CHAPTER 4

Reactivities of monomers

Contents

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Monomer reactivity in emulsion and microemulsion media.

[4.1] Introduction

Monomer reactivity is one of the important parameters that determines the kinetics of a copolymerisation process. In addition, the copolymer properties depend mainly on their monomer reactivities [1] and hence their knowledge helps us to tailor the properties of the resulting copolymer. The determination of monomer reactivity therefore has critical importance. In the case of heterogeneous systems, like emulsion and microemulsion, additional parameters such as monomer partitioning lead to larger spread in the reactivity ratios when feed concentrations have been used for calculations, especially for comonomer pairs involving at least one polar monomer [2 - 4]. Therefore in the present chapter monomer reactivity ratios were recalculated considering the effect of monomer partitioning and were termed as **true reactivity ratios**. Monomer pairs of varying solubility and polarity used for the study in microemulsion are

- Monomers with similar polarity and solubility e.g. ethyl acrylate [EA] and methylmethacrylate [MMA].
- Monomers with different solubility and polarity, e.g. styrene [Sty] and methylacrylate [MA] , styrene - MMA and styrene – acrylonitrile [AN]
- Monomers with similar solubility but different polarity, e.g. styrene [Sty] and butylacrylate [BA].

The first system EA – MMA in emulsion and microemulsion has been extensively studied in our laboratory while the reported microemulsion copolymerisation data [5] for styrene – MA and styrene – BA, has been used for the calculation of the monomer concentration at polymerisation loci and subsequently for the recalculation of the true reactivity ratios.

[4. 2] Copolymerisation of EA - MMA

Polymerisation of a microemulsion comprising 10 g of monomer mixture, 15 g SDS and 75 g water was carried out in a three-neck reaction kettle equipped with a mechanical stirrer, nitrogen inlet and condenser. The reaction mass was purged with nitrogen for 15 min. The reactions were carried out at 70 ^{0}C using 0.76 mM KPS. The copolymer was precipitated with five-fold excess of methanol and washed several times with water. In order to remove the emulsifier completely, the copolymers were dissolved in acetone and reprecipitated in water. Polymerisation of an emulsion comprising 25 g monomer mixture, 0.5 g SDS and 74.5 g water was carried out in a three neck reaction vessel equipped with a mechanical stirrer, nitrogen inlet and condenser. The emulsions were polymerised and processed in the same way as the microemulsions. The products were isolated at less than 5% conversion for all the feed compositions.

The reported copolymerisation data by Xu et al. [5] for the microemulsion copolymerisation of styrene - methylacrylate and styrene - butylacrylate was used to calculate the monomer concentration at the polymerisation loci and subsequently the true reactivity ratios. In their work, 15g mixed monomers were charged into 85 g aqueous solution of sodium 12- hexinoylox-9-octadecenate , SHOA [15 wt% based on water].

Fig 4.1 shows the representative NMR spectrum of EA [0.5] - MMA [0.5] copolymer. The signal for the methyl protons of $O - CH_3$ group from MMA appeared around 3.6 ppm and that for protons from $O - CH_2$ group from ethylacrylate appeared around 4.07 ppm. The MMA mole fraction [F_{MMA}] in the copolymer was calculated from the area under peak for the $O\text{-}CH_3$ protons from MMA and the peak area for $O\text{-}CH_2$

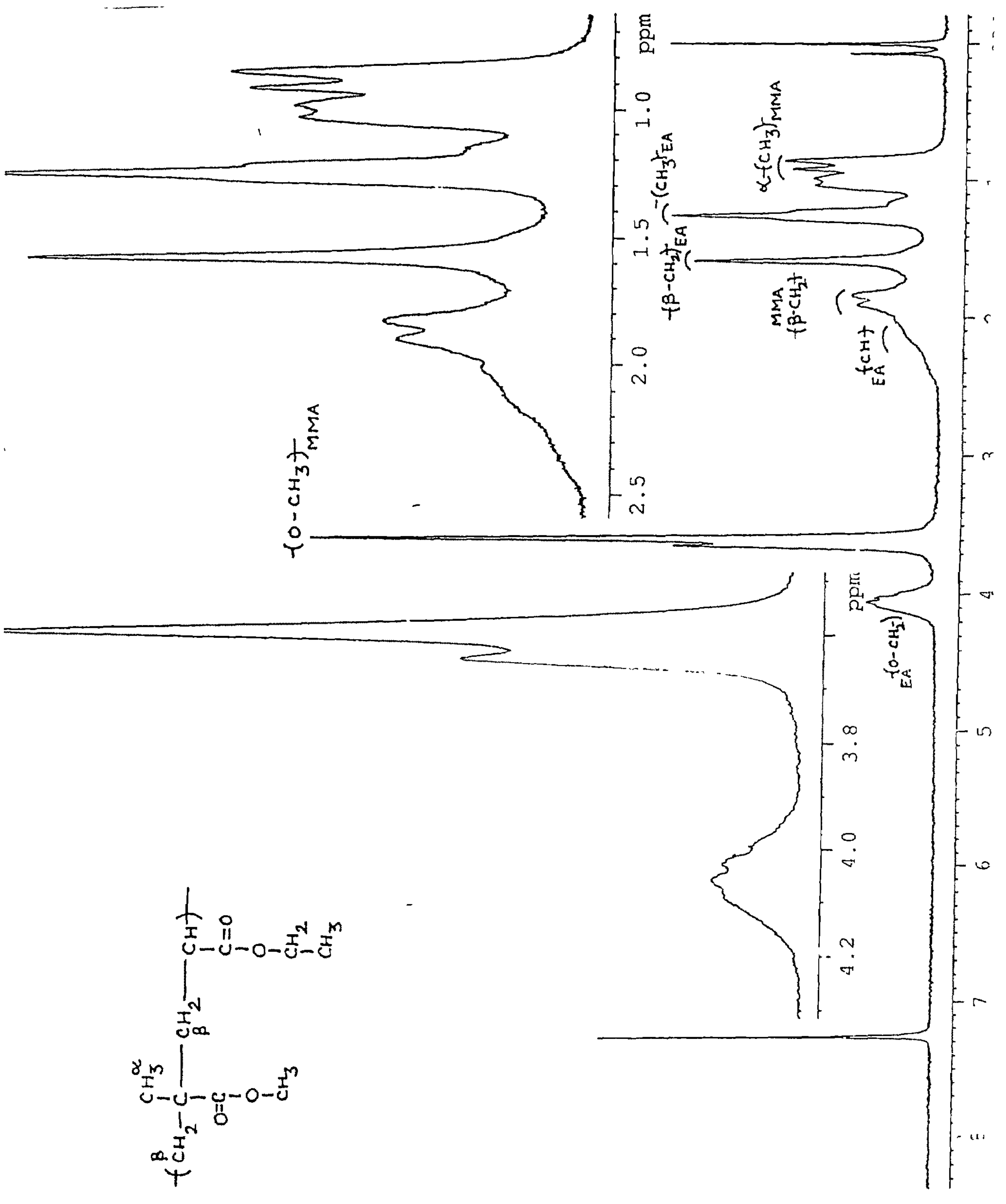


Fig 4.1 : ^{1}H NMR spectra of EA – MMA copolymers synthesized through emulsion polymerisation. MMA in feed 0.5 and in copolymer 0.651.

protons from ethylacrylate using the equation reported for the bulk polymerisation of EA-MMA[6] .

$$F_{MMA} = 2 X A_{MMA} / 2 X A_{MMA} + 3 X A_{EA}$$

The copolymerisation data required for the determination of reactivity ratios of ethylacrylate– methylmethacrylate, styrene-butylacrylate and styrene-methylacrylate is given in Table 4.1, 4.2 and 4.3 respectively and the calculated reactivity ratios are given in Table 4.4. The NMR spectrum in Fig 4 . 2 shows the configurational effect; due to the splitting of the β - methylene protons of MMA in the EA – MMA copolymer synthesised through microemulsion.

Table 4 . 1 : Copolymer composition and monomer concentration at polymerization loci for EA – MMA in microemulsion.

f_{EA}	0.9	0.75	0.66	0.50	0.25	0.1
f_{MMA}	0.1	0.25	0.33	0.50	0.75	0.90
f'_{EA}	0.899	0.749	0.665	0.498	0.249	0.099
f'_{MMA}	0.100	0.250	0.334	0.501	0.75	0.9
f'_{EA} / f_{EA}	0.998	0.998	0.998	0.996	0.996	0.990
f'_{MMA}/f_{MMA}	1.000	1.000	1.003	1.002	1.000	1.000
f'_{EA}/ f'_{MMA}	8.96	2.98	1.991	0.995	0.331	0.11
F_{EA}	0.73	0.52	0.39	0.30	0.13	0.05
F_{MMA}	0.27	0.48	0.61	0.70	0.87	0.95
F'_{EA}	0.72	0.51	0.42	0.29	0.13	0.05
F'_{MMA}	0.28	0.49	0.58	0.71	0.87	0.95
F_{EA} (b)	0.72	0.51	0.42	0.30	0.13	0.05
F_{MMA} (b)	0.28	0.49	0.58	0.70	0.87	0.95

f_{EA} , f_{MMA}: Feed concentrations of ethylacrylate and methylmethacrylate

f'_{EA},f'_{MMA}: Loci Concentration of ethylacrylate and methylmethacrylate .

F_{EA}: Ethylacrylate fraction in copolymer synthesised through microemulsion.

F_{MMA} . MMA fraction in copolymer synthesised through microemulsion polymerisation

F'_{EA} : EA fraction in the copolymer as predicted by Terminal model for microemulsion copolymerisation.

F'_{MMA} : MMA fraction in the copolymer as predicted by Terminal model for microemulsion copolymerisation.

F_{EA} (b): Ethylacrylate fraction in the copolymer synthesised through bulk polymerisation from ref 6.

F_{MMA}(b) : Methylmethacrylate fraction in the copolymer synthesised through bulk polymerisation from ref. 6.

Table 4 . 2 : Copolymer composition and monomer concentration at polymerization loci for Sty – BA in microemulsion.

f_{STY}	0.256	0.338	0.386	0.448	0.495	0.561	0.591	0.652	0.700	0.783	0.827
f_{BA}	0.744	0.662	0.614	0.552	0.505	0.439	0 409	0 348	0 3	0 217	0 173
f'_{sty}	0.199	0.269	0.312	0.369	0.414	0.479	0.510	0.574	0.627	0.722	0.775
f'_{BA}	0.801	0.731	0.688	0.631	0.586	0.521	0.49	0.426	0.373	0.278	0.225
f'_{Sty}/ f_{StY}	0.777	0.795	0.808	0.823	0.836	0.853	0.862	0.880	0.895	0.922	0.937
f'_{BA}/ f_{BA}	1.076	1.104	1.120	1.143	1.160	1.186	1.198	1.224	1.243	1.281	1.3
f'_{STY}/ f'_{BA}	0.247	0.367	0.452	0.584	0.705	0.920	1.04	1.348	1.68	2.597	3.441
F_{Sty}	0.453	0.478	0.49	0 523	0.55	0.587	0.619	0.653	0.693	0.751	0.775
F_{BA}	0.554	0 522	0.51	0.477	0.45	0.413	0.381	0.347	0.307	0.249	0.225
F'_{Sty}	0.421	0.48	0.507	0.54	0.564	0.599	0.615	0.653	0.681	0 742	0.78
F'_{BA}	0.579	0.52	0.493	0.46	0.436	0.401	0.385	0.347	0.319	0.258	0.22
F_{sty} (b)	0.485	0.510	0 544	0.575	0.6	0.647	0.659	0.705	0.737	0.758	0.774
F_{BA} (b)	0.515	0.49	0.456	0.425	0.4	0.353	0.341	0.295	0.263	0.242	0.226

Symbol as in Table 4.1 except Sty represents styrene and BA represent butylacrylate.

Table 4.3: Copolymer composition and monomer concentration at polymerization loci for Sty – MA in microemulsion.

fStY	0.282	0.331	0.404	0.48	0.523	0.667
fMA	0.718	0.669	0.596	0.52	0.477	0.333
f 'StY	0.422	0.479	0.558	0.632	0.671	0.789
f ' MA	0.578	0.521	0.442	0.368	0.329	0 211
f 'StY / fSt y	1.496	1.447	1.381	1.316	1.282	1.182
f ' MA / fMA	0.805	0 778	0 741	0.707	0.689	0.633
f'StY/ f'MA	0.7305	0.920	1 26	1.716	2.039	3.725
FSTY	0.558	0.578	0.637	0.684	0.712	0.791
F MA	0.442	0.422	0.363	0.316	0.289	0.209
F ' StY	0.555	0.588	0.635	0.681	0.707	0.791
F ' MA	0.445	0.412	0.365	0.319	0.293	0 209
F Sty (b)	0.458	0.507	0.545	0.588	0.603	0.727
F MA (b)	0 542	0.493	0.455	0 412	0.397	0.273

Symbol as in Table 4.1 except Sty represents Styrene and MA represents methylacrylate.

[4. 3] Determination of Monomer Reactivity

Conventional monomer reactivity now onwards termed as apparent reactivity, in microemulsion medium, for three different monomer pairs with varying solubility and polarity was calculated from the knowledge of feed concentration and copolymer composition using Finemann Ross , FR [linear method] [7] and Non Linear Least Square method, NLLS [8][Table 4 .4]. The values obtained for Sty – MA and Sty – BA show deviation from bulk values, whereas EA – MMA behaved as an ideally

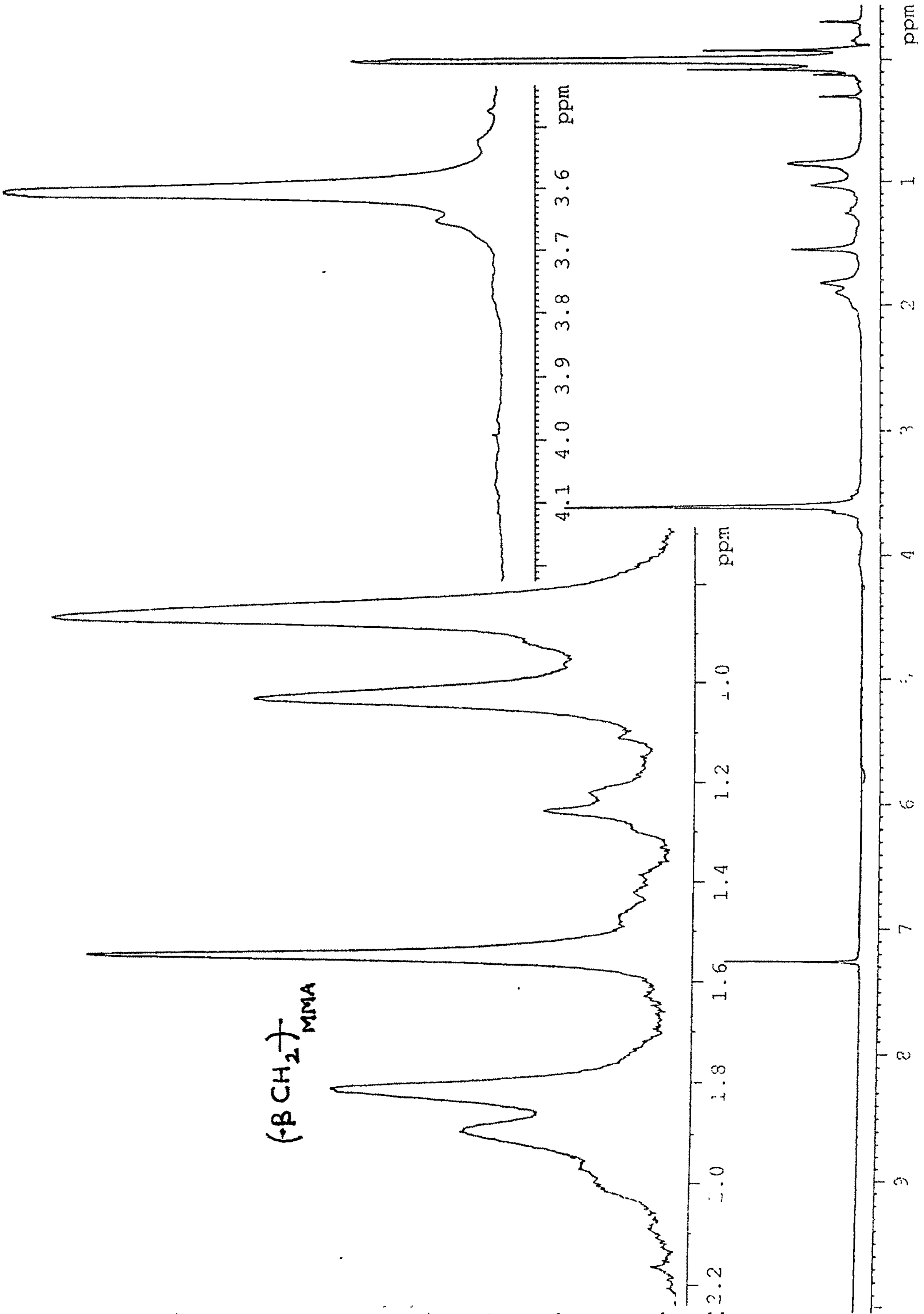


Fig 4. 2 : ^{1}H NMR spectra of EA / MMA copolymer produced by microemulsion copolymerisation. The mole fraction of MMA in the feed 0.9 and that in copolymer 0.95.

compartmentalized bulk polymerization. For bulk polymerisation copolymer composition depends solely on their monomer reactivity at lower conversion. Therefore the bulk values can be taken as a reference system. A deviation from the bulk value for a heterogeneous system like microemulsion is mainly due to the effect of monomer partitioning between aqueous phase and organic phase [monomer droplets]. The deviation becomes more apparent with an increase in the relative difference in solubility and polarity of the comonomers.

In the case of **styrene – MA** there is a large difference in solubility of Sty [0.027 %] and MA [5.2 %]. A predominant polymerisation in the droplets therefore leads to a greater fraction of styrene in the copolymer compared to bulk under identical feed concentration. Monomer partitioning therefore leads to a drift in the copolymer composition.

Very little relative difference in solubility and polarity in the case of EA – MMA monomers leads to insignificant drift in copolymer composition compared to bulk under identical monomer feed concentration [Table 4.1]. Thus the apparent reactivity ratio hardly deviates from the bulk value.

For **styrene – butylacrylate** system both Sty and BA are practically insoluble in water. Their solubility in water is 0.027 and 0.2 % respectively. Therefore both Sty and BA partition mainly in the microdroplets. Since microemulsion is a compartmentalized system predominant polymerization in the microdroplets should result in very close bulk and microemulsion reactivity. But the apparent reactivities both reported and those calculated by us using FR and NLLS method [Table 4 . 4] differ from the bulk value Inorder to gain convergence in these values it is necessary to include the effect of partitioning in the calculation of monomer reactivity.

Table 4 . 4 : Reactivity ratio of Styrene-BA , Styrene-MA and EA-MMA.

Reactivity Ratio in Bulk			**Reactivity Ratio in Microemulsion**					
			Apparent			**True**		
MMA-EA system								
MMA	EA	$r_{MMA}\ r_{EA}$	MMA	EA	$r_{MMA}.r_{EA}$	MMA	EA	$r_{MMA}.r_{EA}$
2.03	0.24	0.49	2.0	0.25	0.52	2.12	0.24	0.51
from Ref. 8 by Mayo- Lewis method			Our work by Fine Mann Ross method					
			2.1	0.25	0.50	2.18	0.25	0.54
			Our work by NLLS method					
Styrene-Methyl acrylate								
Sty	MA	$r_{Sty}\ r_{MA}$	Sty	MA	$r_{Sty}\ r_{MA}$	Sty	MA	$r_{Sty}\ .r_{MA}$
0.84	0.21	0.18	1.50	0.11	0.17	0.81	0.19	0.16
from Ref.5 by Tidwell Mortimer method			Calculated by Fine Mann Ross method using data from ref 5					
			1.35	0.079	0.11	0.80	0.20	0.16
			Calculated by NLLS method using data from Ref.5					
Styrene-Butylacrylate								
Sty	BA	$r_{sty}\ r_{BA}$	Sty	BA	$r_{sty}.\ r_{BA}$	Sty	BA	$r_{sty}.\ r_{BA}$
0.79	0.15	0.12	0.50	0.25	0.12	0.78	0.14	0.12
from Ref.5 by Tidwell Mortimer method			Calculated by Fine Mann Ross method using data from Ref.5					
			0.50	0.25	0.12	0.77	0.14	0.12
			Calculated by NLLS method by using data from Ref.5					

[4.3.1] Effect of monomer partitioning and true reactivity ratio

Monomer partitioning effect can be incorporated using partition coefficient [k] and feed concentration, assuming $\mathbf{f'_A + f'_B = 1}$ where $\mathbf{f'_A}$ and $\mathbf{f'_B}$ are the concentrations of the monomer A and B at the polymerisation loci and $\mathbf{f_A}$ and $\mathbf{f_B}$ are their feed concentrations. Partition coefficient [k] was calculated as per the method reported by Gugliotta et al. [9] using reactivities of monomers in bulk (r') and in microemulsion (r).

$$r_A = r'_A\, k \qquad [2]$$

$$r_B = r'_B / k \qquad [3]$$

$$f'_A / f'_B = k (f_A / f_B) \qquad [4]$$

Earlier reports of microemulsion polymerisation of hydrophobic styrene and hydrophilic counterpart like methylacrylate [5] , acrylonitrile [2] and methylmethacrylate [4] assume $f'_{STY} = f_{STY}$ due to negligible solubility of styrene in water. This would lead to $f'_{MA} = f_{MA}$, $f'_{MMA} = f_{MMA}$ and $f'_{AN} = f_{AN}$ or that the sum of the fractions at the polymerisation loci no longer remains unity. The reported constancy of the f'_{MA} / f_{MA} [5] , f'_{MMA} / f_{MMA} [4] and f'_{AN} / f_{AN} [3] ratio is thus a direct consequence of the definition of partition coefficient and the assumption that $f'_{STY} = f_{STY}$. However, the correctness of this approach has been questioned by Kluperman and Aerdts [10] for the microemulsion copolymerisation of styrene-MMA [4], as the partitioning of MMA will result into the relative styrene concentration at the polymerisation site different from the initial feed concentration. We have therefore calculated the loci concentration considering equation 4 and assuming $f'_A + f'_B = 1$. Moreover, the determination of loci concentration involving both polar monomers becomes impossible using the earlier approach. The loci concentrations were subsequently used to recalculate the reactivity at the actual polymerisation site. The partition coefficient value for EA – MMA calculated from equation 2 and 3 was observed to be 0.99, while the reported values of 0.72 and 1.86 were used for styrene – butylacrylate [5] and styrene – methylacrylate [5] respectively.

Average of partition coefficients for monomers A and B determined by using equation 2 and 3 was considered for the calculation of f'_A and f'_B using equation 4. The reactivity ratios calculated from the actual concentration of monomers at polymerisation loci, considering the effect of monomer partitioning were termed as **true reactivity ratios** and those calculated from the feed ratio were termed as **apparent reactivity ratios** [Table 4 . 4 and Fig 4 . 3].

[4.3.2] Prediction of copolymerisation locus

For a microemulsion, polymerisation locus is decided by its microstructure. Recent reports [11 - 13] reveal that for microemulsion various microstructures ranging from discrete spherical micelles and droplets to a bicontinuous micellar network evolve with the variation in the microemulsion composition. The report by Nyden et al. [11] for a didodecyldimethylammonium sulphate [DDAS] / water / hydrocarbon, microemulsion shows that at high water contents discrete spherical micelles exists at all surfactant to oil ratios in microemulsion region. Their results were supported by NMR self – diffusion experiments, which showed equal diffusion for surfactant and hydrocarbon. At intermediate oil to surfactant ratio, the spherical micelles were reported to change its shape to prolate and also grow in size. As the water content decreases further, a bicontinuous structure was reported to evolve, indicating a smaller self-diffusion of surfactant than that of the hydrocarbon.

In the present work, the compositions [given in experimental section] selected for the polymerisation of EA – MMA [our work] and that selected by Xu et al. for styrene - methylacrylate and styrene – butylacrylate microemulsions lies in high water concentration region, with a relatively low oil to surfactant ratio. The surfactant to oil ratio was reported to be 0. 85 for styrene - methylacrylate and styrene – butylacrylate

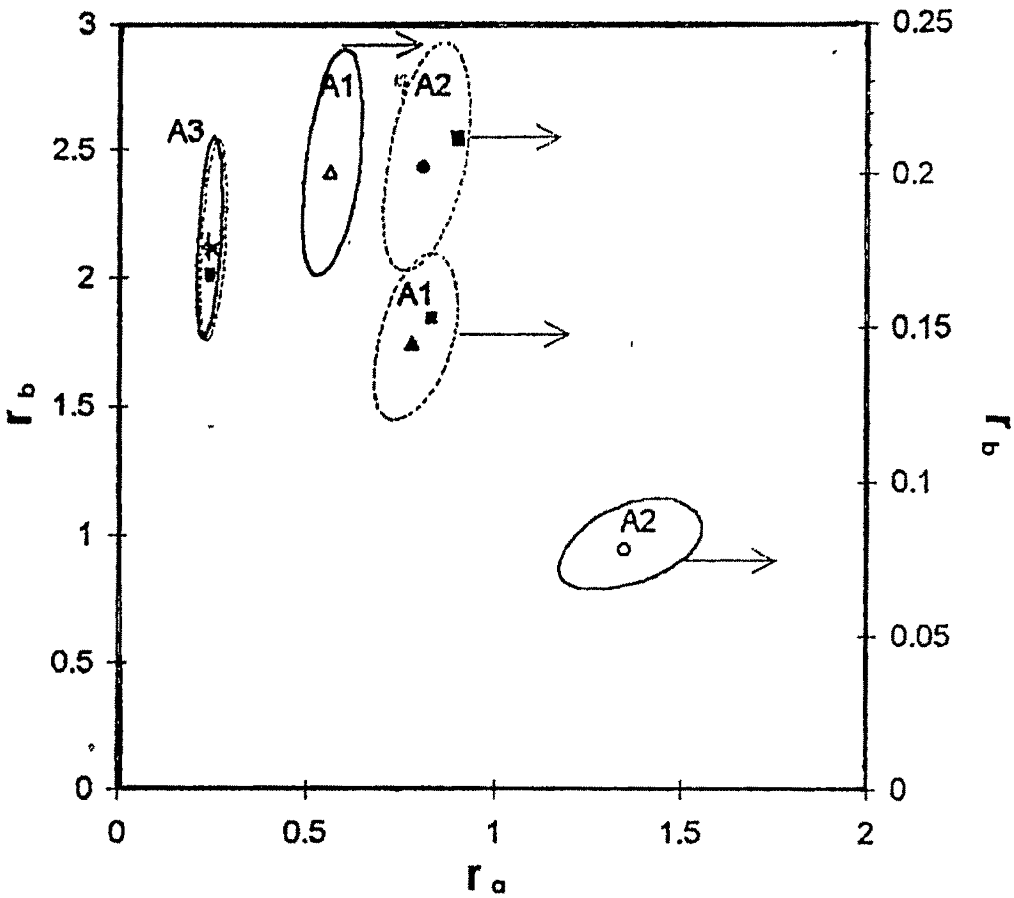


Fig 4.3 : 95% joint confidence curves by EVM.

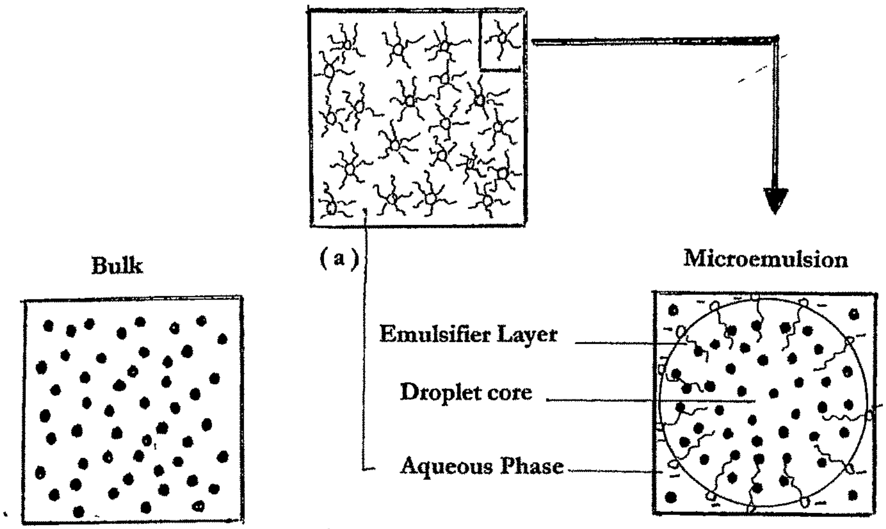
—— Based on monomer concentration in feed.

….. Based on monomer concentration in the loci.

- A1 : Styrene - Butylacrylate system , A2 : Styrene - Methylacrylate system , A3 : Ethylacrylate - Methylmethacrylate system.
- r_a = Reactivity ratio of Styrene and EA.
- r_b = Reactivity ratio of BA, MA, MMA.
- Reactivitiy ratios based on monomer concentration in feed for Styrene - BA (Δ) , Styrene - MA (O) and EA - MMA (+) in microemulsion.
- Reactivity ratios based on monomer concentration in loci for Styrene - BA (▲) , Styrene - MA (●) and EA - MMA (x) in microemulsion.
- Reactivity ratios in bulk for, EA - MMA (■) , Styrene - MA (■) and Styrene - BA (■)

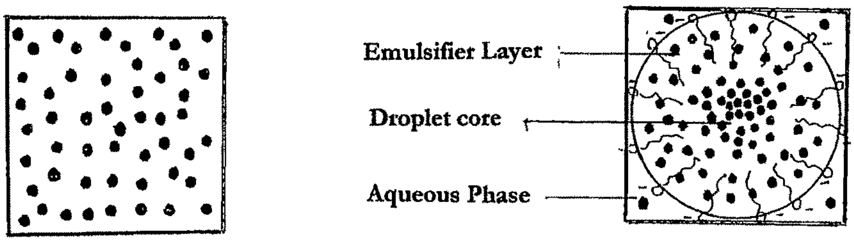
respectively. In our system it is 1.5 for ethylacrylate – methylmethacrylate. Therefore the most probable microstructure is assumed to be the discrete spherical micelles and or monomer droplets as shown in Fig 4.4 a. Point ‘A’ of the phase diagram [Fig 3 .12] for EA [0. 5] - MMA [0. 5]/ SDS / Water shows the location of the selected composition in our work . These micro emulsified droplets have been widely reported as the predominant locus of polymerisation for oil / water microemulsion [14,15]. Now, if a droplet is visualized at microlevel the homogeneity of monomer distribution within droplet is affected by the polarity of the monomer and is shown in Fig 4 4 b’, 4.4c’ and 4.4 d’. The corresponding bulk systems have been shown as 4.4 b, 4.4 c and 4.4 d. More polar part of the monomer tends to reside near the surface of o/w droplets, whereas the hydrophobic monomer will tend to be at the core of the droplet. In addition to this, the actual concentration of the monomers at droplet differs from that taken in feed, due to the partitioning of the monomers between oil droplet and aqueous phase. This results in the variation in actual monomer concentration at the monomer droplet, which affects the copolymer composition. As a result reactivities calculated considering this effect will be different than those calculated by conventional way without considering the partitioning effect.

[a] EA – MMA system has monomers with similar polarity and solubility. Using k values , monomer concentration in the droplet was calculated and is given as f'_{EA} and f'_{MMA}. From the results in Table 4.1 it is observed that f'_{EA}/f_{EA} and f'_{MMA}/f_{MMA} i.e ratio of monomer concentration in droplet and in feed is constant. f'_{EA}/f_{EA} and f'_{MMA}/f_{MMA} values very near to one indicate an uniform distribution of monomers in the droplet. It also indicates that although both the monomers are partitioning between oil and water phase the mole ratios of monomers at the droplet [f'_{EA}/f'_{MMA}] and in



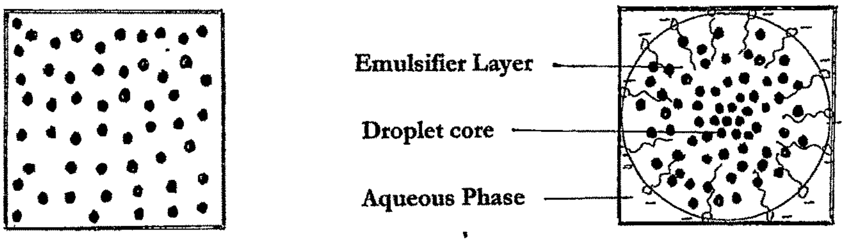
(b) (●) EA, (●) MMA (b') (●) EA, (●) MMA

Diagram showing homogeneous distribution of EA and MMA in droplet similar to bulk. o⁀⁀⁀⁀ SDS



(c) (●) Styrene, (●) MA (c') (●) Styrene, (●) MA

Diagram showing a higher concentration of MA in the emulsifier layer for Styrene - MA, but overall styrene concentration in droplet is higher due to partitioning of MA in aqueous phase. o⁀⁀⁀⁀ SHOA



(d) (●) Styrene, (●) BA (d') (●) Styrene, (●) BA

Diagram showing a greater concentration of BA in the emulsifier layer for Styrene – BA system. o⁀⁀⁀⁀ SHOA

Fig 4. 4 : Diagramatic representation of the microstructure with respect to monomer distribution within the droplet.

(a) A typical oil / water / surfactant microemulsion.
(b) EA, MMA (bulk), (c) Styrene, MA (bulk), (d) Styrene, BA (bulk).
(b') EA, MMA distribution within the microemulsion droplet.
(c') Styrene, MA distribution within microemulsion droplet.
(d') Styrene, BA distribution within microemulsion droplet.

feed [f_{EA} / f_{MMA}] do not vary due to their similar solubility and polarity. This should lead to the similar values of true and apparent reactivities. Our observed values by NLLS method , given in Table 4 . 4 and Fig 4 . 3 are very close to each other and are **r_{MMA} = 2.1** and **2.18, r_{EA} = 0.25** and **0.25** respectively as apparent and true reactivities. The observed good agreement in the experimentally obtained copolymer composition for bulk [6] and microemulsion [present work] indicates that microemulsion copolymerisation of EA-MMA resembles to bulk and monomer partitioning has no effect on copolymer composition and hence on reactivity ratios. Fig 4.4 b' shows a homogeneous distribution of EA and MMA within a microdroplet without any preferential site for polymerisation.

[b] For Styrene – Butylacrylate the reported [5] copolymer composition for microemulsion showed a greater fraction of more polar monomer, butylacrylate for identical bulk feed concentration and is given in Table 4.2. The variation in copolymer composition results in the reported partition coefficient [k] value to be 0.76 rather than unity This indicates internal partitioning of monomers within a microdroplet. Therefore true reactivity ratio was calculated by us considering the effect of monomer partitioning. This approach indeed gives very close reactivity ratios to bulk polymerisation [Table 4.4 and Fig 4.3]. Based on higher concentration of BA 30 % and lower concentration of styrene 20% in the microemulsion droplets and the observed lower Tg for the copolymers synthesized through microemulsion compared to that synthesized through bulk using identical feed concentration, Xu et al. [5] have reported emulsifier layer as the preferential copolymerisation locus. Fig 4.4d' gives a pictorial representation showing higher concentration of butylacrylate in the emulsifier layer arising due to the higher polarity of BA.

[c] In Styrene – MA system there is a difference in both solubility and polarity of the monomers. The solubility of styrene and MA in water is 0.027% and 5.2% respectively. The greater partitioning of MA in aqueous phase relative to styrene increases the styrene concentration in the microdroplet. This leads to a greater styrene fraction in the copolymer compared to bulk for identical feed [Table 4.3]. The apparent reactivity ratios calculated by us from Xu et al's data [5], using NLLS and FR method but without considering partitioning of monomers are very much different from the bulk values [Table 4.4 and Fig 4.3]. The divergence in apparent and bulk reactivity ratio arises mainly due to the effect of monomer partitioning. Therefore the partitioning effect was included in calculating the true reactivity ratios. The reported [5] partition coefficient value k = 1.86 was used for the calculation. Thus the true reactivity ratios calculated by us were very close to the bulk values [Table 4.4 and Fig 4.3]. The calculated $\mathbf{f'_{MA}/\ f_{MA}}$ values increase with increase in feed concentration of [MA] while **f ' sty / f sty** values decrease with increase of styrene in feed. This indicates that there exists a preferential site of polymerisation within a droplet having a higher concentration of MA. Within a droplet, the higher MA concentration is expected in the emulsifier layer due to its higher polarity as shown clearly in Fig 4.4 c'. This can also be supported by the cosurfactant effect of lower acrylates in microemulsion polymerisation as reported by Antoniette et al.[16]. On this basis it is suggested that the probable copolymerisation locus might be the emulsifier layer rather than the droplet core. Had there been no preferential site, the $\mathbf{f\ '_{MA}\ /\ f_{MA}}$ and **f ' sty / f sty** values would have been constant as in the case of EA - MMA, where there exists no concentration gradient within a microdroplet. The closeness of true reactivity ratio with bulk has also been observed in case of styrene – MMA and styrene – acrylonitrile. The true reactivity ratios calculated by NLLS method were found to be $r_{STY} = 0.72$ and $r_{AN} = 0.031$ and $r_{STY} = 0.5$ and $r_{MMA} = 0.34$ whereas the bulk values reported are $r_{STY} = 0.41$, $r_{AN} = 0.04$ and $r_{STY} = 0.47$, $r_{MMA} = 0.45$ [3,4]. In all the cases the monomer fraction in the copolymer obtained experimentally agrees with that obtained theoretically using Terminal Model [17] by using the true reactivity ratios and concentration at loci for the respective monomers as shown in Table 4.1, 4.2 and 4.3.

It has been discussed at lengths in past the importance of microenvironment on reactivities of monomers. In case of micro emulsion the microenvironment depends on monomer solubility and polarity. The importance of actual concentration at polymerisation loci is reflected in the observed reactivities [Table 4.4 and Fig 4.3]. In the case of EA – MMA, very little difference in relative solubility and polarity results in insignificant drift in composition from the initial feed ratio for EA – MMA resulting into similar true and apparent reactivity ratio. In the case of styrene - MA considerable difference in solubility as well as polarity results into significant difference in true and apparent reactivity ratios. In the case of styrene – BA though the solubility is similar the difference in polarity results into concentration gradient within the droplet resulting into somewhat different reactivities. However, the difference in the true and apparent value is less than that observed in styrene – MA and higher than that observed in EA – MMA. In all the cases, the true reactivity ratios, calculated by considering the effect of monomer partitioning lead to a close resemblance in microemulsion and bulk reactivity ratios. This indicates a greater accuracy of the values since copolymer composition in case of bulk polymerisation depends only on reactivity ratio at lower conversion. The insignificant difference in the microemulsion and bulk reactivity ratio has also been observed by Kluperman and Aerdts [10] on the re-evaluation report for microemulsion copolymerisation of styrene and MMA reported by Gan et al [4].

In addtion reactivity ratios of EA – MMA emulsion system were compared with the results obtained for microemulsion and bulk. The 95% joint confidence curves for emulsion and microemulsion or bulk system show considerable difference in the values irrespective of the similarity in the solubility of EA and MMA in water as shown in Fig 4.5 and Table 4.5. The difference arises due to higher degree of polymerisation in aqueous phase, leading to a higher loci concentration of the more water soluble monomer EA [Table 4.6] and correspondingly a higher fraction of EA in the copolymer than in bulk or microemulsion [Table 4.7] for conversions below 6 % in all the cases. While the true reactivity ratio matches with the bulk values for both emulsion and microemulsion. This again proves that multiplication of the initial feed ratio with a suitable constant i.e. the partition coefficient [which includes the effect of partitioning of both the monomers] gives the monomer concentration corresponding to the copolymer obtained as in the case of bulk polymerisation where the initial feed corresponds closely to the copolymer composition at very low conversions.The partition coefficient value , calculated using equation was found to be 1 47.

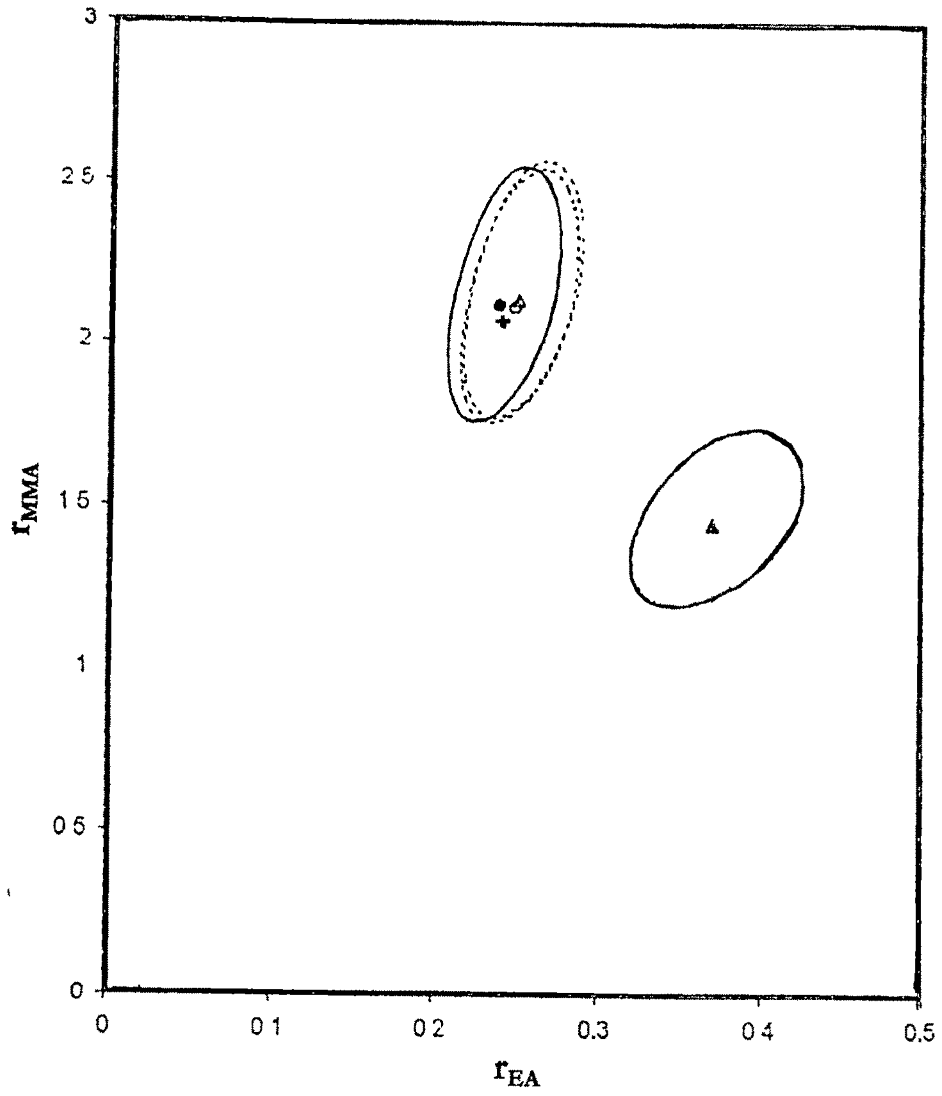


Fig 4. 5 : 95 % joint confidence curves by EVM.

Based on monomer concentration in feed. (———)

Based on monomer concentration in the loci. (.......)

r_{EA} = Reactivity ratio of EA.

r_{MMA} = Reactivity ratio of MMA.

Reactivitiy ratios based on monomer concentration in feed for EA – MMA in microemulsion (●) , in emulsion (▲).

Reactivity ratios based on monomer concentration in loci for EA – MMA in microemulsion (o) , in emulsion (Δ).

Reactivity ratios in bulk for, EA – MMA (+)

Table 4.5 : Reactivity ratio of EA - MMA using various methods for emulsion and microemulsion copolymerisation.

Method	Bulk (from Ref 6.)			Emulsion (our Work)			Microemulsion(our ork)		
	r_{EA}	r_{MMA}	$r_{EA}.r_{MMA}$	r_{EA}	r_{MMA}	$r_{EA}.r_{MMA}$	r_{EA}	r_{MMA}	$r_{EA}.r_{MMA}$
ML	0.24	2.03	0.48	-	-	-	-	-	-
FR (App)				0.44	1.55	0.68	0.26	2.0	0.52
KT (App)				0.37	1.41	0.52	0.26	2.02	0.52
NLLS(App)				0.37	1.44	0.53	0.25	2.12	0.53
FR (True)				0.30	2.28	0.68	0 26	2.10	0.54
NLLS(True)				0.25	2.13	0.53	0.25	2.11	0.52

FR : Finemann Ross method , KT : Kelen Tudos , NLLS : Non Linear Least Square Mothod , ML . Mayo-Lewis,
App : apparent reactivities, True : True reactivities

Table 4 .6 : Composition of EA / MMA in feed and copolymerisation loci.

Emulsion						
f_{EA}	0.9	0 75	0.66	0.5	0.25	0.10
f_{MMA}	0.1	0.25	0.33	0 5	0.75	0.90
f'_{EA}	0.929	0.815	0.746	0.595	0.329	0.140
f'_{MMA}	0.070	0.184	0.253	0.404	0.670	0.859
f'_{EA} / f_{EA}	1.032	1.086	1.130	1.19	1.316	1 40
f'_{MMA} / f_{MMA}	0.70	0.736	0.766	0 808	0.893	0 954
Microemulsion						
f'_{EA}	0.899	0.749	0.665	0.498	0.249	0.099
f'_{MMA}	0.1	0.25	0.334	0.501	0.750	0.900
f'_{EA} / f_{EA}	0.998	0.998	1.007	0.996	0.996	0.990
f'_{MMA} / f_{MMA}	1.00	1.00	1.012	1.002	1.00	1.00

f_{EA} , f_{MMA} : Concentration of EA and MMA in feed.

f'_{EA} , f'_{MMA} : Concentration of EA and MMA at polymerisation loci

Table 4 .7 : Composition of EA / MMA copolymer synthesied in bulk, emulsion and microemulsion.

Feed Concentration		Emulsion		Microemulsion		Bulk	
f_{EA}	f_{MMA}	F_{EA}	F_{MMA}	F_{EA}	F_{MMA}	F_{EA}	F_{MMA}
0.9	0.1	0.814	0.185	0.729	0.27	0.72	0.27
0.75	0.25	0.583	0.416	0.52	0.479	0.51	0.49
0.66	0.33	0.478	0.521	0.384	0.615	0.42	0.57
0.5	0.5	0.348	0.651	0.3	0.699	0.30	0.7
0.25	0.75	0.187	0.812	0.136	0.863	0.13	0.86
0.1	0.9	0.102	0.897	0.051	0.948	0.05	0.94

f_{EA} , f_{MMA} : Feed concentrations of ethylacrylate and methylmethacrylate.

F_{EA} ,F_{MMA} EA and MMA fraction in copolymer synthesised through emulsion , microemulsion and bulk polymerisation .

[4. 4] Copolymer Configuration

From DSC analysis, one observes a Tg of 114 °C and 117 °C respectively for microemulsion and emulsion based copolymer synthesised from feed composition rich in MMA [0.9 MMA / 0.1 EA][Fig 3. 25]. The higher Tg obtained for the Poly-[MMA] samples synthesised through emulsion and microemulsion were 125 and 123 respectively. This might indicate a greater contribution due to syndiotactic mode of addition of the monomer units in the copolymer as reported by Wittmann and Kovacs on the basis of triad analysis of Poly – [MMA] [18]. Fig 4.2 shows the expected singlet due to syndiotactic resonence of the β - methylene protons appearing around 1.8 – 2.0 δ, although broadened and complicated by the residual isotactic resonance for the microemulsion copolymerisation of EA – MMA. Similar splitting patterns for β - methylene protons observed for emulsion system. Roy and Devi [19] have also reported syndiotactic mode of addition for pure Poly – [MMA] synthesised in emulsion. The nature of these multiplets for β - methylene protons has been reported to be an absolute measure of the polymer's predominant configuration [20].

[4 . 5] Characterisation

[4 . 5 . 1] NMR analysis

The composition of the copolymer was determined from ^{1}H NMR recorded on 200 MHz Bruker DPX 200 instrument using TMS as an internal reference and 2 % w / v sample solution in $CDCl_3$. Fig 4.1 shows the NMR spectrum of EA - MMA copolymer.

[4 . 5 . 2] Thermal analysis

The Tg's of the purified Poly [EA - co – MMA] synthesized from emulsion and microemulsion were determined at MMA[0.9] / EA[0.1] feed concentrations and are shown in [Fig 3.25].

[4 . 6] Conclusion

1. The concentration of commoner at the polymerisation loci can be determined from the ratio of concentration of the commoners at the polymerisation loci, assuming that the sum of the loci concentrations of the commoners equals unity rather than considering the equivalency of loci and feed concentrations, for hydrophobic monomers like styrene to overcome the error arising due to the partitioning of the other monomer.
2. Recalculation of the reactivity ratios termed as true reactivity ratios, in microemulsions considering the concentration of monomers at the polymerisation loci and not in the feed leads to very close values for those calculated for bulk polymerisation.
3. Prediction regarding the actual copolymerisation locus can be done on the basis of values of f'_A / f_A and f'_B / f_B ratios.
4. Calculation of loci concentration of both polar monomers requires an assumption of their concentration at the polymerisation site to be unity.
5. Emulsion copolymerisation shows a greater composition drift compared to microemulsion polymerisation of polar monomers.

References

1. Wall FT , Florin RE and Delbeq CJ , *J . Am . Chem . Soc .* , **72** , 4769 (1950).
2. Lee KC , Gan LM and Chew CH , *Polymer*, **36** , 3719 (1995)
3. Sanghvi PG , Patel A C , Gopalkrishnan KS , Devi S . *European Polymer Journal* , **36** : 2275 (2000).
4. Gan LM , Lee K C , Chew C H , Ng SC , Gan L H . *Macromolecules* , **27**, 6335 (1994)
5. Xu X , Ge X , Zhang Z , Zhang M . *Polymer* , **39** , 5321 (1998).
6. Grassie N , Torrance BJD , Fortune JD, *Polymer*, **6** , 653 (1965).
7. Finemann M and Ross SD , *J . Polymer . Sci .*, **5** , 269 , (1950).
8. Koening , Chemical microstructure of polymer chains , John Wiley , New York, 1980, Chapter 3.
9. Gugliotta L M , Arzamendi G and Asua J M . *J Appl . Polym . Sci* , **55** , 1017 (1995).
10. Klumperman B , Aerdts A M . *Macromolecules* , **29** , 6619 (1996).
11. Nyden M , Sodermam O , Hansson P. *Langmuir* , **17** , 6794 (2001).
12. Silas JA , Kaler EW . *J. Colloid and Interface Science* , **243** , 248 (2001).
13. Summers M, Eastoe J , Heenan RK , Steyler D , Grillo I . *J . Dispersion Science and Technology* , **22** , 597 (2001).
14. Gou JS, Sudol ED, Vanderhoff JW and El – Aasser MS , *J . Poly . chem . Ed* , **130** , 691,(1992).
15. Full AP, Kaler EW, Arellano J and Puig JE , *Macromolecules* , **29** , 2764 , (1996).
16. Antonietti M , Lohmann S and Van Niel C . *Macromolecules* , **25** , 1139 (1992).
17. Mayo FR , Lewis FM . *J. Amer. chem . Soc.* , **66** , 1594 (1944).
18. Wittmann JC, Kovacs AJ , *J . Polym . Sci . C .* , **16** , 4443 (1969).
19. Roy S and Devi S, *J . Appl. Polym . Sci .* **62** , 1509 , (1996).
20. Bovey FA , High Resolution NMR of Macromolecules , Academic Press, London , Chapter 3 , 73 (1972).