylonitrile[8] deviations from the predictions of Eq. (5) in the emulsion copolymerization of acrylonitrile and butyl acrylate are observed.

The sets of experimental data given in Table I were fitted in Eq. (3) to estimate the relative transfer constants to monomer and the rate of initiation. The estimated values of the transfer constants to monomer and the rates of initiation at two different concentrations of initiator and emulsifier are listed in Table II. For these calculations the literature values of propagation rate constants for homopolymerizations of acrylonitrile and butyl acrylate and reactivity ratios for acrylonitrile/butyl acrylate comonomer system were used. The propagation rate constants k_{pAA} (acrylonitrile) and k_{pBB} (butyl acrylate) were taken to be $5.0 \cdot 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $2.0 \cdot 10^3 \text{ dm}^3 \cdot \text{ mol}^{-1} \text{ s}^{-1}$ (ref.[9]). The reactivity ratios r_A and r_B were taken to be 1.082 and 0.816 (ref.[10]), respectively.

The rate of initiation can be obtained from equation

$$R_i = 2fk_d[I] . \tag{6}$$

TABLE I

Overall polymerization rate (R_p) and number-average degree of polymerization $(\bar{P}_n)$ in the emulsion copolymerization of acrylonitrile and butyl acrylate (x_B denotes mole fraction of this comonomer). Systems (the concentrations in $10^{-2} \text{ mol cm}^{-3}$ related to water volume): 1 [E] = = 7.32, [I] = 2.28; 2 [E] = 7.32, [I] = 1.4; 3 [E] = 0.63, [I] = 2.28

x_B	$R_p \times 10^3$, mol dm^{-3} s^{-1}			$\bar{P}_n \times 10^{-3}$		
	1	2	3	1	2	3
0.788	30.5	29.0	8.5	8.5	7.2	7.3
0.625	35.3	25.0	8.7	8.5	7.1	6.9
0.435	23.5	23.0	8.5	9.2	7.4	6.2
0.410	26.0	20.0	10.9	10.0	7.8	7.2

If we estimate k_d (the decomposition rate constant) at 70°C to be $7 \cdot 0 \cdot 10^{-5}$ s^{-1} (refs[11,12]) and f (the initiator efficiency) is estimated to be 0·7 (ref.[3]) using initiator concentration (related to water volume) $2 \cdot 28 \cdot 10^{-2}$ mol dm^{-3} (used in the systems *1* and *3*) and $1 \cdot 4 \cdot 10^{-2}$ mol dm^{-3} (in the system *2*), the calculated rates of initiation are $2 \cdot 23 \cdot 10^{-6}$ mol dm^{-3} s^{-1} and $1 \cdot 3 \cdot 10^{-6}$ mol dm^{-3} s^{-1}, respectively. The values of R_i calculated from Eq. (6) are somewhat higher than those listed in Table II. A small deviation from the calculated value is observed in the system *3* with the lowest emulsifier concentration (around CMC of E). If the copolymerization of acrylonitrile and butyl acrylate is carried out at a lower concentration of initiator (system *2*), the magnitude of R_i (see Table II) is by an order lower than that calculated by Eq. (6). This effect may be explained in terms of the retardation of the polymerization process by E itself[13]. The interaction of the primary radicals derived from persulfate and/or of oligomer radicals with emulsifier molecules may lead to deactivation of an active radical center and to the decrease of the rate of initiation. On the other hand it was confirmed[14,15] that the rate of thermal decomposition of persulfate increases considerably in the presence of the emulsifier. Thus the free radicals derived from the emulsifier molecules may either take part in the initiation of the polymerization processes within the micelles and the poylmer particles or in the aqueous phase or in the retardation of the initiation step when the radicals are enought stable.

The monomer transfer constants for acrylonitrile and butyl acrylate in the systems *1* and *2* (with the high [E]) are nearly by an order of magnitude higher the than those for the system *3* (with lower [E]). The monomer transfer constants in the system with the low [E] are similar to those reported by other authors[16,17] for homogeneous polymerization of acrylonitrile ($C_A = 2 \cdot 6 \cdot 10^{-5}$) and butyl acrylate ($C_B = 4 \cdot 0 \cdot 10^{-5}$).

The sum of the cross-transfer constants ($C_{AB} + C_{BA}$) is higher than the sum of

TABLE II

Rate transfer constants (k_{AA} and k_{BB}), relative transfer constants ($C_{AA} = k_{AA}/k_{pAA}$, $C_{BB} = k_{BB}/k_{pBB}$), the sum of cross-transfer constants to monomer ($C_{AB} + C_{BA}$), and the rate of initiation (R_i) of the emulsion copolymerization of acrylonitrile (A) and butyl acrylate (B). Systems *1*, *2*, and *3* as denoted in Table I

System	$\dfrac{k_{AA}}{\text{dm}^3\,\text{mol}^{-1}}$	$\dfrac{k_{BB}}{\text{s}^{-1}}$	$c_{AA} \cdot 10^5$	$c_{BB} \cdot 10^5$	$(C_{AB} + C_{BA}) \cdot 10^5$	$\dfrac{R_i \cdot 10^6}{\text{mol dm}^{-3}\,\text{s}^{-1}}$
1	0·28	0·21	5·7	10·5	29	1·4
2	0·51	0·25	10·2	12·5	31	0·13
3	0·166	0·065	33·33	3·33	8·0	2·0

homotransfer constants. This is not to be expected from this pair of monomers since each reactivity ratio is about 1·0. The results show that the probability of cross-transfer ractions exceeds that of homotransfer by a factor 1·8 in the system *1*, 1·36 in the system *2*, and 1·2 in the system *3*.

According to Eq. (*3*), the value of $\bar{P}_n$ is related to the monomer feed ratio *L* as shown. As a reaction proceeds the feed composition in acrylonitrile/butyl acrylate system drifts[8] and the molecular weight of copolymer being produced will also change as a functions of reaction time[18,19]. Hence, the molecular weight of copolymer samples withdrawn from the reaction mixture should be measured at the beginning of the interval 2. The study of acrylonitrile/butyl acrylate system, however, was based on values of the molecular weight that were measured for copolymers withdrawn in the interval 3. This could have resulted in values of the molecular weight which were lower than produced at interval 2 (refs[18,19]) and yielded relative transfer constants to monomer and rates of initiation that were relative high.

It is reasonable to suppose that the magnitude of both transfer constants to monomer and the initiation rate depends on the applicability of Eq. (*3*) for measured values of rate of polymerization and molecular weight of copolymers. It is necessary to discuss the effect of *n* in Eq. (*3*) on the magnitude of calculated parameters. For homogeneous polymerization *n* denotes the mode of termination, *i.e.*, *n* is 2 when termination (here between two macroradicals) occurs by coupling and 1 when termination occurs by disproportionation. In the emulsion systems the termination within polymer particles takes place between macroradicals and primary or oligomer radicals. Consequently, the mode of termination within latex particles can not influence the molecular weight of polymer former, *i.e.*, the molecular weight of polymer is given by the chain length of macroradicals. The chain termination is regulated mainly by the rate of entry of free radicals into monomer-swollen polymer particles. Smith and Ewart[6] previously reported that no two radicals can coexist in a particle. If the radical enters the growing particle, it will immediatelly terminate the growth of the chain. Thus, each particle contains one radical for half time an the average-number of radicals *per* particle (*Q*) is 0·5. It follows that every second entering radical can initiate the growth of the chain and therefore the value of *n* (in Eq. *3*) was taken to be 2. However, as it was shown[6-8] this assumption holds only for polymerization of monomers with very low water solubility. In the acrylonitrile/butyl acrylate system copolymerizations have proceeded at high initiation rate and one of the monomers (acrylonitrile) has a high water solubility. This could have resulted in some deviation from Eq. (*3*) for the present copolymer system.

Molecular weight of polymer is found to be function of the rate constants for free radical propagation, entry of radicals to polymer particles, exit of radicals from latex particles and bimolecular termination[19,20]. Besides, the high water souilblity of monomer predicts the high rate of radical desorption from polymer particles[20], which rather decreases the rate of polymerization.

The procedure described here does not takes into account the chain transfer to polymer and emulsifier. The chain transfer to polymer does not affect the number--average molecular weight and the new polymer radical would not reinitiate the polymerization selectively. Therefore it is not necessary to considere the chain transfer to polymer and add the additional term to Eq. (*3*). On the basis of literature data[3,7] the emulsifier was thought to be inactive agent which does not influence the rate of polymerization and the molecular weight of polymer. Emulsion polymerization data obtained recently in the presence of sodium dodecylphenoxybenzenedisulphonate indicate that the emulsifier temperately decreases the polymerization rate[5,8]. It proposes that some additional terms should be added to the right-hand side of Eq. (*3*). This would lead to complicated calculation of all parameters.

It should be emphasized, however, that the values of the relative transfer constants to monomer and the rate of initiation calculated by simplified Eq. (*3*), have not been checked by other calculations or actual measurements. While the estimated values are plausible, they probably reflect discrepancies between the simple mode Eq. (*3*) and the real systems.

These observation reveal the complex character of the present comonomer system and final conclusion about the nature of the chain transfer mechanism is still open to theoretical and experimental verification.

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