Colloid Polym Sci 273:822–827 (1995)

ORIGINAL CONTRIBUTION

P.C. Dwivedi
S.D. Pandey
A. Tandon
S. Singh

Polymerization of methyl methacrylate with aminoalcohols and carbon tetrachloride initiated by charge-transfer mechanism

Received: 2 September 1994
Accepted: 1 April 1995

Dr. P.C. Dwivedi (✉) · S.D. Pandey
A. Tandon · S. Singh
Department of Chemistry
H.B. Technological Institute
Kanpur, 208002 India

Abstract Polymerization of methylmethacrylate (MMA) with aminoalcohols, namely ethanolamine (EA), diethanolamine (DEA) and triethanolamine (TEA) in the presence of carbontetrachloride (CCl_4) has been investigated in the dimethylsulfoxide (DMSO) medium by employing a dilatometric technique. The rate of polymerization (R_p) has been evaluated under the conditions $\frac{CCl_4}{[amine]} < 1$ and > 1. The kinetic data reveal the possible participation of a charge-transfer complex in the polymerization reaction. In the absence of either CCl_4 or amine, no polymerization of MMA was observed under the present experimental conditions. The polymerization of MMA was inhibited by hydroquinone, indicating a free radical initiation.

Key words Charge-Transfer – free radical – nitrogen donor

Introduction

Much attention has been focussed in the past two decades on the polymerization of MMA by charge-transfer mechanism [1–10]. Majority of these studies involve nitrogen atom of the aliphatic amines as the donor site in the formation of the charge-transfer complex. Thus, the polymerization of MMA initiated by charge-transfer complexes formed by *n*-butylamine [11], isopropylamine [12], cyclopentylamine, heptylamine [13], *n*-pentylamine, *n*-hexylamine, and *n*-octylamine [6], etc. in the presence of carbon tetrachloride has been investigated in detail. Such charge-transfer initiated polymerisation can be accelerated by Lewis acids like Fe^{3+} [14], Cu^{2+} [15], Rb^{3+} [16] and Ru^{2+} [16]. Two mechanisms have been proposed for the initiation of the polymerization of MMA by these charge-transfer complexes. One is the initiation by the charge-transfer complex formed between the amine donor and carbon tetrachloride acceptor [17] (mechanism 1), while the other involves the charge-transfer complex formed between the amine donor and the monomer acceptor as the initiator [3] (mechanism 2). Dass and coworkers [11–13] as well as Dwivedi and coworkers [6] presumed that both the mechanisms are possible and presented experimental evidence for the predominance of mechanism 1 under the condition $[CCl_4]/[amine] \leq 1$ and mechanism 2 under the condition $[CCl_4]/[amine] > 1$.

Recently, Baruah and coworkers [18] have reported the polymerization of MMA by charge-transfer mechanism with ethanolamine (EA) and CCl_4 in N, N-dimethylformamide medium. This report prompted us to carry out detailed investigations on the polymerization of MMA using a variety of aminoalcohols in the presence of CCl_4. In this paper, we have used one member each of a primary, secondary and tertiary aminoalcohol namely, ethanolamine (EA), diethanolamine (DEA) and triethanolamine (TEA) respectively in DMSO medium. EA has been included in this study for the sake of comparison.

Experimental

MMA, DMSO and carbon tetrachloride were purified by the standard methods [6]. EA, DEA and TEA were distilled under reduced pressure before use. The procedure for polymerization and evaluation of the rate of polymerization (R_p) of MMA is described elsewhere [6]. The intrinsic viscosity (η_{int}) of the polymer was determined in benzene solution at 30 °C with a Ubbelohde viscometer. The average degree of polymerization ($\bar{P}_n$) was calculated by using Eq. (1) [19].

$$\eta_{int} = 3.36 \times 10^{-3} \bar{P}_n^{0.73} \quad (1)$$

Equation (2) [20] was used to evaluate the molecular weight (m_n) of the polymer.

$$\eta_{int} = 5.2 \times 10^{-5} m_n^{0.76} \quad (2)$$

Results and discussion

MMA was polymerised by EA, DEA and TEA in the presence of CCl_4 in DMSO medium. However, no polymerization of MMA could be observed in the absence of the aminoalcohols or CCl_4 under the present experimental conditions. The rate of polymerization (R_p) of MMA was found to be dependent on the concentration of MMA, aminoalcohols, CCl_4 and hydroquinone.

The rate of polymerization of MMA was measured at various concentrations of MMA keeping the concentrations of the aminoalcohol and CCl_4 constant and the results are presented in Table 1. When $[CCl_4]/[\text{aminoalcohol}] \leq 1$, the monomer exponent values calculated from the slope of the linear plot of $\log R_p$ versus log[MMA] were found to be nearly unity indicating a first order variation of R_p with [MMA] in all the cases. A typical plot is shown in Fig. 1 for TEA. This first order variation of R_p with [MMA] was further supported by the linear plots of $\log [a/(a-x)]$ versus time for EA, DEA and TEA. Such a typical plot is given in Fig. 2 for DEA. Here, a and $(a-x)$ represent the concentrations of MMA (which may be

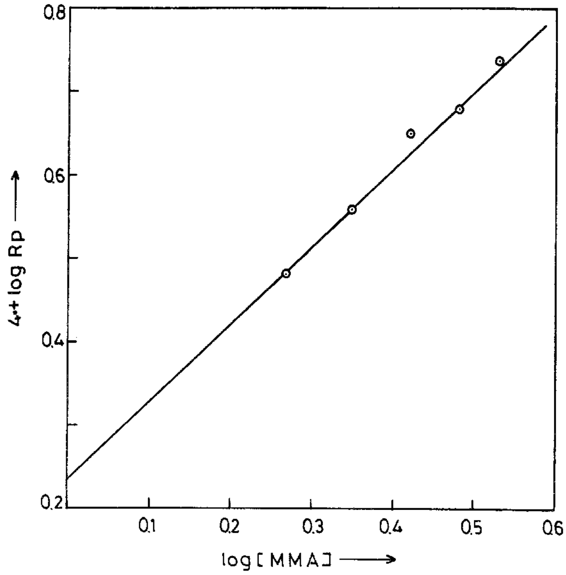


Fig. 1 Log [MMA] vs. $\log R_p$ plot for the polymerization of MMA in DMSO solution ([TEA] = 0.32 mol l^{-1}; $[CCl_4]$ = 0.20779 mol l^{-1})

Table 1 Effect of concentration of MMA on R_p in DMSO medium at 40 °C.[a]

MMA (mol l^{-1})	$R_p \times 10^4$ (mol l^{-1} s^{-1})					
	$[CCl_4]/[\text{amine}] < 1$			$[CCl_4]/[\text{amine}] > 1$		
	EA[b]	DEA[c]	TEA[d]	EA[e]	DEA[f]	TEA[g]
1.504	2.022	1.618	–	1.498	1.772	–
1.880	2.622	2.037	2.996	1.977	2.397	3.195
2.256	2.996	2.097	3.595	2.097	2.741	4.494
2.632	3.221	2.397	4.494	2.561	3.296	5.692
3.008	3.371	2.547	4.794	2.996	3.895	7.939
3.384	4.494	2.996	5.543	3.265	4.344	8.688
3.76	5.138	3.146	–	–	4.494	–

[a] For EA at 30 °C
[b] [EA] = 1.32 mol l^{-1}, $[CCl_4]$ = 0.83 mol l^{-1}
[c] [DEA] = 0.76 mol l^{-1}, $[CCl_4]$ = 0.4158 mol l^{-1}
[d] [TEA] = 0.32 mol l^{-1}, $[CCl_4]$ = 0.2077 mol l^{-1}
[e] [EA] = 0.33 mol l^{-1}, $[CCl_4]$ = 0.83 mol l^{-1}
[f] [DEA] = 0.76 mol l^{-1}, $[CCl_4]$ = 1.24 mol l^{-1}
[g] [TEA] = 0.32 mol l^{-1}, $[CCl_4]$ = 2.077 mol l^{-1}

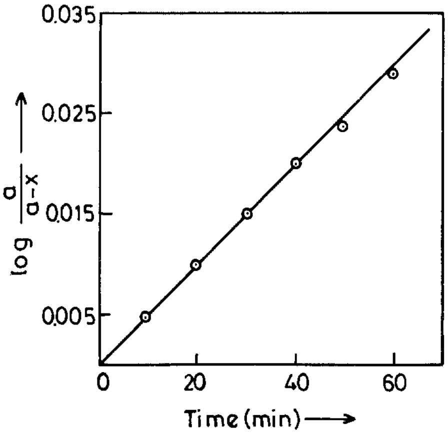


Fig. 2 Plot of $\log[a/(a-x)]$ vs. time for the polymerization of MMA in DMSO solution ($[\text{MMA}] = 3.384$ mol l^{-1}, $[\text{CCl}_4] = 1.24$ mol l^{-1}; $[\text{DEA}] = 0.76$ mol l^{-1})

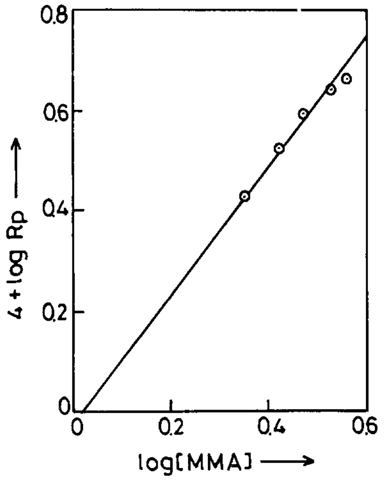


Fig. 3 Log [MMA] vs. $\log R_p$ plot for the polymerization of MMA in DMSO solution ($[\text{DEA}] = 0.76$ mol l^{-1}; $[\text{CCl}_4] = 1.24$ mol l^{-1})

taken as proportional to the volume of MMA solution in the dilatometer) initially and at time t. The first order rate constants, k, evaluated from these plots are $5.03 \times 10^{-5}\,\text{s}^{-1}$, $1.91 \times 10^{-5}\,\text{s}^{-1}$ and $2.2 \times 10^{-5}\,\text{s}^{-1}$ for EA, DEA and TEA, respectively.

The data for the variation of R_p with MMA concentration at a fixed concentration of the aminoalcohol and CCl_4 when $[\text{CCl}_4]/[\text{aminoalcohol}] > 1$ are given in Table 1. The order of reaction with respect to MMA under this condition was determined from the slope of the linear plot of $\log R_p$ versus log [MMA] and was found to be between 1.3 and 1.47. A typical plot is shown in Fig. 3 for DEA.

R_p of MMA measured at different concentrations of CCl_4 while keeping the concentration of the aminoalcohol and MMA constant was found to increase with an increase in the concentration of CCl_4 and became independent of it when $[\text{CCl}_4]/[\text{aminoalcohol}] > 1$. A typical plot of R_p versus $[\text{CCl}_4]$ is shown in Fig. 4 for TEA. When $[\text{CCl}_4]/[\text{aminoalcohol}] < 1$, R_p was found to be proportional to $[\text{CCl}_4]^{0.5}$ as evidenced by the plots in Fig. 5.

R_p of MMA increased with an increase in the concentration of aminoalcohol at fixed concentrations of MMA and CCl_4 and was found to be proportional to $[\text{aminoalcohol}]^{0.5}$ under both the conditions, $[\text{CCl}_4]/[\text{aminoalcohol}] < 1$ and > 1. A typical plot of R_p versus $[\text{aminoalcohol}]^{0.5}$ is shown in Fig. 6 for TEA. The linear plots of R_p versus $[\text{aminoalcohol}]^{0.5}$ yield intercept on the $[\text{aminoalcohol}]^{0.5}$ axis which give the limiting values of the concentration of aminoalcohols for the formation of the associated complex with DMSO [21]. Thus, the aminoalcohols upto these limiting concentrations were not free to initiate the polymerization of MMA. Above this limiting concentration the free aminoalcohol

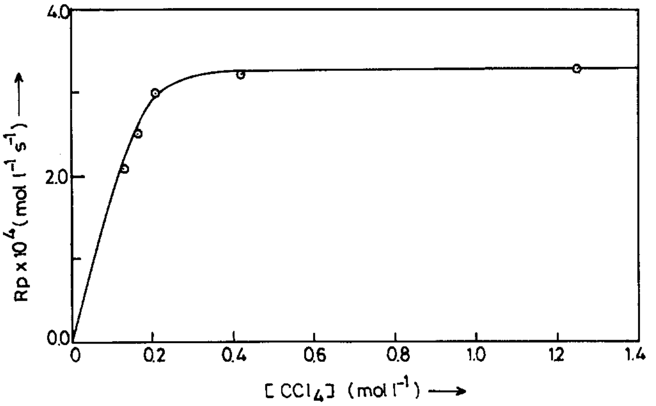
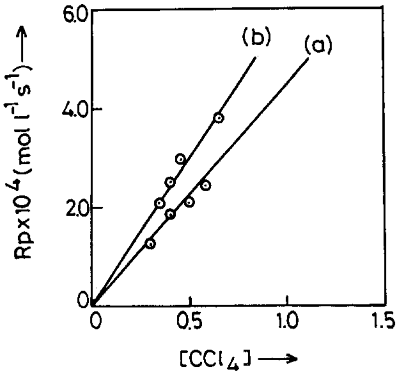


Fig. 4 Plot of R_p vs. $[\text{CCl}_4]$ for the polymerization of MMA in DMSO solution ($[\text{MMA}] = 1.88$ mol l^{-1}; $[\text{TEA}] = 0.32$ mol l^{-1})

Fig. 5 Plots of R_p vs. $[\text{CCl}_4]^{0.5}$ for the polymerization of MMA in DMSO solution (a) $[\text{EA}] = 1.32$ mol l^{-1}; $[\text{MMA}] = 1.88$ mol l^{-1}; (b) $[\text{TEA}] = 0.32$ mol l^{-1}; $[\text{MMA}] = 1.88$ mol l^{-1}



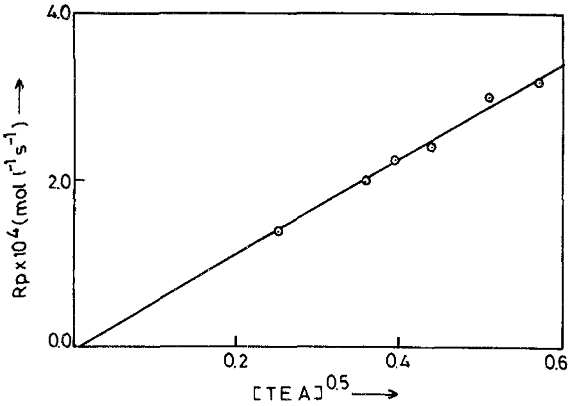


Fig. 6 Plot of R_p vs. $[TEA]^{1/2}$ for the polymerization of MMA in DMSO solution ([MMA] = 1.88 mol l^{-1}; $[CCl_4]$ = 2.0779 mol l^{-1})

was available for the formation of a charge-transfer complex with MMA and CCl_4 and the initiation of the polymerization was possible.

The polymerization of MMA was inhibited by hydroquinone (see Table 2) indicating a free radical mechanism for the polymerization.

R_p of MMA increased with an increase in temperature. The overall energies of activation (Ea) evaluated from the slopes of the Arrhenius plots were found to be 27.6, 29.4 and 31.2 kjmol^{-1} for EA, DEA and TEA respectively. It is interesting to note that these Ea values follow the same trend as the R_p values measured at the same concentration of MMA aminoalcohol and CCl_4 as can be seen from the data given below:

Aminoalcohol	$R_p^a \times 10^4$ (mol l^{-1} s^{-1})
EA	5.69
DEA	4.34
TEA	3.59

[a] At 40 °C
[MMA] = 1.88 mol l^{-1}
$[CCl_4]$ = 0.83 mol l^{-1}
[aminoalcohol] = 0.33 mol l^{-1}

The $k_p/k^{1/2}$ values in Table 3 exhibit a similar trend. With the exception of TEA, the first order rate constants (k) also vary in the same direction. The foregoing observations seem to suggest that the polymerization of MMA in these systems is initiated by the formation of a charge-transfer complex in which the aminoalcohol acts as an electron donor.

The molecular weights of the poly(methyl methacrylate) (PMMA) were found to increase with the increase in the concentration of MMA and CCl_4. However, the molecular weights of PMMA decreased with increase in concentration of the aminoalcohol. This is to be expected because there is a possibility of termination by aminoalcohol also.

Table 2 Effect of Hydroquinone on the rate of Polymerization of DEA at 40 °C in DMSO solution[a]

Concentration of hydroquinone (mol l^{-1})	$R_p \times 10^4$ (mol l^{-1} s^{-1})
0.0	2.921
1.81×10^{-2}	2.247
3.63×10^{-2}	2.097
5.42×10^{-2}	1.498

[a] [MMA] = 1.8 mol l^{-1}, [DEA] = 0.76 mol l^{-1}, $[CCl_4]$ = 1.24 mol l^{-1}

Mechanism of initiation of polymerization of MMA

The polymerization of MMA was inhibited by hydroquinone indicating a free radical mechanism for the polymerization. These free radicals are generated by the decomposition of the charge-transfer complex formed by the aminoalcohol as electron donor. Two mechanisms have been proposed for the initiation of polymerization of MMA by charge-transfer complexes involving amine donors in the presence of CCl_4. According to mechanism 1 [17], the initiation of polymerization is due to charge-transfer complex (I) formed by the interaction of the amine with CCl_4 which decomposes to produce $\dot{C}Cl_3$ as shown in the following scheme:

$$RNH_2 + CCl_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \qquad (3)$$

$$I \xrightarrow{k_2} R\dot{N}^+H_2Cl^- + \dot{C}Cl_3$$

$$M + \dot{C}Cl_3 \longrightarrow \dot{R}_1 \qquad (4)$$

where M = MMA, R = alkyl group of the amine, $\dot{R}_1$ = $\dot{M}CCl_3$ and I = charge-transfer complex.

Mechanism 2 [3] assumes that a charge-transfer complex (II) is formed by the interaction between amine and MMA which initiates polymerization in the presence of CCl_4 according to the following scheme:

$$RNH_2 + MMA \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} II \qquad (5)$$

$$II + CCl_4 \xrightarrow{k_4} \dot{R}_1 + R\dot{N}^+H_2Cl^- \qquad (6)$$

Table 3 $[\eta_{int}]$, molecular weight, $\bar{P}_n$ and $k_p/k_t^{1/2}$ data[a] for polymerization of MMA[b]

Amine	[MMA] $(mol\,l^{-1})$	$[\eta_{int}]$	$\bar{P}_n$	Molecular weight	$k_p/k_t^{1/2}$ $(l\,mol^{-1}\,s)^{1/2}$
Ethanolamine	1.504	0.42	745.4	1,35,400	
	1.88	0.47	869.8	1,60,400	
	2.256	0.54	1052.0	1,92,800	0.230
	2.632	0.59	1188.0	2,16,500	
	3.008	0.64	1327.0	2,40,900	
	3.384	0.68	1442.0	2,61,000	
	3.76	0.72	1560.0	2,81,400	
Diethanolamine	1.504	–	–	–	
	1.88	0.275	417.3	79,270	
	2.256	0.35	580.8	1,08,800	
	2.632	0.40	697.4	1,29,800	0.183
	3.008	0.425	757.7	1,40,600	
	3.384	0.49	920.8	1,69,500	
	3.76	0.53	1024.0	1,87,800	
Triethanolamine	1.504	–	–	–	
	1.88	0.29	447.6	85,000	
	2.256	0.37	626.6	1,17,100	0.111
	2.632	0.43	770.0	1,43,000	
	3.008	0.54	1052.0	1,92,500	
	3.384	0.66	1385.0	2,50,800	
	3.76	–	–	–	

[a] At 30 °C
[b] $[EA] = 1.33\,mol\,l^{-1}$, $[CCl_4] = 0.83\,mol\,l^{-1}$
$[DEA] = 0.76\,mol\,l^{-1}$, $[CCl_4] = 1.24\,mol\,l^{-1}$
$[TEA] = 0.32\,mol\,l^{-1}$, $[CCl_4] = 2.0779\,mol\,l^{-}1$

$R\dot{N}^+H_2Cl^-$ formed in Eq. 4 and 6 is expected to undergo dissociation in DMSO (which is a polar solvent) to give $R\dot{N}^+H_2$ which may react with CCl_4 to produce $\dot{C}Cl_3$ as suggested by Takemoto and coworkers [22]

$$RN^+H_2Cl^- \longrightarrow R\dot{N}^+H_2 + Cl^-$$

$$R\dot{N}^+H_2 + CCl_4 \longrightarrow RNHCl + \dot{C}Cl_3 + H^+$$

Investigations on the polymerization of MMA using a number of aliphatic amines in the presence of CCl_4 [6, 11–13] have established that both the mechanisms are possible. Recently, Baruah and Subrahmanyam [9] have carried out gel permeation chromatographic studies on the polymerisation of butyl methacrylate by charge-transfer mechanism with EA in the presence of carbon tetrachloride. They have found that polymers with sufficiently excess EA in the system have a bimodal molecular weight distribution, whereas the polymers with less EA in the system have a unimodal and sharp distribution curve. These studies also suggest the coexistence of two polymerization mechanisms whose relative contribution depends on EA.

When $[CCl_4]/[amine] < 1$, mechanism 1 predominates and R_p is given by the equation,

$$R_p = \frac{k_p k_1^{1/2}}{k_t^{1/2}}[M][A]^{1/2}[CCl_4]^{1/2} \tag{7}$$

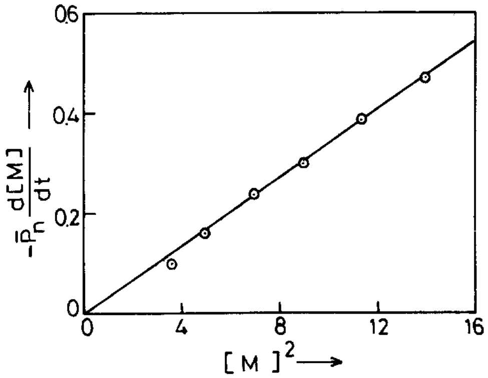


Fig. 7 $-\bar{P}_n[d[M]/dt]$ vs. $[M]^2$ plot for the polymerization of MMA ($[DEA] = 0.76\,mol\,l^{-1}$; $[CCl_4] = 1.24\,mol\,l^{-1}$)

When $[CCl_4]/[amine] \gg 1$, mechanism 2 predominates and R_p is given by the equation,

$$R_p = \frac{k_p k_3^{1/2}}{k_t^{1/2}}[M]^{3/2}[A]^{1/2} \tag{8}$$

Here, $[M] = [MMA]$ and $[A] = [amine]$ and k_p and k_t represent the rate constants of propagation and termination, respectively.

Our experimental results with EA, DEA and TEA agree well with Eqs. (7) and (8) indicating that the initiation of polymerization studied here involves the same mechanisms as proposed for the amine donors. As some of the monomer is used up in the initiation step, the experimentally observed order is slightly less than the theoretical value.

As the polymerization of MMA in the presence of CCl_4 and the aminoalcohol is initiated by free radicals produced from the charge-transfer complex, Eq. (9) should be applicable:

$$-\bar{P}_n\left[\frac{d[\mathrm{M}]}{dt}\right]=\frac{k_p^2}{k_t}[\mathrm{M}]^2 \qquad (9)$$

where $\bar{P}_n$ is the degree of polymerization, $-d[\mathrm{M}]/dt = R_p$ and [M] is the concentration of MMA in mol litre^{-1}. The $\bar{P}_n$ values for the systems examined here are given in Table 3. The plots of $-\bar{P}_n[d[\mathrm{M}]/dt]$ versus $[\mathrm{M}]^2$ were indeed found to be linear. Such a typical plot is shown in Fig. 7 for DEA. Slopes of these plots yielded values of $k_p/k_t^{1/2}$ given in Table 3. It is worth mentioning that some of the typical values of $k_p/k_t^{1/2}$ reported for such systems are 0.1436 [23], 0.160 [24], 0.109 and 0.134 [13], 0.125 [25], 0.198 [26], and 0.196–0.319 [27]. These $k_p/k_t^{1/2}$ values are comparable to our data and thus, lend support to the free radical mechanism for polymerization of MMA initiated by charge-transfer complexes.

References

1. Matsuda M, Ishiroshi Y (1970) J Polym Sci A-1 8:387
2. Oshiro Y, Shirota Y, Mikawa M (1974) J Polym Sci A-1 12:2199
3. Rosin H, Daren SLJ, Asscher M, Vofsi D (1972) J Appl Polym Sci 16:1687
4. Matsuda M, Ishiroshi Y, Seki K (1976) J Polym Sci Polym Chem Ed 14:1337
5. Dodgson K, Ebdon JR (1977) Eur Polym J 13:791
6. Dwivedi PC, Srivastava Archana, Rathi RS (1990) J Polym Sci Polym Chem Ed A 28:3279
7. Baruah SD, Dass NN (1979) Makromol Chem 180:1351
8. Mahato PK, Dass NN (1991) Indian J Chem 30A:418
9. Baruah SD, Subrahmanyam B (1991) Colloid Polym Sci 269:543
10. Baruah SD, Aradhana, Dass NN (1992) Polym J 24:719
11. Sen SR, Dass NN (1982) Eur Polym J 18:477
12. Baruah SD, Dass NN (1980) Eur Polym J 16:11
13. Dass NN, Gogoi AK (1983) J Macromol Sci Chem A 20:807
14. Begum SS, Dass NN (1982) J Polym Sci Polym Lett Eds 20:297
15. Dass NN (1984) Prog Polym Sci 10:51
16. Sen SR, Dass NN (1983) J Polym Sci A-1 21:3381
17. Latenberger WJ, Jones EA, Miller JG (1968) J Am Chem Soc 90:1110
18. Baruah SD, Subrahmanyam B (1990) J Macromol Sci Chem A 27:237
19. Baysat B, Tobolsky AV (1952) J Polym Sci 9:171
20. Pinner SH (1961) A short course in polymer chemistry Pergamon Oxford p 28
21. Pimental GC, McClellan (1960) The Hydrogen Bond, Reinhold New York p 373
22. Inaki Y, Ishiyama M, Hibino K, Takemoto K (1975) Makromol Chem 176:3135
23. Saha SK, Chaudhuri AK (1988) J Polym Sci Polym Chem A 26:901
24. Matsuda M, Hirayama T (1967) J Polym Sci A-1 5:2769
25. Bevington JC (1957) Trans Faraday Soc 53:997
26. Gogoi AK, Dass NN (1983) J Polym Sci A-1 21:3517
27. Dass NN, Gogoi AK (1984) J Poly Mater 1:183