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Cyclopolymerization of N,N'-methylenebisacrylamide with N,N-dimethylaniline-trichloroacetic acid and N,N-dimethylaniline-benzoyl chloride systems in aqueous medium

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ABSTRACT

The kinetics of cyclopolymerization of N,N'-methylenebisacrylamide (MBA) was carried out using a novel charge-transfer complexes of N,N-dimethylaniline(DMA)-Benzoyl chloride (BoCl) and N,N-dimethylaniline-Trichloroacetic acid (TCA). The reactions were carried out under various conditions of concentrations at constant temperature of 52ºC in aqueous medium. The dependence of rate of polymerization on various experimental conditions such as different concentrations of monomer MBA, donor DMA and acceptors BoCl and TCA were studied. The order with respect to monomer, donor and acceptors was found to be 1, 0.5 and 0.5 respectively. The kinetic results were interpreted by a suitable mechanic sequence. Absence of gelation is attributed to the formation of a cyclic polymer. Jobs method of continuous variation studies show that 1:1 complex formation.

Keywords: cyclopolymerization, non-conjugated divinyl monomer, N,N-dimethylaniline-Benzoylchloride, N,N-dimethylaniline-Trichloracetic acid charge-transfer complex

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INTRODUCTION

Butler and his co-workers reported that monomer containing three or four cyclic groups lead to the formation of insoluble polymers. A chain growth mechanism was proposed which involved alternation, intra-inter molecular steps which for the first time familiarly brought out at cyclopolymerization [1]. N,N'-methylenebisacrylamide [MBA], which is a symmetrical non-conjugated diolefin having double bond at terminal position and is a well-known cross-linking monomer used in the preparation of hydrogels, which are studied for the development of self-regulated insulin delivery system [2], potent anticancer drug. The insoluble gel formation was due to the three dimensional growth of the polymer.

This type of monomer can also polymerize without cross linking to give soluble gel-free polymer [3-5]. The cyclopolymerization of N,N'-methylenebisacrylamide initiated by eosin – ascorbic acid system is reported. The rate of polymerization is proportional to [MBA] and [Ascorbic acid] [6]. In our laboratory the cyclopolymeriztion of non conjugated divinyl monomer N,N'-methylenebisacrylamide with redox pair of Mn(VII)-Thiol in a homogeneous gel free state was reported [7].

Charge-Transfer complexes studied as initiator of vinyl polymerization, were not employed for initiation of cyclopolymerisation. N,N-dimethylaniline(DMA) is a well n-donor. It also behaves as a π-acceptor, when it interacts with suitable π acceptor [8]. The present study of cyclopolymerisation initiated by CT complexes indicate that N,N-dimethylaniline function as a lone-pair n donor of the increvalent type.

The survey of literature reveals free radical existence through the formation of CT complex DMA seems to undergo CT interaction with a variety of acceptor and leading to radical polymerization [9,10]. Tertiary amines are potential donors with anhydrides acylchlorides as acceptor involving in the vinyl polymerization. In many of the above cases the formation of CT complex is evidenced by the appearance of the CT band and a few by ESR spectral investigation. In most of these cases a first order rate dependence of monomer and a square root dependence of donor and acceptor are reported [11-19]. DMA-Trichloroacetic acid [TCA] initiated vinylpolymerization and a mechanism involving bimolecular reaction between the donor and acceptor followed by the decomposition of the complex to give initiating free radical resulting in the polymerization is reported [20].

In recent past numerous reports have appeared using charge-Transfer complexes as initiator of vinyl polymerization. In our laboratory we have reported cycopolymerization of divinyl monomer using various redox pair and DMA-Benzene sulphony chloride charge transfer complex[21-27]. Still it has been the topic of extensive investigation. To the best of our knowledge CT complex has not been used as initiator for cyclopolymerization. The present study of cyclopolymerization initiation by CT complexes indicates that, N,N—dimethylaniline function as a lone pair n-donor of the increvalent type. In the present investigation, Benzoylchloride and Trichloroacetic acid are chosen as acceptors.

EXPERIMENTAL SECTION

Purification of the monomer and the polymerization procedure were all as reported earlier [7]. N,N-dimethylaniline, Benzoylchloride, Trichloroacetic acid and, acetonitrile were purified by standard procedure.

RESULTS AND DISCUSSION

In this study under the specified experimental conditions employed DMA or BoCl or TCA alone could not initiate any effective polymerization. No initiation of polymerization was observed in aerated conditions or in the presence of hydroquinone, all of which revealed the free radical nature of the polymerization reaction. No induction period was observed and light did not alter the reaction kinetics as was proved by same kinetic results in presence and the absence of light. Nevertheless all experiments were carried out in reaction vessel covered with block cloth.

EFFECT OF MONOMER CONCENTRATIONS ON CHARGE-TRANSFER COMPLEXES:

In both the systems of study the monomer concentration was varied in the order of $5x10^{-2}molL^{-1}$ to $50x10^{-2}$ $molL^{-2}$ at constant [DMA], constant [TCA] or at constant [BoCl],(Tab1,2;Fig 1,2). In both systems of study, log R_p vs log [MBA] was found to be linear with the slope, one and the plots of R_p vs [MBA] were straight lines passing through the origin, from the slope of which the complex rate parameters were calculated.

When the concentration of monomer and the acceptor were kept constant, the concentration of DMA was varied from $1.5x10^{-2}$ $molL^{-1}$ to $8.0x10^{-2}$ $molL^{-1}$. The plots log R_p vs log [DMA] were found to be a straight line with the slope of 0.5 and the plots of Rp against $[DMA]^{0.5}$ passing through the origin, permit the calculation of the complex parameter (Tab.3,4;Fig3,4).

The Concentration of TCA and BoCl were carried from $0.33x10^{-2}molL^{-1}$ to $3.33x10^{-2}molL^{-1}$. The rate of cyclopolymerization was observed to have square root dependence on the concentration of the acceptor and the plots of R_p vs $[ACC]^{0.5}$ passed through the origin (Tab5,6;Fig5.6).

The value of overall rate constant, $k_p k_t^{-0.5} (2k_d K)^{0.5}$ was obtained from the plots of the rate of polymerization versus the monomer concentration and from the plots of the rate of polymerization versus the square root of the concentration of the initiators . The value is $3x10^{-2}$ $molLs^{-1}$ for DMA-BoCl system and $6x10^{-3}$ $molLs^{-1}$ for DMA-TCA system.

Jobs method of continuous variation (Tab.7; Fig.7) studies shows that 1:1 complex formation and it is thermally decomposed to give primary radical. The formation of charge – transfer complex between the DMA and Acceptors have been assumed as follows.

$$DMA + ACC \underset{k_d}{\overset{K}{\rightleftharpoons}} C\ (Complex)$$

$$C \longrightarrow Ro$$

R^o is the initiating free radical.

$$MBA + R^o \xrightarrow{k_d} M1^o$$

$$M_1^o \xrightarrow{k_c} M_2^o$$

In the termination step, solvent also be involved or by primary radical deactivation or by reinitiation.

$$Mn^o + Mn^o \xrightarrow{k_c} Polymer$$

$$R^o + DMA \xrightarrow{k^o} products$$

$$R^o + BsCl \xrightarrow{k'^o} products$$

Primary radical deactivation

$$M^o + S \xrightarrow{ktr,s} polymer + S^o$$

$$S^o + MBA \xrightarrow{k_i'} SM^o$$

All the type of initiation, propagation and termination steps were considered and expression were derived for the rate of polymerization.

$$Rp = kp \frac{(k_i/k_t)^{0.5} (2k_d K)^{0.5} [M]^{1.5} [C]^{0.5}}{k_i[M] + k^o [D] + [A]^{0.5}}$$

[D] and [A] are the initial concentration of the donor and acceptor respectively. Under experimental condition $1>>[A]_{eq}$ and $[D]_{eq}$, $C=K[D]_T[A]_T$

$$Rp = \frac{kp (k_i/k_t)^{0.5} (2k_d K)^{0.5} [M]^{1.5}[A]^{0.5} [D]^{0.5}}{k_i[M] + k_o [D] + k_o'[A]^{0.5}}$$

Assuming $k_i [M]>>k_o[D] + k_o' [A]$,

$$Rp = kp\ k_t^{0.5} (2k_d K)^{0.5} M [A]^{0.5} [D]^{0.5}$$

The structure of the polymer unit of similar non-conjugated divinyl monomer [6,7] and also the polymer of MBA were studied by spectral analysis and reported to consist of five member and seven – member units respectively, which provides conclusive evidence for cyclopolymerization of MBA.

TABLE-1

[Bod]:1.33 [DMAl]:1.66				[Bod]:1.33 [DMAl]:15.0			
[MBA]	R_p	2+log[MBA]	6+logRp	[MBA]	R_p	2+log[MBA]	6+logRp
10.3	4	1.0136	1.6021	10.3	6.02	1.0136	1.7795
15.5	6.1	1.188	1.7853	15.5	8.52	1.188	1.9304
20.6	8.32	1.3147	1.9201	20.6	11.6	1.3147	2.064
31	12	1.4908	2.0791	31	16	1.49	2.2041
41.3	16	1.6157	2.2041	41.3	22.5	1.6157	2.3521

All concentrations are expressed in 10^{-2} mol litre^{-1}.

R_p values in 10^{-5} molL^{-1}s^{-1}.

TABLE-2

[TCA]:1.33 [DMAl]:3.33				[TCA]:1.33 [DMAl]:1.66			
[MBA]	R_p	3+log[MBA]	7+logRp	[MBA]	R_p	3+log[MBA]	7+logRp
1.4	1.58	1.1473	1.1986	1.46	1.3	1.1643	1.1139
2.8	3.57	1.4483	1.5526	2.92	2.6	1.4655	1.4154
4.21	5.36	1.6255	1.7291	4.38	3.95	1.6414	1.5966
5.61	7.75	1.7493	1.8893	5.84	5.26	1.7664	1.721
8.42	11.5	1.9255	2.0606	8.76	7.71	1.9425	1.8871

All concentrations are expressed in 10^{-2} mol litre^{-1}.

R_p values in 10^{-5} molL^{-1}s^{-1}.

TABLE-3

[MBAl]:16.74 [Bocl]:1.33					[MBAl]:10.6 [Bocl]:1.33				
[DMA]	R_p	3+log[DMA]	6+logRp	$[DMA]^{0.5}$	[DMA]	R_p	3+log[DMA]	6+logRp	$[DMA]^{0.5}$
1.66	5.67	1.2201	1.7528	12.8	1.66	4.07	1.2201	1.6096	12.8
3.33	6.6	1.5224	1.5224	18.2	3.33	5.1	1.5224	1.7076	18.2
5	8.4	1.699	1.699	22.3	5	6.36	1.699	1.8035	22.3
6.7	9	1.8261	1.8261	25.8	6.7	6.9	1.8261	1.8335	25.8
8	9.86	1.9031	1.9031	28.2	8	7.4	1.9031	1.8692	28.2

All concentrations are expressed in 10^{-2} mol litre^{-1}.

R_p values in 10^{-5} molL^{-1}s^{-1}.

$[DMA]^{0.5}$ values in 10^{-2}(molL^{-1})$^{0.5}$

TABLE-4

[MBAl]:2.80 [TCA]:1.33					[MBAl]:8.40 [TCA]:1.33				
[DMA]	R_p	3+log[DMA]	7+logRp	$[DMA]^{0.5}$	[DMA]	R_p	3+log[DMA]	7+logRp	$[DMA]^{0.5}$
1.67	2	1.2227	1.301	13	1.67	8.1	1.2227	1.9085	13
2.5	3.1	1.3979	1.4914	15.8	2.5	9.55	1.3979	1.98	15.8
3.33	3.57	1.5224	1.5526	18.2	3.33	11.2	1.5224	2.0492	18.2
4.16	4.5	1.6201	1.1532	20.4	4.17	12.2	1.6201	2.0864	20.4
5	4.67	1.699	1.699	22.3	5	14	1.699	2.1461	22.3

All concentrations are expressed in 10^{-2} mol litre^{-1}.

R_p values in 10^{-5} molL^{-1}s^{-1}.

$[DMA]^{0.5}$ values in 10^{-2}(molL^{-1})$^{0.5}$

$[TCA]^{0.5}$ values in 10^{-2}(molL^{-1})$^{0.5}$

TABLE-5

	[MBAl]:3.00 [DMAl]:3.33				[MBAl]:16.7 [DMA]:3.39				
[Boc]	R_p	3+log[Bocl]	6+logRp	$[Bocl]^{0.5}$	[Boc]	R_p	3+log[Bocl]	6+logRp	$[Bocl]^{0.5}$
3.3	1.6	0.5185	1.1248	5.74	0.33	3.3	0.5185	1.7403	5.74
4.5	2.32	0.8195	1.3636	8.12	0.66	4.5	0.8195	1.892	8.12
5.91	2.9	1	1.4623	10	1	5.91	1	1.9772	10
6.45	3.32	1.1231	1.5211	11.5	1.33	6.45	1.1238	2.0413	11.5
6.87	3.71	1.2041	1.5693	12.6	1.66	6.87	1.2041	2.0681	12.6

All concentrations are expressed in 10^{-2} mol litre^{-1}.

R_p values in 10^{-5} molL^{-1}s^{-1}.

$[Bocl]^{0.5}$ values in 10^{-2}(molL^{-1})$^{0.5}$

TABLE-6

	[MBAl]:4.20 [DMAl]:3.33				[MBAl]:5.62 [DMA]:3.33				
[TCA]	R_p	3+log[TCAl]	7+logRp	$[TCA]^{0.5}$	[TCA]	R_p	3+log[TCAl]	7+logRp	$[TCA]^{0.5}$
0.67	3.68	0.8241	1.5658	8.18	0.67	5.5	0.8241	1.7403	8.18
1.33	5.3	1.1239	1.7242	11.5	1.33	7.8	1.1239	1.892	11.5
2	6.45	1.301	1.8095	14.1	2	9.49	1.301	1.9772	14.1
2.67	7.5	1.4265	1.875	16.3	2.67	11	1.4265	2.0413	16.3
3.33	8.35	1.5224	1.9216	18.2	3.33	11.7	1.5224	2.0681	18.2

All concentrations are expressed in 10^{-2} mol litre^{-1}.

R_p values in 10^{-5} molL^{-1}s^{-1}.

$[TCA]^{0.5}$ values in 10^{-2}(molL^{-1})$^{0.5}$

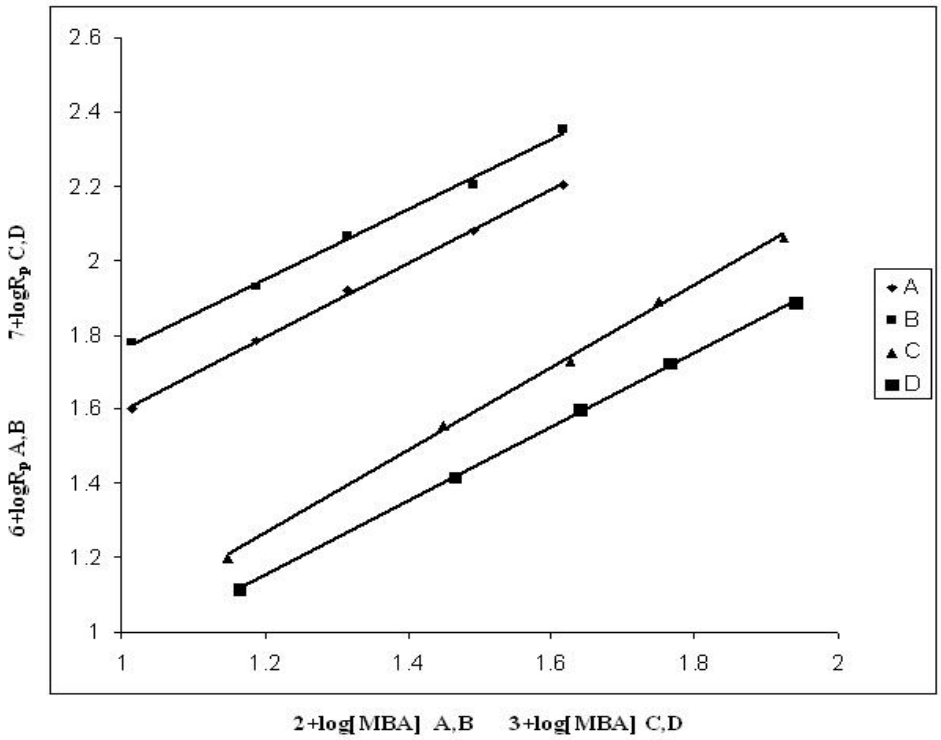

Fig.1. Dependence of $\log R_p$ on $\log[MBA]$; (A)[Bocl]=1.33×10^{-2} [DMA]=1.66×10^{-2}, (B) [Bocl]= 1.33×10^{-2} [DMA]= 5.0×10^{-2}; (C) [TCA]= 1.33×10^{-2} [DMA]= 3.33×10^{-2}; (D) [TCA]= 1.33×10^{-2} [DMA]= 1.66×10^{-2}; Concentrations in $molL^{-1}$,Temp.55°C.

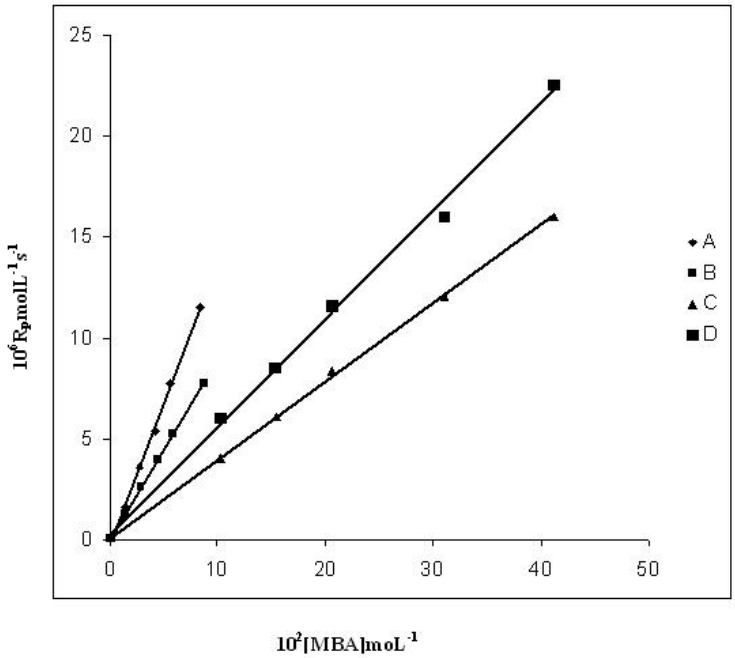

Fig.2. Dependence of R_p on [MBA]; (A)[Bocl]=1.33×10^{-2} [DMA]=1.66×10^{-2}, (B) [Bocl]= 1.33×10^{-2} [DMA]= 5.0×10^{-2}; (C) [TCA]= 1.33×10^{-2} [DMA]= 3.33×10^{-2}; (D) [TCA]= 1.33×10^{-2} [DMA]= 1.66×10^{-2}; Concentrations in $molL^{-1}$,Temp.55°C.

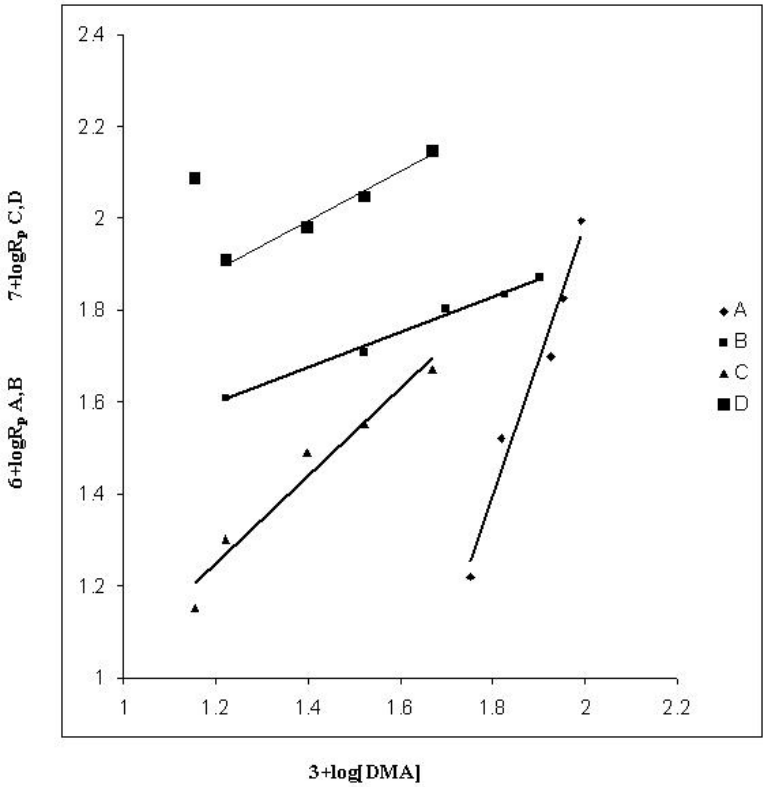

Fig.3. Dependence of $\log R_p$ on $\log[DMA]$; (A)[Bocl]=$1.33x10^{-2}$ [MBA]=$16.74x10^{-2}$, (B) [Bocl]= $1.33x10^{-2}$ [MBA]= $10.6x10^{-2}$; (C) [TCA]= $1.33x10^{-2}$ [MBA]= $2.80x10^{-2}$; (D) [TCA]= $1.33x10^{-2}$ [MBA]= $8.40x10^{-2}$; Concentrations in $molL^{-1}$, Temp.55°C.

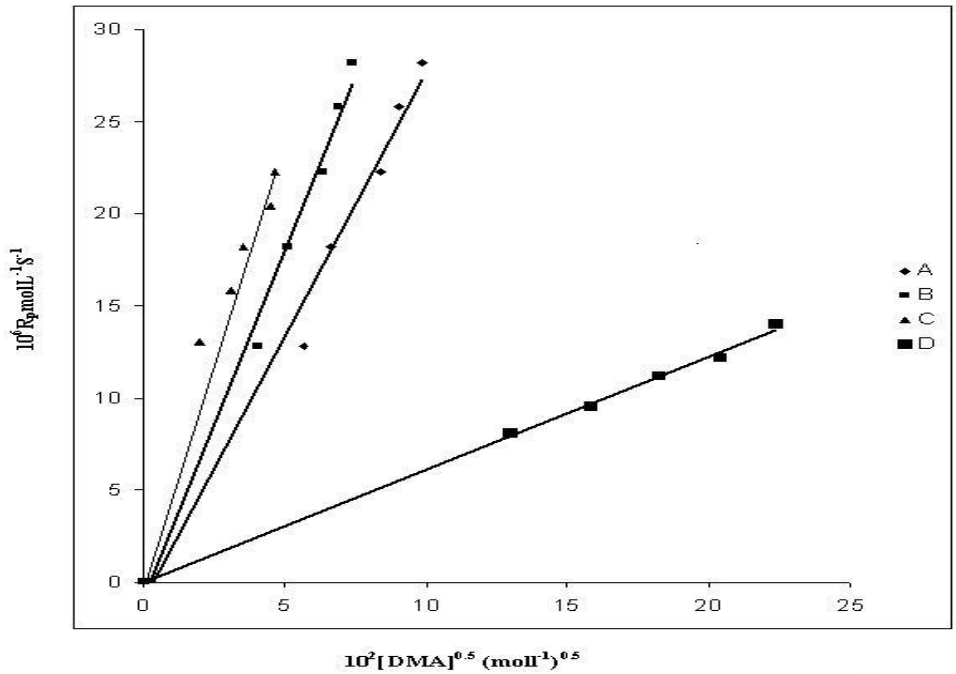

Fig.4. Dependence of R_p on [DMA]; (A)[Bocl]=$1.33x10^{-2}$ [MBA]=$16.74x10^{-2}$, (B) [Bocl]= $1.33x10^{-2}$ [MBA]= $10.6x10^{-2}$; (C) [TCA]= $1.33x10^{-2}$ [MBA]= $2.80x10^{-2}$; (D) [TCA]= $1.33x10^{-2}$ [MBA]= $8.40x10^{-2}$; Concentrations in $molL^{-1}$, Temp.55°C.

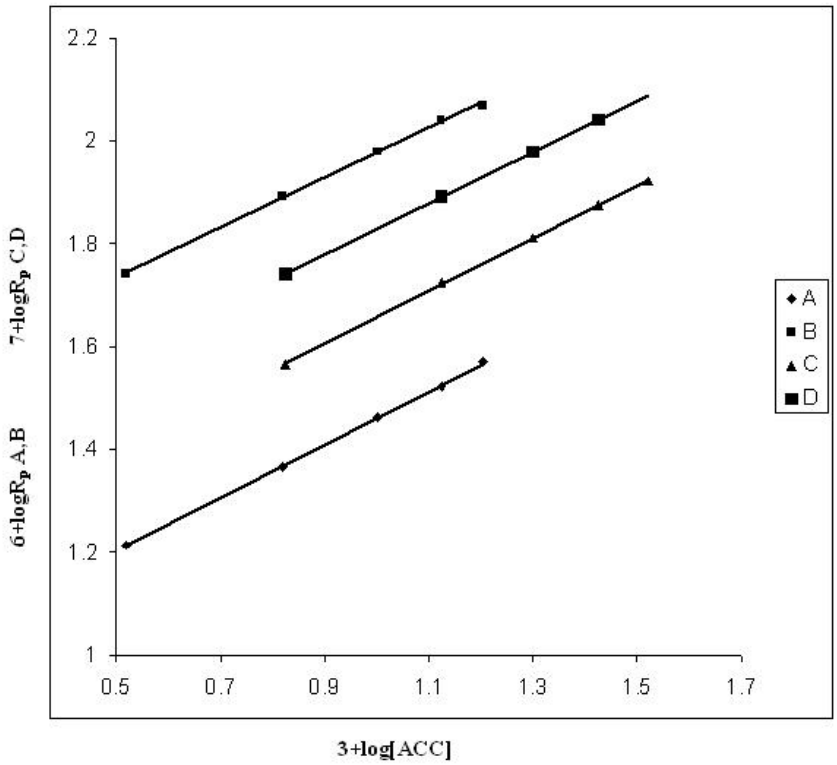

Fig.5 Dependence of $\log R_p$ on log[ACC]; (A)[DMA]=3.39×10^{-2} [MBA]=16.74×10^{-2}, (B) [DMA]= 5.00×10^{-2} [MBA]= 15.4×10^{-2}; (C) [DMA]= 3.33×10^{-2} [MBA]= 4.20×10^{-2}; (D) [DMA]= 3.33×10^{-2} [MBA]= 5.62×10^{-2}; Concentrations in $molL^{-1}$,Temp.55°C.

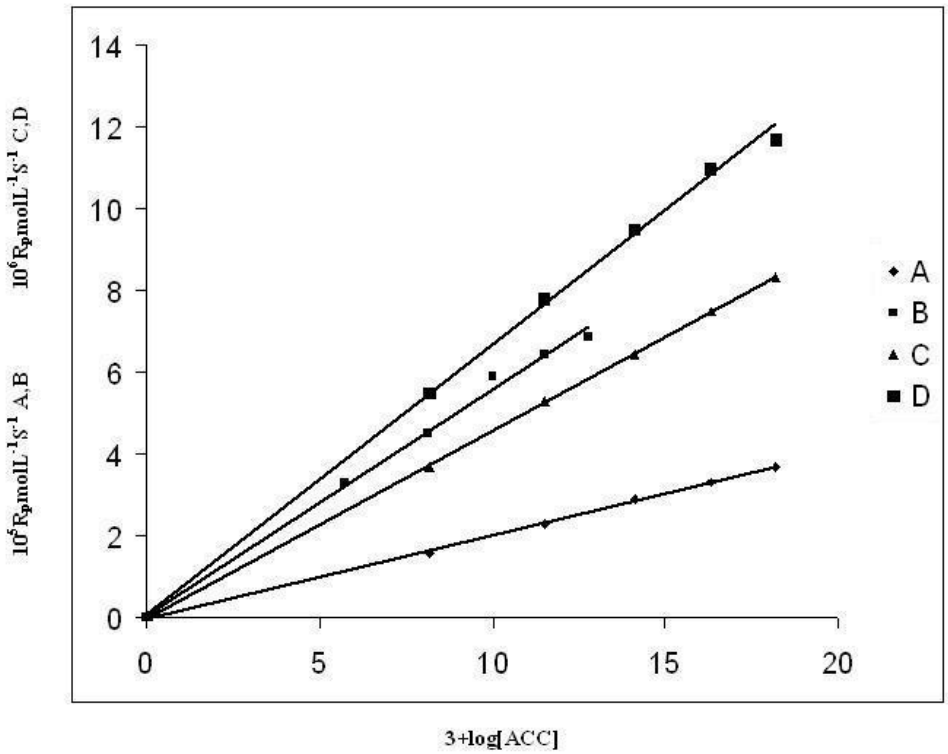

Fig.6. Dependence of R_p on [ACC]; (A)[DMA]=3.39×10^{-2} [MBA]=16.74×10^{-2}, (B) [DMA]= 5.00×10^{-2} [MBA]= 15.4×10^{-2}; (C) [DMA]= 3.33×10^{-2} [MBA]= 4.20×10^{-2}; (D) [DMA]= 3.33×10^{-2} [MBA]= 5.62×10^{-2}; Concentrations in $molL^{-1}$,Temp.55°C

TABLE-7

Job's Method of continuous variation

	[DMA]+[Bocl]=1.0	[DMA]+[TCA]=0.37	
Mole percentage of DMA	Mole percentage of the acceptors	DMA-Bocl at 245nm	DMA-TCAat 247 nm
10	90	0.37	0.16
20	80	0.56	0.28
30	70	0.68	0.36
50	50	0.75	0.44
70	30	0.55	0.37
80	20	0.32	0.29
90	10	0.22	0.1

All concentrations are expressed in 10^{-2} mol litre^{-1}.

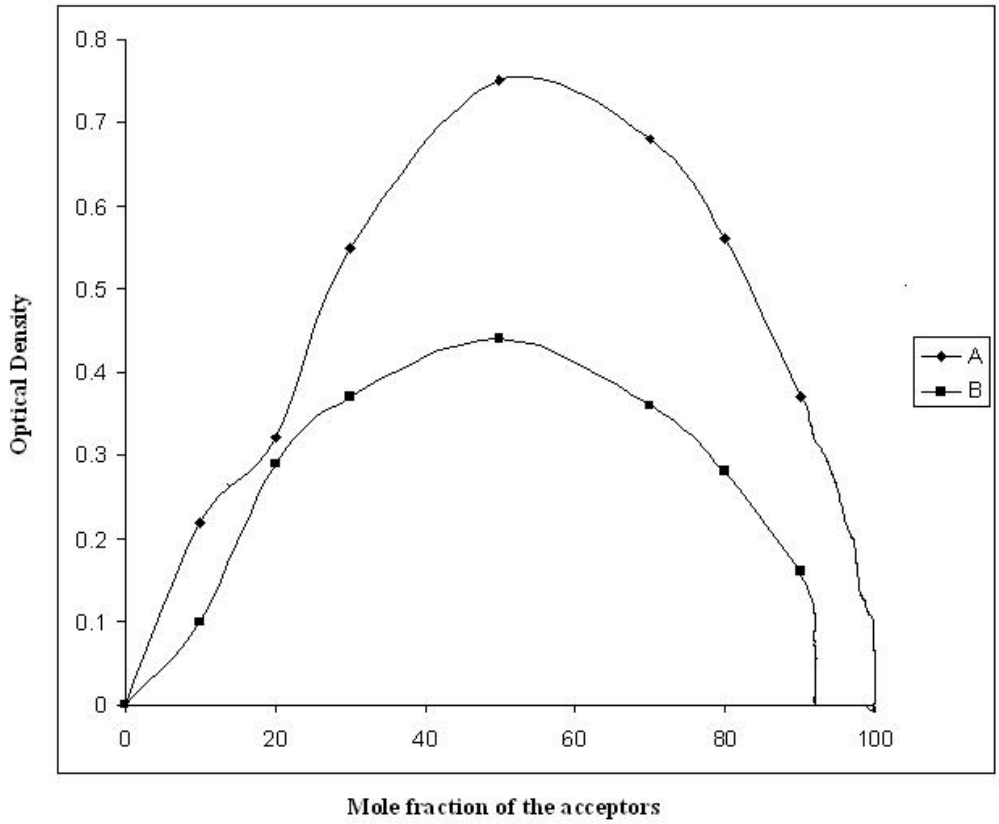

Fig.7. Optical Density vs mole fraction o f acceptor; (A).[DMA]+[Bocl]=1.0; (B).[DMA]+[TCA]=1.0; All Concentrations are expressed in 10^{-2} molL^{-1}; Temp.27ºC

CONCLUSION

In this study we have demonstrated the utilization of CT complexes initiator for cyclopolymerization reaction. We found that the R_p was proportional to $[MBA]^1$, $[DMA]^{0.5}$, $[Bscl]^{0.5}$. . The overall rate constant were found to be $3x10^{-2}$ and $6x10^{-3}$ respectively.

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