

CHAPTER - 4

**STUDIES ON COPOLYMERIZATION OF ACRYLAMIDE WITH
DIACETONE ACRYLAMIDE AND N-tert-BUTYLACRYLAMIDE BY
Fe(III)-TU REDOX COUPLE ON MONTMORILLONITE SURFACE**

4.1 INTRODUCTION AND REVIEW OF PREVIOUS WORK

Copolymers of acrylamide have shown a number of properties lending themselves to a variety of industrial applications. Of growing importance are those related to use as water soluble viscofiers and displacement fluids in enhanced oil recovery.²⁴²⁻²⁴⁷ Two of the critical limitations of polyelectrolytes are, however, loss of viscosity in the presence of mono or multivalent electrolytes (viz. NaCl, CaCl₂, etc.) and ion binding to the porous reservoir rock substrates. Copolymers of acrylamide and acrylates can be synthesized by several methods including those of solution²⁴⁸⁻²⁵⁹ and emulsion²⁶⁰⁻²⁶³ polymerizations. The physical properties of the copolymers in some cases, are dependent on the method of preparation. The copolymers of AM with sodium acrylate in aqueous ammonium persulfate solution was conducted at 70° for 60 min. producing a honeylike copolymer which had molecular weight 1.25×10^6 as reported by Soltez and co-workers.²⁴⁸ Cationic free radical copolymers of acrylamide with dimethylaminoethyl methacrylate and dimethylaminoethyl acrylate had been prepared by Baade and Hunkeler²⁴⁹ with azocyano valeric acid and K₂S₂O₈ at 45°-60°C. Lafuma and Durand have found that during random copolymer formation of acrylamide and a quaternary ammonium acrylate monomer, the cleavage of the ester function occurred in mild alkaline medium with a simultaneous inter-chain reaction resulting in imide group formation.²⁵⁰ Lavrov and co-workers have reported that copolymerization of 2-hydroxy ethyl methacrylate with acrylamide in aqueous solution in the presence of (NH₄)₂S₂O₈/ascorbic acid redox catalyst proceeded without the gel effect characteristic of bulk polymerization²⁵¹. The reactivity ratios of the dimethylamino ethyl methacrylate methyl chloride salt with acrylamide at 54° C were 1.54 and 0.30 respectively when redox azo compounds were used as catalyst²⁵². The molecular weight of copolymers of auxin-containing monomers with acrylamide was determined to be in the range of $5.5 - 18.0 \times 10^4$ when a 4-pyrrolidinopyridine and dicyclohexyl carbodiimide²⁵³ catalysts were used. For AM - Na acrylate copolymer, prepared in aqueous solution at room temperature

and at pH 7.4 - 12.1, the reactivity ratios were 0.9 - 1.18 and 0.32 - 0.48 respectively²⁵⁴. McCormick and Salazar have reported that the increasing randomness in the copolymers of acrylamide with Na-3-acrylamido - 3-methylbutanoate is observed if prepared in NaCl solution rather than in distilled water²⁵⁶. The polyelectrolytes had inherent hydrogen bonding capacity and pseudo plasticity and exhibited large dimension in aqueous solution²⁵⁷. In inverse microemulsion copolymerization of AM with methylacrylate initiated with AIBN by Vaskova was a typical "dead - end" polymerization²⁶⁰. In inverse emulsion polymerization method, incorporation of high hydrophile - lyophile balance coemulsifier in addition to the water-in-oil type main emulsifier increased the rate of polymerization significantly. Free radical copolymerization of acrylamide with butylacrylamide or isopropyl methacrylate in the presence of AIBN in DMF at 60°C was investigated by Srinivasula, Rao and co-workers²⁶¹⁻²⁶². The chemical structures of random copolymers of acrylamide with Na - 2 - sulfoethylmethacrylate in dextran were determined by McCormick in order to gain a more complete understanding of the structure - property relations and performance under simulated field conditions encountered in enhanced oil recovery²⁶³. The synthesis and characterization of copolymers of acrylamide with N-alkylacrylamide were investigated by McCormick and Nonaka and co-workers in aqueous solution utilizing Na-dodecyl sulfate as a surfactant and $K_2S_2O_8$ as the initiator²⁶⁴. A remarkable increase in apparent viscosity was observed at low mol. fractions of N-alkylacrylamide in the copolymer at a critical concentration which is a function of alkyl chain length in the monomer and copolymer molecular weight. The viscosity behaviour is interpreted in terms of a concentration dependent model involving interchain hydrophobic association in aqueous solution²⁶⁴. The copolymer microstructures and reactivity ratios of copolymers of acrylamide with N-(1,1-dimethyl-3-oxo-butyl)-N-(n-propyl) acrylamide were studied by McCormick and Blackmon and the value of r_1, r_2 determined to be 2.20 (ref 265). The copolymer of acrylamide with N-(1,1 - dimethyl 3 - oxo-butyl) acrylamide yielded a r_1, r_2 value of 0.75 and the copolymer of AM with N, N-dimethyl acrylamide provided a r_1, r_2 value of 0.86 as reported by

McCormick and Chen²⁶⁶. Monoazeotropic and non ideal copolymers were prepared during copolymerization of methyl methacrylate with AM, N-methylacrylamide and N,N-dimethylacrylamide in 1,4 Dioxan solution at 65°C using AIBN as initiator²⁶⁷. Low molecular weight water soluble copolymers of acrylamide with itaconic acid, methacrylic acid and acrylic acid were prepared in the presence of $K_2S_2O_8$ and thioglycerin by Sumi and co-workers²⁶⁸. Granular copolymers of ethylacrylate (EAC) and acrylonitrile (ACN) had been prepared by Thomas with dispersed bentonite when EAC and ACN were dissolved in ethanol and heated under reflux condition with benzoyl peroxide for six hours²⁶⁹. The copolymerization of methyl methacrylate with acrylonitrile and methacrylonitrile were studied by Bhattacharyya in the presence of HM/thiourea redox couple²⁷⁰.

In the present work, attempts have been made to prepare water soluble copolymers of acrylamide with N - (1, 1 - Dimethyl - 3 - oxybutyl) acrylamide (commonly referred to as Diacetone acrylamide, DAAM) and N-t butyl acrylamide (N-t BAM) on the montmorillonite surface by interlayer trapped Fe(III) ions in the presence of TU. Importance of the study lie in the fact that (I) the applied technique provides high molecular weight polymers having high intrinsic viscosities and (II) at least one of the above copolymers has already shown some promises by not losing its solution viscosities in the presence of added electrolytes¹¹. The success in copolymerization would result in relatively pure copolymer without subsequent solvent extractions. Moreover, the structure of the clay mineral would, perhaps, control the structure and physico-chemical property of the copolymer. This chapter deals with the studies on copolymerization of AM with DAAM and N-tert BAM and including microstructures and reactivity ratios of the polymers. Copolymerization of vinyl monomers on clay surface have not been studied so far in detail. Attempts have, therefore, been made to use FeM/TU initiating system in the copolymerization reactions.

4.2. EXPERIMENTAL

4.2.1 Materials and purification

Reagents

The purification techniques of acrylamide(reagent grade, Fluka) and thiourea (Merck) were discussed in previous section 3.2. Method of preparation and the characteristics of Fe(III) - montmorillonite (FeM) were similar to those as already described in section 3.2.

N-(1,1-dimethyl-3-oxybutyl) acrylamide(reagent grade, Fluka) was recrystallised twice from methanol and vacuum dried. N-t butyl acrylamide (reagent grade, Fluka) was used as received.

Polymerization

Poly(acrylamide-co-N,N-dimethylacrylamide)

The copolymerization of acrylamide with N, N dimethylacrylamide (DAAM) was conducted in aqueous solution at 50°C using 0.50%(w/v) of FeM and 0.04 M of thiourea as initiator. Table-23 lists reaction parameters for four series of reactions in which the ratio of monomers in the feed and reaction times were varied. A specified amount of DAAM dissolved in distilled water was added to the mixtures of acrylamide and thiourea solutions of known concentrations in 100 ml stoppered pyrex bottles under nitrogen. In another set of bottles, known amounts of aqueous FeM suspensions were degassed and, finally added to the former bottles under nitrogen atmosphere. The pH of the final mixture was adjusted to 2.0 ± 0.1 by drop-wise addition of 0.01M HCl solution, well shaken and immediately placed in thermostatic bath of appropriate temperature. pH adjustment was necessary to ensure the formation

of adequate amount of the amido-sulfenyl primary radicals to initiate the copolymerization reaction¹⁴. After the designated reaction intervals, the copolymerization reactions were stopped by diluting the reaction mixtures with chilled water, keeping the reaction vessel in ice bath and FeM was separated by centrifugation (1.5×10^4 r. p. m.). AM-DAAM copolymers were precipitated out by the addition of excess acetone. The copolymers and FeM were washed separately by acetone and water respectively. The copolymers and FeM were then dried at 60°C under vacuum for 48 hrs. Conversions were determined gravimetrically.

Poly (acrylamide-co-N-tert-butylacrylamide)

Since N-t-butylacrylamide is insoluble in water, the monomer was dissolved in micellar pseudo-phase of non ionic surfactant Triton-X-100(R). Four series of copolymerization of acrylamide with N-t-butylacrylamide having a total monomer concentration of 0.42M were conducted in aqueous solution at 50°C using 0.50% FeM (w/v) and 0.04M TU as the initiator. Reaction parameters for four series of reactions are given in Table-24. The reaction procedures were same as those described for the preparation of copolymers of AM with DAAM.

Elemental Analysis

Elemental analysis for carbon and nitrogen for the AM-DAAM and AM-N-t BAM in copolymers were conducted by Regional Sophisticated Instrumentation Centre (RSIC), Chandigarh, India (Table 23 and 24). The copolymer compositions were calculated based on C/N ratios because of the variability of absolute values due to the hygroscopic nature of the polymers. Elemental analyses were conducted at polymer conversion levels, i.e. low and high, to assess drift in the copolymer composition.

Viscosity Measurements

A series of copolymer solutions of different concentrations in aqueous 0.1 M NaCl are prepared from the 0.5% stock solution. The intrinsic viscosity measurement technique has already been mentioned in Section 3.2.

4.3 RESULTS AND DISCUSSION

The study of copolymerization involves the calculation of reactivity ratios of the monomers. Present investigation involves the copolymers of DAAM and N-tert BAM with AM. Such monomer conjugates have been chosen because (I) the groups attached to the vinyl groups are electron withdrawing (II) the position occupied by the methyl group in both the monomers (DAAM and N-tert BAM) is similar with respect to the vinyl carbon atom. It is clear from the Table - 22 that, in case of AM-DAAM, the monomer conversion decreases with decreasing AM-DAAM ratios. However, at lower monomer ratios than 4:1, no copolymers were detected. But in presence of Triton X-100 (R), the monomer conversion increases with decreasing monomer composition ratios. The monomer conversion was also increased with decreasing the AM : DAAM ratio when the concentration of Triton X-100(R) was changed from 0.01 mol.L⁻¹ to 0.02 mol.L⁻¹. On the other hand, in case of AM-N-t BAM, copolymerization reaction proceeds efficiently in presence of surfactant, Triton X-100(R). The monomer conversion increases with decreasing AM-N-tert BAM ratios. High conversion is also observed by FeM/TU initiating system (Table-22).

Table - 22

Copolymerization of 0.4 M AM (0.7108 g) in aqueous medium (25 ml) with DAAM and N-t BAM in presence of 0.04 M TU and 0.50% (w/v) FeM at 50°C (pH 2.01) in presence of varying amounts of DAAM and N-t BAM.

[AM] mol.L ⁻¹	[DAAM] mol.L ⁻¹	AM]/[DAAM]	Triton-X-100(R) mol.L ⁻¹	Conversion ^a %
0.40	0.02	20.0	0.01	11.70
0.40	0.04	10.0	0.01	36.01
0.40	0.06	6.6	0.01	33.30
0.40	0.08	5.0	0.01	32.50
0.40	0.02	20.0	0.02	18.53
0.40	0.04	10.0	0.02	40.30
0.40	0.06	6.6	0.02	34.60
0.40	0.08	5.0	0.02	33.50
0.40	0.02	20.0	—	45.6 ^b
0.40	0.04	10.0	—	27.5
0.40	0.06	6.6	—	14.6 ^b
0.40	0.08	5.0	—	14.5 ^b
0.40	0.09	4.4	—	— ^c
0.40	0.17	2.3	—	— ^c
[AM]	[N-t BAM]	[AM]/N-t BAM]		Conversion ^a
0.40	0.01	41.0		53.8 ^b
0.40	0.02	20.0		54.1 ^b
0.40	0.03	13.3		59.8 ^b
0.40	0.04	10.0		56.6 ^b

^aCopolymer yield after 4.5 hrs, ^bIn absence of surfactant, ^cNo copolymer formed.

Reactivity Ratios

The variation in feed ratios and the resultant copolymer compositions (Table 23 and 24) as determined from elemental analyses were used to calculate the reactivity ratios for the AM-DAAM and AM-N-t BAM copolymer systems. The Fineman - Ross method²⁷¹ and Kelen - Tüdös method²⁷² were employed to determine the monomer reactivity ratios at low conversion, whereas an integrated form of the Mayo-Lewis equation²⁷³ was used for higher conversion copolymerization data. Figure 52 is the Fineman - Ross plot for acrylamide (M_1) and diacetoneacrylamide (M_2). The reactivity ratios r_1 and r_2 for the monomer pair M_1 and M_2 can be determined by

$$F(f-1)/f = r_1 (F^2/f) - r_2 \quad (44)$$

Where $f = d(M_1)/d(M_2)$, $F = (M_1)/(M_2)$.

The reactivity ratio r_1 was determined to be 0.69 ± 0.03 from the slope and $r_2 = 0.62 \pm 0.05$ from the intercept. The reactivity ratios are however calculated as 6.18 ± 0.17 and 1.06 ± 0.06 respectively for AM and DAAM on changing the index on monomer as acrylamide (M_2) and diacetone acrylamide (M_1) (Table 26). Similarly, the Kelen - Tüdös approach was applied for evaluation of reactivity ratios for the same monomer pair according to

$$v = r_1 \xi - r_2 (1 - \xi) / \alpha \quad (45)$$

where $v = G/\alpha + H$ and $\xi = H/\alpha + H$.

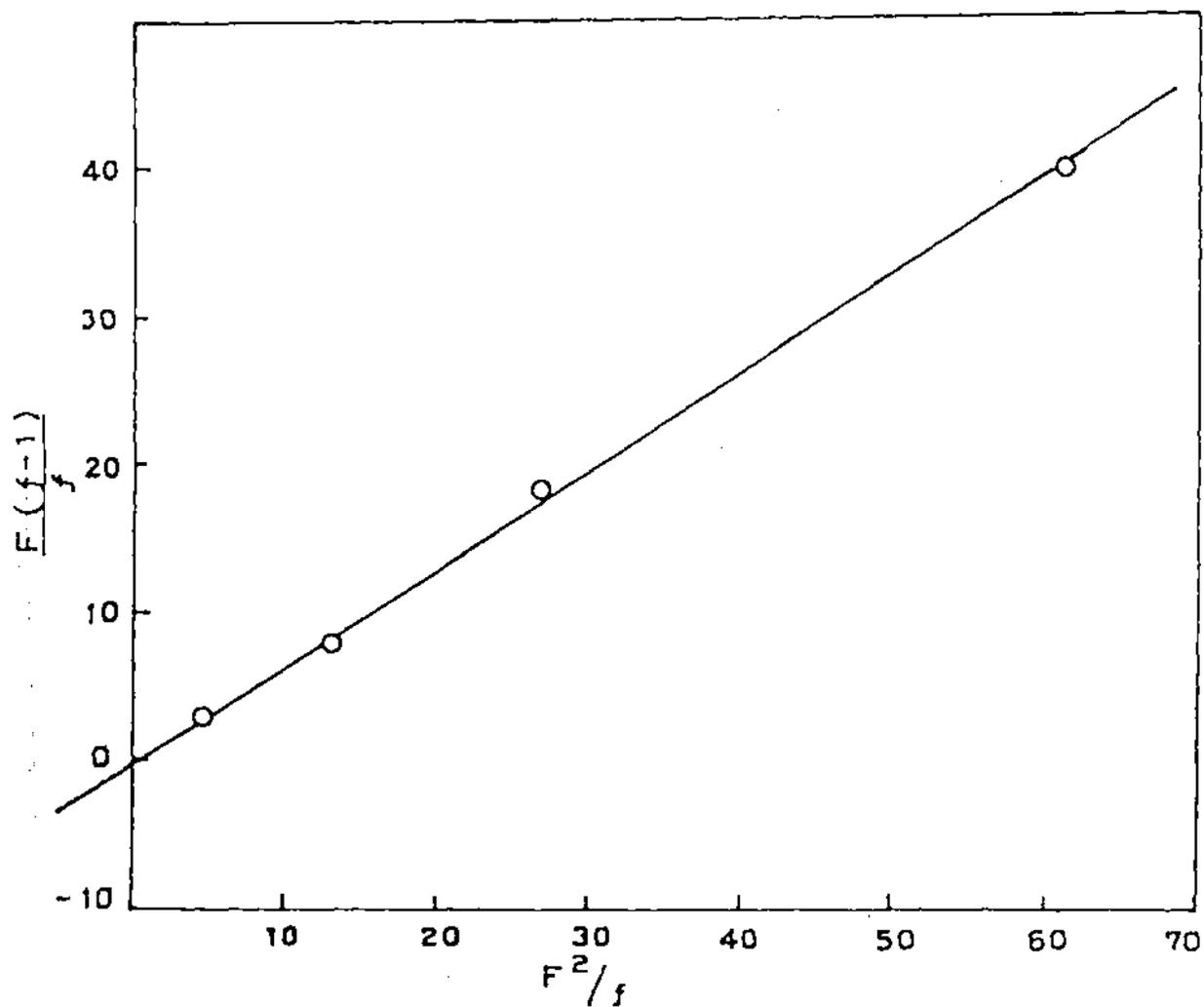


Fig. 52 Determination of reactivity ratios for copolymerization of AM with DAAM by Fineman-Ross method.

Table - 23

Reaction parameters for the copolymerization of AM with DAAM at 50°C in Distilled water (Total Monomer concentration = 0.42 M)

Sample number	Monomer concentration in the feed (M)			Reaction time (min.)	Conversion(%)	Elemental Analysis (wt%)		Mol % DAAM in copolymer	[η] ml.g ⁻¹
	[AM]	[DAAM]	[AM]/[DAAM]			C	N		
DAAM-10-1	0.41	0.01	41	90	37.10	41.46	15.03	3.60 ± 0.04	
DAAM-10-2	0.41	0.01	41	150	48.13	41.72	15.15	3.52 ± 0.04	420
DAAM-10-3	0.41	0.01	41	210	54.19	42.62	14.82	5.91 ± 0.04	
DAAM-20-1	0.40	0.02	20	90	23.37	42.08	14.51	6.32 ± 0.08	
DAAM-20-2	0.40	0.02	20	150	31.84	42.03	14.26	7.32 ± 0.09	350
DAAM-20-3	0.40	0.02	20	210	40.54	43.05	14.81	6.54 ± 0.09	
DAAM-30-1	0.38	0.04	9.5	90	6.00	43.47	13.51	12.52 ± 0.20	
DAAM-30-2	0.38	0.04	9.5	150	15.40	43.30	13.52	12.24 ± 0.20	340
DAAM-30-3	0.38	0.04	9.5	210	30.37	44.31	14.11	11.05 ± 0.20	
DAAM-40-1	0.34	0.08	4.25	90	11.10	45.28	12.36	21.22 ± 0.30	
DAAM-40-2	0.34	0.08	4.25	150	6.47	45.25	11.39	27.23 ± 0.40	333
DAAM-40-3	0.34	0.08	4.25	210	7.41	46.23	12.70	20.71 ± 0.30	

Table - 24

Reaction Parameters for the copolymerisation of AM with N-t BAM At 50°C (Total Monomer Concentration = 0.42 M)

Sample number	Monomer concentration in the feed (M)			Reaction time (min.)	Conversion(%)	Elemental Analysis (wt%)		Mol % N-t BAM in copolymer	[η] ml.g ⁻¹
	[AM]	[N-t-BAM]	[AM]/[N-t BAM]			C	N		
	N-t-BAM-10-1	0.41	0.01			41	90		
N-t-BAM-10-2	0.41	0.01	41	150	35.81	40.32	15.53	1.66 ± 0.04	430
N-t-BAM-10-3	0.41	0.01	41	210	55.61	42.28	15.50	4.57 ± 0.06	
N-t-BAM-20-1	0.40	0.02	20	90	36.27	40.91	15.62	1.31 ± 0.04	
N-t-BAM-20-2	0.40	0.02	20	150	40.78	40.94	15.08	4.15 ± 0.04	415
N-t-BAM-20-3	0.40	0.02	20	210	52.79	42.02	15.07	6.32 ± 0.08	
N-t-BAM-30-1	0.38	0.04	9.5	90	28.58	42.10	14.21	11.42 ± 0.20	
N-t-BAM-30-2	0.38	0.04	9.5	150	31.81	41.11	14.94	5.21 ± 0.05	403
N-t-BAM-30-3	0.38	0.04	9.5	210	34.53	43.58	12.79	24.33 ± 0.30	
N-t-BAM-40-1	0.34	0.08	4.25	90	28.38	42.35	14.29	11.44 ± 0.20	
N-t-BAM-40-2	0.34	0.08	4.25	150	39.40	41.96	14.30	10.57 ± 0.20	300
N-t-BAM-40-3	0.34	0.08	4.25	210	40.98	43.67	13.10	22.25 ± 0.30	

The transformed variables G and H are given by

$$G = \frac{[M_1]/[M_2] \left[\left(\frac{d[M_1]}{d[M_2]} - 1 \right) \right]}{d[M_1]/d[M_2]} \quad (46)$$

$$H = \frac{\left(\frac{[M_1]}{[M_2]} \right)^2}{d[M_1]/d[M_2]} \quad (47)$$

The parameter α is calculated by taking square root of the product of the lowest and highest values of H for the copolymerization series. A plot of the data according to the Kelen - Tüdös method is shown in Figure 53. Reactivity ratios were determined for AM : DAAM monomer pair as $r_1 = 0.71$ and $r_2 = 0.61$ respectively. The observed data in the Kelen - Tüdös plot are linear, an indication that these copolymerization follow the conventional copolymerization kinetics under a prerequisite that the reactivity of a polymer radical is only determined by the terminal monomer unit²⁷⁴. Table - 25 lists the parameters used to statistically determine reactivity ratios from the Mayo-Lewis method at high conversion [equation 48].

$$r_2 = \frac{\log \frac{[M_{2,0}]}{[M_2]} - \frac{1}{p} \log \left(\frac{1 - p[M_1]/[M_2]}{1 - p[M_{1,0}]/[M_{2,0}]} \right)}{\log \frac{[M_{2,0}]}{[M_2]} + \log \left(\frac{1 - p[M_1]/[M_2]}{1 - p[M_{1,0}]/[M_{2,0}]} \right)} \quad (48)$$

Where p is an integration constant defined by $(1-r_1) / (1-r_2)$, the initial concentrations of AM and DAAM are represented by $[M_{1,0}]$ and $[M_{2,0}]$ respectively. Values of 0.76 and 0.58 were obtained for r_1 and r_2 respectively (Fig. 54). Closely comparable values of r_1 and r_2 were obtained from Fineman - Ross, Kelen - Tüdös, and Mayo - Lewis treatments for the copolymerization of acrylamide with diacetone acrylamide on montmorillonite surface and are listed

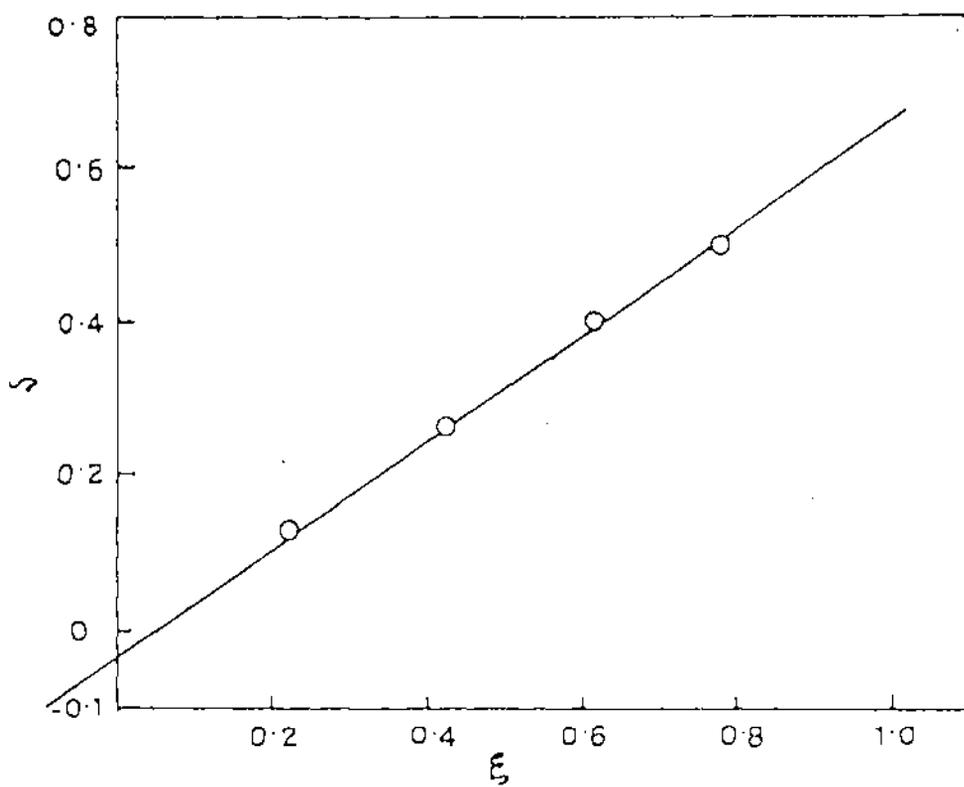


Fig. 53 Determination of reactivity ratios for copolymerization of AM with DAAM by Kelen-Tüdös method.

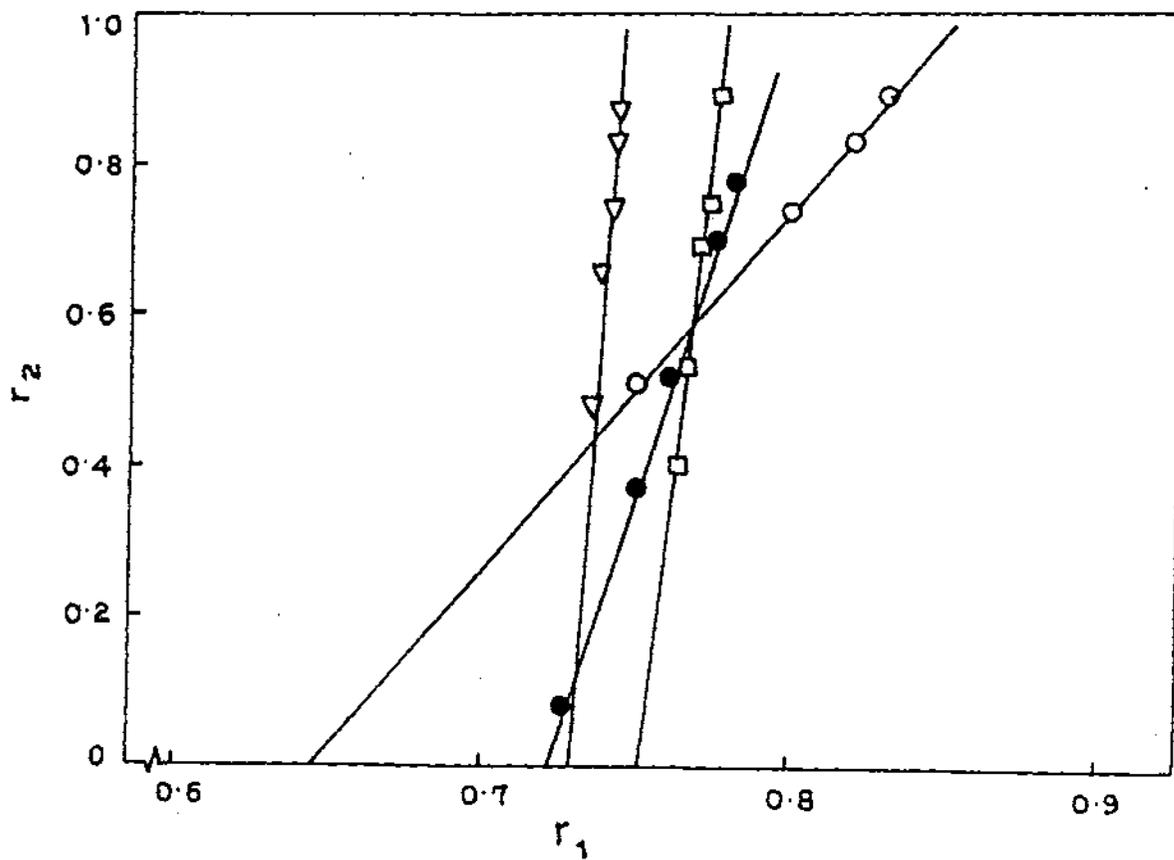


Fig. 54 Mayo-Lewis plot of AM-DAAM copolymer (high conversion).

Table - 25

Variables for the Evaluation of the Reactivity Ratios by the Lewis - Mayo Method

Sample number	$M_{1,0}$	$M_{2,0}$	Q_1	M_1	M_2	Q	F_1	F_2	r_1	r_2
DAAM-10-2	0.41	0.01	41	0.218	0.004	53.17	0.47	0.59	0.76 ± 0.02	0.58 ± 0.04
DAAM-20-3	0.40	0.02	20	0.244	0.011	23.24	0.39	0.47		
DAAM-30-3	0.38	0.04	9.50	0.269	0.026	10.25	0.29	0.34		
DAAM-40-3	0.34	0.08	4.25	0.316	0.074	4.29	0.07	0.08		

$M_{1,0}$ = initial concentration of AM

$M_{2,0}$ = initial concentration of DAAM

$Q_1 = M_{1,0}/M_{2,0}$

M_1 = residual AM in solution

M_2 = residual DAAM in solution

$Q = M_1/M_2$

$F_1 = 1 - M_1/M_{1,0}$

$F_2 = 1 - M_2/M_{2,0}$

r_1 = reactivity ratio of AM

r_2 = reactivity ratio of DAAM

in Table 26.

Reactivity ratio studies were also conducted for the copolymerization of acrylamide (M_1) with N-t-butylacrylamide (M_2) using Fineman-Ross (Figure 55) and Kelen-Tüdös (Figure 56) methods. Mayo-Lewis treatment did not give desirable results. The calculated reactivity ratios are listed in Table 27. Figure 57 shows the composition as a function of the acrylamide in the feed based on the experimentally determined reactivity ratios in the copolymerization of AM with DAAM and with N-t-BAM. The AM-DAAM copolymers with $r_1 r_2 = 0.43$ and the AM-N-t BAM copolymers with $r_1 r_2 = 0.70$ exhibit an opposite tendency toward alternation. Experimental points on the figure are, however, restricted upto 80 mole % of AM in the feed because no copolymer was formed below that value. Previous study on the copolymerization of AM with DAAM by potassium persulfate initiator showed a variation of r_1 and r_2 values from 0.76 to 0.83 and 0.92 to 0.99 respectively for the three methods applied.²⁶⁶ These values are, however, higher than those obtained in the present study. Current investigation also shows that r_1 values for the copolymerization of AM with

Table - 26

Reactivity Ratios for copolymerization of AM (r_1) with DAAM (r_2) Method

Method	r_1	r_2
Fineman - Ross ^a	0.69 ± 0.03	0.62 ± 0.05
Fineman - Ross ^b	6.18 ± 0.17	1.06 ± 0.06
Kelen - Tüdös	0.70 ± 0.08	0.60 ± 0.09
Mayo - Lewis	0.76 ± 0.02	0.58 ± 0.04

^a $M_1 = AM, M_2 = DAAM$; ^b $M_1 = DAAM, M_2 = AM$

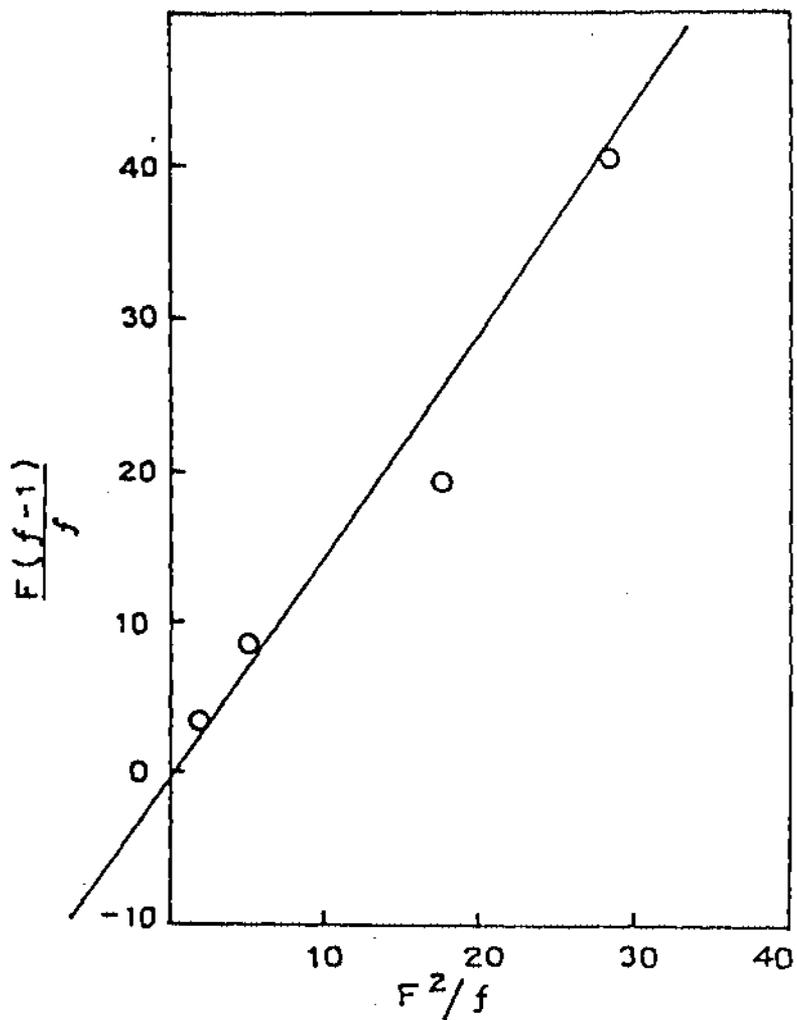


Fig. 55 Determination of reactivity ratios for copolymerization of AM with N-t-BAM by Fineman-Ross method.

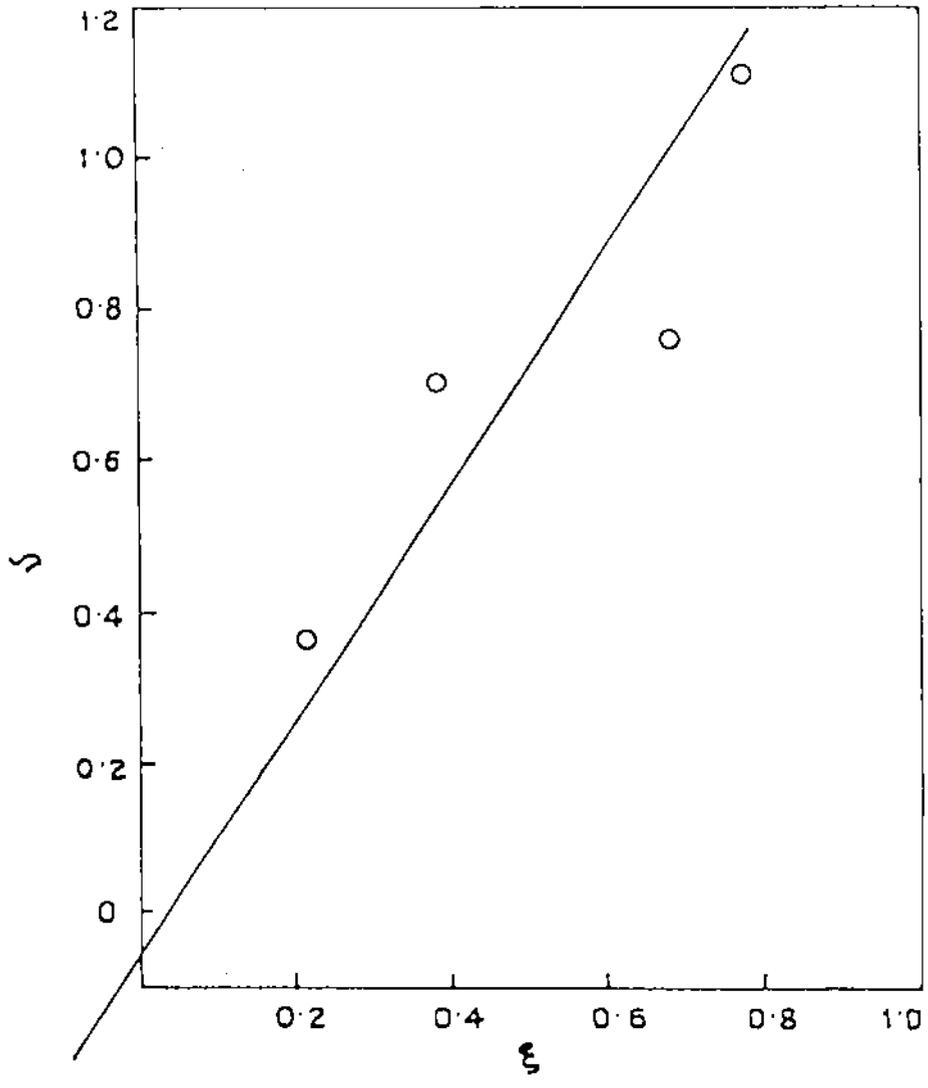


Fig. 56 Determination of reactivity ratios for copolymerization of AM with N-t-BAM by Kelen-Tüdös method.

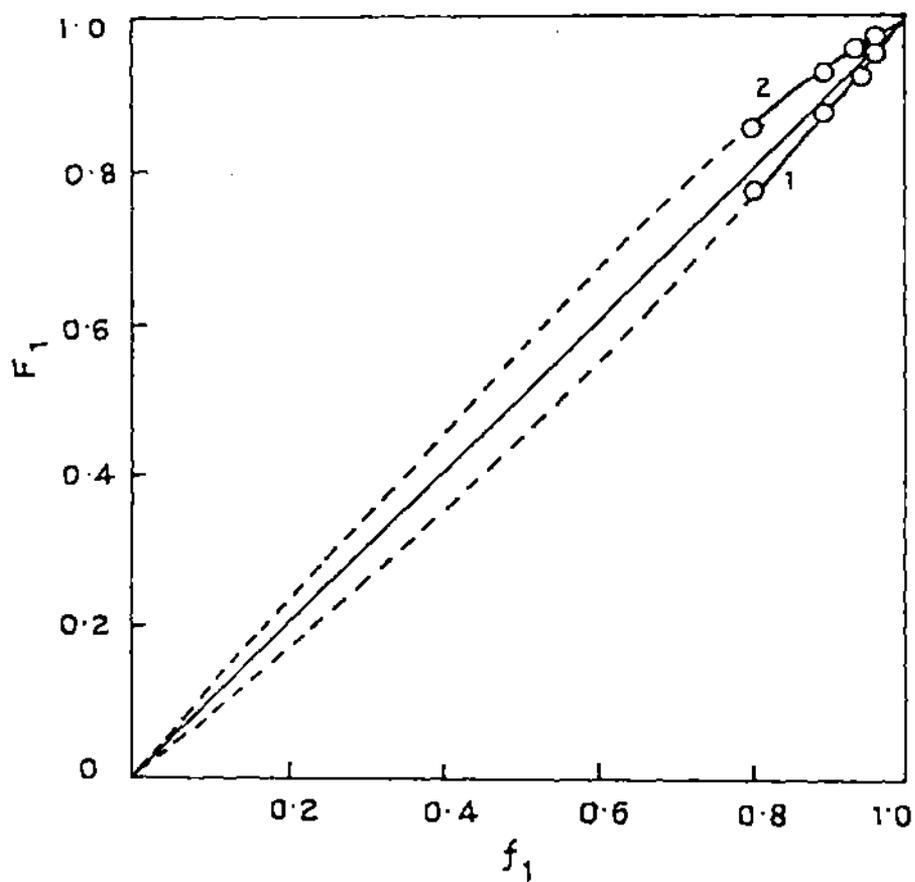


Fig. 57 Copolymer composition as a function of feed composition for the copolymerization of AM with DAAM (curve 1) and AM with N-t-BAM (curve 2).

Table - 27

Reactivity Ratios for copolymerization of AM(r_1) with N-t BAM (r_2)

Method	r_1	r_2
Fineman - Ross ^a	1.50 ± 0.10	0.50 ± 0.04
Fineman - Ross ^b	1.39 ± 0.08	0.75 ± 0.06
Kelen - Tudos	1.50 ± 0.10	0.46 ± 0.04

^a $M_1 = AM, M_2 = N-t-BAM;$ ^b $M_1 = N-t-BAM, M_2 = AM$

N-t-BAM is considerably higher than AM-DAAM copolymers, where as, those of r_2 are smaller in the case AM-N-t BAM than that of the other copolymer.

Copolymer microstructure

The microstructures of the AM-DAAM and AM-N-t BAM copolymers are expected to be important in determining the solution properties of copolymers. As mentioned earlier, observed data follow the conventional copolymerisation equation and the adherence of the data to this equation is an important point in establishing the validity of the statistical microstructure analyses. The statistical distribution of monomer sequences, $M_1 - M_1, M_2 - M_2,$ and $M_1 - M_2$ may be calculated utilizing equations²⁷⁵⁻²⁷⁶.

$$X = \phi_1 - 2\phi_1(1 - \phi_1)/\{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1 - \phi_1)]\}^{1/2} \quad (49)$$

$$Y = (1 - \phi_1) - 2\phi_1(1 - \phi_1)/\{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1 - \phi_1)]\}^{1/2} \quad (50)$$

$$Z = 4\phi_1(1 - \phi_1)/\{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1 - \phi_1)]\}^{1/2} \quad (51)$$

The mole fractions of $M_1 - M_1, M_2 - M_2$ and $M_1 - M_2$ sequences in the copolymer are designated by X, Y and Z respectively. The copolymer

composition is ϕ_1 and, r_1 and r_2 are the reactivity ratios, for the respective monomer pairs. Mean sequence lengths, μ_1 and μ_2 , can be calculated utilizing equation (52) and (53) with the consideration of compositional drift.²⁷⁵

$$\mu_1 = 1 + r_1 [M_1]/M_2 \quad (52)$$

$$\mu_2 = 1 + r_2 [M_2]/M_1 \quad (53)$$

The intermolecular linkage and mean sequence length distributions for the AM-DAAM and the AM-N-t BAM copolymers are listed in Table 28 and 29 respectively. The Kelen - Tüdös values of reactivity ratios were used for sequence distribution calculation. For the series of AM-DAAM copolymers, the mean sequences length of acrylamide, μ_{AM} , varied from 30.03 at an 96.36/3.64 mol ratio of AM/DAAM in the copolymer to 4.01 with a 78.77/21.23 mol ratio. For those compositions, values of μ_{DAAM} were 1.01 and 1.14 respectively. On the other hand, the AM-N-t BAM copolymers had μ_{AM} value of 62.50 and 7.37 at 98.33/1.67 and 89.42/10.58 mol ratios of AM/N-t BAM respectively. Above values for μ_{N-tBAM} were 1.01 and 1.11 respectively.

Effect of Feed Composition

The effect of feed composition on intrinsic viscosity of copolymers synthesized at high conversion was studied for both AM-DAAM and the AM-N-t BAM copolymers listed in Table 23 and 24 respectively. Figure 58 illustrates the effect of feed composition on the intrinsic viscosity for each copolymer series. The observed decrease in intrinsic viscosity with increasing diacetoneacrylamide or N-tert-butylacrylamide co-monomer concentrations may be explained by increased cross-termination rates of copolymerization as compared to the very low rate of termination observed for acrylamide, resulting in the decrease of the overall molecular weight of the copolymers^{278,279}.

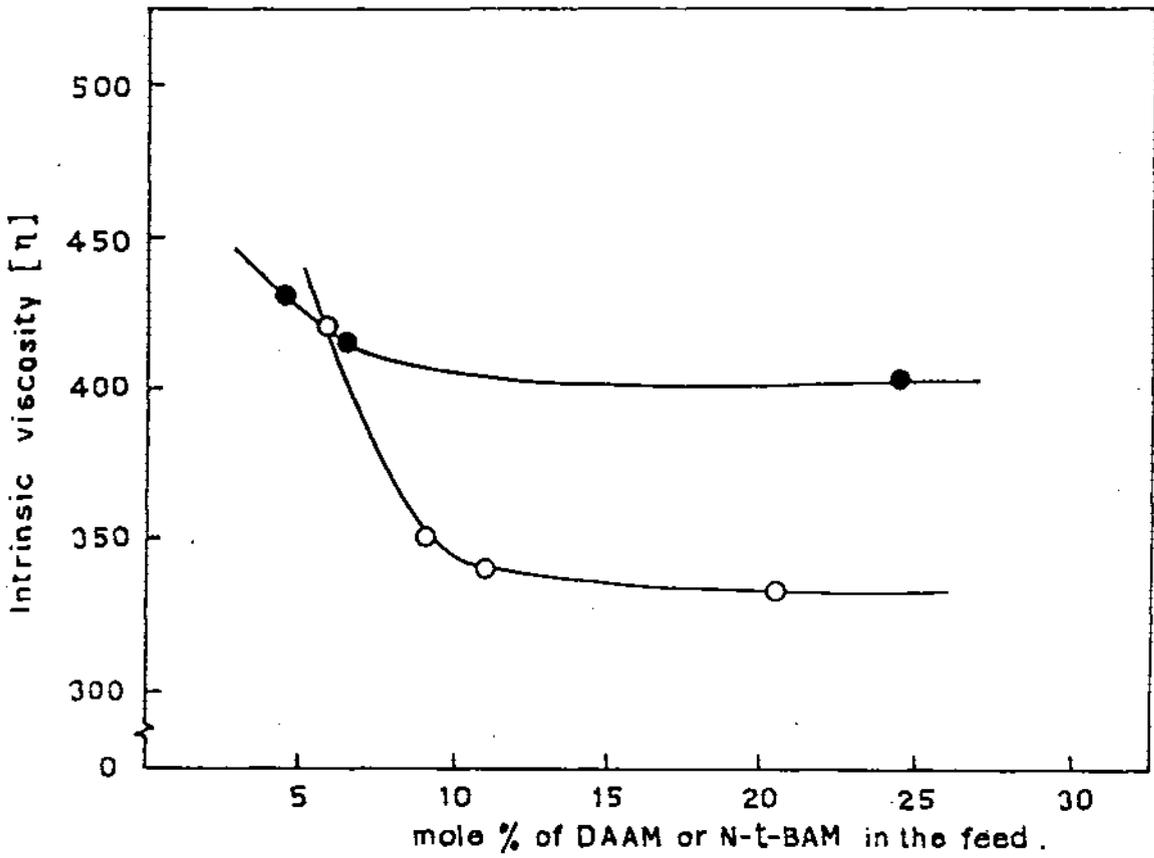


Fig. 58 Effect of feed composition on the intrinsic viscosity of AM-DAAM (o) and AM-N-t-BAM (●) copolymers.

Table- 28
Structural Data for the copolymers of AM with DAAM

Sample Number	Composition ^a (mole%)		Block ness ^b (mole%)		Alternation ^b (mole%)	Mean Sequence length		μ_{AM}/μ_{DAAM}
	AM	DAAM	AM-AM	DAAM-DAAM	AM - DAAM	μ_{AM}	μ_{DAAM}	
DAAM-10-1	96.36	3.64	92.78	0.06	7.16	30.03	1.01	29.58
DAAM-20-1	93.61	6.39	87.41	0.19	12.40	15.16	1.03	14.71
DAAM-30-1	87.44	12.56	75.67	0.79	23.54	7.72	1.06	7.29
DAAM-40-1	78.77	21.23	60.05	2.51	37.43	4.01	1.14	3.51
DAAM-10-2	96.46	3.54	92.97	0.06	6.97	30.03	1.01	29.58
DAAM-20-2	92.69	7.31	85.70	0.32	13.98	15.16	1.03	14.71
DAAM-30-2	87.73	12.27	76.21	0.76	23.03	7.72	1.06	7.29
DAAM-40-2	72.76	27.24	50.00	4.47	45.54	4.01	1.14	3.51
DAAM-10-3	94.08	5.92	88.32	0.16	11.51	30.03	1.01	29.58
DAAM-20-3	93.49	6.51	87.17	0.20	12.62	15.16	1.03	14.71
DAAM-30-3	88.94	11.06	78.48	0.60	20.92	7.72	1.06	7.29
DAAM-40-3	79.22	20.78	60.83	2.40	36.77	4.01	1.14	3.51

^a Calculated from elemental analysis ; ^b Statistically calculated from the reactivity ratios.

Table- 29
Structural Data for the copolymers of AM with N-t BAM

Sample Number	Composition ^a		Block ness ^b		Alternation ^b		Mean Sequence length		μ_{AM}/μ_{N-tBAM}
	(mole%)		(mole%)		(mole%)				
	AM	N-t BAM	AM-AM	N-t BAM- N-t BAM	AM	N-t BAM	μ_{AM}	μ_{N-tBAM}	
N-t-BAM-10-1	93.78	6.22	87.84	0.28	11.87		62.50	1.01	61.80
N-t-BAM-20-1	98.61	1.39	97.23	0.01	2.75		31.00	1.02	30.30
N-t-BAM-30-1	88.59	11.41	78.16	0.98	20.86		15.25	1.05	14.52
N-t-BAM-10-1	88.56	11.44	78.10	0.98	20.91		7.37	1.11	6.64
N-t-BAM-10-2	98.33	1.67	96.68	0.01	3.30		62.50	1.01	61.80
N-t-BAM-20-2	95.82	4.18	91.77	0.12	8.11		31.00	1.02	30.30
N-t-BAM-30-2	94.75	5.25	89.70	0.20	10.10		15.25	1.05	14.52
N-t-BAM-40-2	89.42	10.58	79.68	0.84	19.48		7.37	1.11	6.64
N-t-BAM-10-3	95.44	4.56	91.03	0.46	8.82		62.50	1.01	61.80
N-t-BAM-20-3	93.68	6.32	87.65	0.29	12.06		31.00	1.02	30.30
N-t-BAM-30-3	75.62	24.38	56.05	4.80	39.14		15.25	1.05	14.52
N-t-BAM-40-3	77.77	22.23	3.95	3.95	36.55		7.37	1.11	6.64

^aCalculated from Elemental Analysis

^bStatistically calculated from Reactivity Ratios.