

# Kinetics of N, N-Dimethylaniline-Benzenesulphonylchloride Charge-Transfer Complex Initiated Cyclopolymerization of Divinyl Monomer

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## Abstract

Polymerization of non-conjugated divinyl monomer N,N'-methylenebisacrylamide was studied using a novel charge-transfer complex of N,N-dimethylaniline-benzenesulphonyl chloride in a homogeneous gel-free state, under varying conditions of concentration and temperature. The reactions were carried out under various concentrations at a constant temperature of 52 °C in acetonitrile media. The dependence of the rate of polymerization on various experimental conditions, such as different concentrations of monomer N,N'-methylenebisacrylamide, donor N,N-dimethylaniline, acceptor benzenesulphonyl chloride, and temperature were studied. The order with respect to monomer, donor, and acceptor were found to be 1, 0.5, and 0.5 respectively. The kinetic results were interpreted by a suitable mechanistic sequence. Absence of gelation is attributed to the formation of a cyclic polymer. Jobs method of continuous variation studies shows 1:1 complexformation.

**Keywords:** Cyclopolymerization, Non-conjugated divinyl monomer, N,N-dimethylaniline-benzenesulphonyl chloride, Charge-transfer complex

## 1. Introduction

Modern technology development needs reliable high-performance polymers for advanced applications. Bulk synthesis of polymers involves various kinetic factors. Kinetic studies play a major role in the industrial synthesis of many high-performance polymers (Michael A. Meador., 2003). N,N'-methylenebisacrylamide (MBA), which is a symmetrical non-conjugated diolefin having a double bond in the terminal position, is a well-known cross-linking monomer used in the preparation of hydrogels, which are studied for the development of self-regulated insulin delivery systems (Satis, et al., 2006) and as a potent anticancer drug. The formation of insoluble gel 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 (Gopalan, et al., 1982; Subbaratnam, et al., 1986; Ratnasabapathy, et al., 1988). Butler and his co-workers reported that a monomer containing three or four cyclic groups leads to the formation of insoluble polymers. A chain growth mechanism was proposed involving an alternation of intra and intermolecular steps, which for the first time was found to lead to cyclopolymerization (Butler, et al., 1957). The cyclopolymerization of N,N'-methylenebisacrylamide initiated by an eosin-ascorbic acid system is reported. The rate of polymerization is proportional to [MBA] and [Ascorbic acid] (Parthasarathy, et al., 2004). The cyclopolymerization of non-conjugated divinyl monomer N,N'-methylenebisacrylamide with a redox pair of Mn(VII)-Thiol in a homogeneous gel-free state in the authors' laboratory is also reported here (Umayavalli et al., 1996). Park et al. is reported the selective cyclopolymerization of alpha, omega-dienes (Park, et al., 2006).

Recently, the Pd (II)-dimine catalysts initiate cyclopolymerization of isopropylidene diallylmalonate(1) to produce the polymer containing trans-1,2-disubstituted cyclopentane groups has been reported (Park, et al., 2010).

A charge-transfer complex has not been studied previously as an initiator for cyclopolymerization. The present investigation of cyclopolymerization of non-conjugated divinyl monomer initiated by N,N-dimethylaniline-benzene sulphonyl chloride charge-transfer complex indicates that N,N-dimethylaniline (DMA) functions as a lone pair n-donor of the increvalent type. This is proved by its ineffectiveness in initiating polymerization in the presence of hydrochloric acid. It is a well known n-donor. It also behaves as a  $\pi$ -acceptor when it interacts with another suitable  $\pi$ -acceptor (Kothandaraman, et al., 1986a; Kothandaraman, et al., 1984b). The reasons for choosing benzenesulphonyl (Bscl) chloride as an acceptor were its simplicity and its structure which is analogous with that of O-toluene sulphonyl chloride.

Studies of charge-transfer complexes involving aromatic sulphonyl chloride are relatively rare. The charge-transfer interaction of DMA with O-toluene sulphonyl chloride has been investigated, and this complex-initiated vinyl polymerization of methyl methacrylate and acrylamide in acetonitrile medium has been presented as a radical mechanism. The initiating radical is formed by thermal decomposition of the complex. It was found to be first order to [monomer] and of order 0.5 to [DMA] and [OTscl] (Kothandaraman, et al., 1984c).

## 2. Methods and Materials

The reagents used were purified using standard procedures. The kinetics of polymerization was studied by batch process. The polymerization experiment was carried out as described below.

A solution containing the required amount of monomer, acceptor was taken in the reaction vessel and made up to the fixed volume (20mL) with acetonitrile. The solution was then deaerated for 20 minutes with purified nitrogen as to ensure inert atmosphere as well as through stirring. The tube was thermostated at the appropriate temperature in the thermostat. At the end of 20 minutes, required amount of donor DMA solution was added into the polymer tube through a micro funnel, which was subsequently rinsed with 2mL of acetonitrile. The passage of nitrogen was continued for 5 more minutes. The inlet and outlet tube were closed to maintain the nitrogen atmosphere till the end of a fixed reaction time. Air was blown to arrest the reaction. The blank test was also conducted under the same experimental condition. The rate of monomer disappearance,  $R_p$  was determined by bromometry.

## 3. Results and Discussion

In this study, under the specified experimental conditions used, neither DMA alone nor Bscl alone could initiate 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 obtaining the same kinetic results in the presence and the absence of light. Nevertheless, all experiments were carried out in a reaction vessel covered with black cloth. The role played by acetonitrile in charge-transfer complex formation must be minimal, as indicated by the fact that there was no shift in the DMA absorption band in acetonitrile and that no polymerization occurred in the presence of dimethylaniline alone in acetonitrile medium. This is similar to the CT complex formation and thermal decomposition behavior of a DMA-OTscl system (Kothandaraman, et al., 1984c).

Absorption measurements for the DMA-Bscl mixture in acetonitrile are presented, and the UV spectra of DMA-Bscl are reported (Figure 1). When the concentration of DMA was increased, the optical density of the CT bands increased also, revealing that these bands could be directly correlated to the donor action of the DMA. Increase in the acceptor concentration also resulted in an increase in the absorption of the CT band.

A series of mixtures of the donor and the acceptor in different ratios was prepared by keeping the total concentration constant, and absorption measurements were made for each solution mixture at  $\lambda_{\max}$ . If components of the mixture were found to have an absorption maximum, this value was subtracted from the observed absorption value. However, the components of the CT complex studied here were chosen to have negligible individual absorption at the absorption wavelengths exhibited by the CT complex. The optical density was plotted against mole fraction, confirming the formation of a 1:1 complex (Table 1; Figure 2). The complex then underwent thermal decomposition, yielding primary radicals. The polymerization process through the intermediate formation of a charge-transfer complex was indicated by the identification of a charge transfer band at 336nm. Taking all these factors into consideration, the formation of a CT complex between DMA and benzene sulphonyl chloride is shown in Figure 3.

### 3.1 Evidence for cyclopolymerization

The polymer solution formed is found to have no unsaturation which confirms the involvement of both the double bonds in the propagation step, otherwise known as cyclopolymerization. The IR and NMR spectra of the polymer

formed which gave the conclusive evidence for the seven membered cyclized ring units in polymer (Hatada, et al., 1986; Ohya, et al., 1983) as detailed below.

The IR spectral details of the polymer and monomer are given in Figure 4. The absorption at  $1700\text{cm}^{-1}$  due to carbonyl function is not affected in the polymer and in the monomer, MBA. However the absence of  $-\text{CH}=\text{CH}_2$  stretching frequency at  $1630\text{cm}^{-1}$  in the polymer which well pronounced in the monomer is of significance. This observation clearly indicates the cyclization propagation sequence (Figure 7 step III or IV) and not through intermolecular addition propagation as observed with monovinyl monomers (Figure 7 step II), in which case the pendant double bonds could be detected. It is also noted that the polymers formed do not consume bromine by addition as decided by bromometric estimations.

The results of NMR analysis of the polymer also support the cyclization propagation (step III or IV) rather than the vinyl propagation (step II) as proved by the absence of any signal at  $6.15\delta$  due to the pendant  $\text{CH}_2=\text{CH}-$  in the polymer (Figure 5). In the cyclopolymerization of acrylic anhydrides (Corfield, et al., 1972; Hatada, et al., 1986; Ohya, et al., 1983), the difference in the chemical shift for methylenic protons in the six membered rings and that for the two intermittent methylenic protons in the five membered rings were differentiated, recorded and ratio of HH/HT intramolecular cyclization was also calculated.

On this basis, similar observation could be expected in cyclopolymerization of MBA also. The observed NMR spectra of MBA polymer is shown in Figure 5. For comparison the NMR spectra of polymethacrylate and polymethylmethacrylate are also indicated (as model compounds) in Figure 6, where total HT addition involving six membered rings and 30% HH cyclization were reported (Corfield, et al., 1972). By analysis of these spectral data it is clear that the MBA undergoes a total cyclopolymerization and it could be only seven membered rings with two intermittent methylenic groups (Figure7, Step III) constituting the polymer and this conclusion supports our earlier prediction of this type of cyclic units.

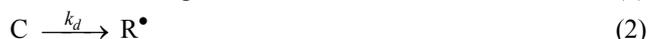
### 3.2 Effect of monomer concentrations on charge-transfer complexes

The rate of cyclopolymerization at various monomer concentrations with constant [DMA] and [BscI] was studied. It was found that the rate constant was dependent on the first power of [MBA]. The  $\log R_p$  vs.  $\log [\text{MBA}]$  plot was a straight line with a slope of one. The  $R_p$  vs. [MBA] plot passed through the origin. The slope of this plot permitted the calculation of the complex rate parameter,  $k_p k_t^{-0.5} (2k_d K)^{0.5}$ . Using K and  $k_d$  values taken from the literature, (Kothandaraman, et al., 1986a; Kothandaraman, et al., 1984b; Kothandaraman, et al., 1984c). It is possible to obtain  $k_p k_t^{-0.5}$  in all three monomer variation studies.

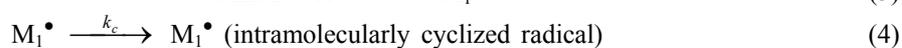
Under constant concentrations of monomer and BscI, the DMA concentration was varied from  $6.7\text{mmol}\cdot\text{L}^{-1}$  to  $33.3\text{mmol}\cdot\text{L}^{-1}$ . The  $\log R_p$  vs.  $\log [\text{DMA}]$  plot gave a straight line with a slope of 0.5, and the  $R_p$  vs.  $[\text{DMA}]^{0.5}$  plot was a straight line passing through the origin. The slope obtained from the latter plot permitted the recalculation of  $k_p k_t^{-0.5}$  using the value obtained from the monomer variation experiments. To study the effect of BscI concentration on the rate of polymerization at constant [MBA] and constant [DMA], BscI concentration was varied from  $4.5 \times 10^{-2}\text{mol}\cdot\text{L}^{-1}$  to  $36.4\text{mol}\cdot\text{L}^{-1}$ . It was observed that the rate of polymerization varied with  $[\text{BscI}]^{0.5}$ . The  $R_p$  vs.  $[\text{BscI}]^{0.5}$  plot passed through the origin. From these plots, it was possible to calculate  $k_p k_t^{-0.5}$ , obtaining a value in agreement with that calculated from [monomer] variation and [DMA] variation (Table 2; Figures 8 & 9).

The value of the overall rate constant,  $k_p k_t^{-0.5} (2k_d K)^{0.5}$ , was obtained from plots of the rate of polymerization versus monomer concentration and from plots of the rate of polymerization versus the square root of the concentration of the initiators; the value obtained was  $1.5 \times 10^{-2}$ .

To accommodate the observed results, the following reaction mechanism is proposed:

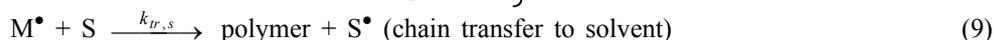
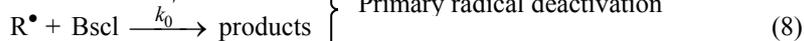


where  $\text{R}^\bullet$  is the initiating free radical.



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





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

$$R_p = k_p \frac{(k_i k_t)^{0.5} (2k_d)^{0.5} [M]^{1.5} [C]^{0.5}}{k_i [M] + k_o [D] + k_o' [A]^{0.5}}$$

The equilibrium constant is

$$K = \frac{[C]}{[D]_{\text{eq}} [A]_{\text{eq}}}$$

Where  $[D]_{\text{eq}}$  and  $[A]_{\text{eq}}$  represent the equilibrium concentration of the donor and acceptor respectively.

$$[D]_{\text{eq}} = \frac{[D]_T}{1 + K[A]_{\text{eq}}}$$

$$[A]_{\text{eq}} = \frac{[A]_T}{1 + K[D]_{\text{eq}}}$$

Where  $[D]_T$  and  $[A]_T$  are the initial concentration of the donor and acceptor respectively.

$[D]$  and  $[A]$  are the initial concentrations of the donor and acceptor respectively. Under experimental conditions,  $1 \gg [A]_{\text{eq}}$  and  $[D]_{\text{eq}}$ ,  $C = K [D]_T [A]_T$ .

$$R_p = k_p \frac{(k_i k_t)^{0.5} (2k_d)^{0.5} [M]^{1.5} [D]^{0.5} [A]^{0.5}}{k_i [M] + k_o [D] + k_o' [A]^{0.5}}$$

Assuming that  $k_i [M] \gg k_o [D] + k_o' [A]$ ,

$$R_p = k_p k_t^{-0.5} (2k_d)^{0.5} K^{0.5} M [D]^{0.5} [A]^{0.5}.$$

The experimental results for MBA polymerization indicate that the mechanism just described may be operative. The initiation proposed was of radical nature, and the decomposition of the charge-transfer complex proceeded without the participation of the monomer.

#### 4. Conclusions

Cyclopolymerization kinetics of N,N'-methylenebisacrylamide monomer has been investigated exclusively using charge-transfer complex. Kinetic parameters are obtained from plots of the rate of polymerization versus monomer concentration and from plots of the rate of polymerization versus the square root of the concentration of the initiators. These results will serve as a new process to synthesis many high-performance polymers.

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Table 1. Job's method of continuous variation

[DMA] + [BscI] = 0.2 mol·L <sup>-1</sup>		
Mole percentage of DMA	Mole percentage of the acceptors	O.D. $\lambda_{\max}$ DMA-BscI 336 nm
10	90	0.42
20	80	0.68
30	70	0.83
50	50	0.95
70	30	0.73
80	20	0.52
90	10	0.26

Table 3. Dependence of  $R_p$  on [MBA], [DMA] and [BscI]

Effect of [MBA] [BscI]:9.1 [DMA]:1.33				Effect of [DMA] [MBA]:4.9 [BscI]:9.1					Effect of [BscI] [MBA]:3.87 [DMA]:3.33				
[MBA]	$R_p$	$3+\log R_p$	$6+\log R_p$	[DMA]	$R_p$	$3+\log[\text{DMA}]$	$6+\log R_p$	$[\text{DMA}]^{0.5}$	[BscI]	$R_p$	$3+\log R_p$	$6+\log R_p$	$[\text{BscI}]^{0.5}$
2.94	1.61	1.4692	1.2068	0.67	2.4	0.826	1.3802	8.16	4.55	1.6	1.6580	1.2041	21.3
3.92	2.3	1.5942	1.3617	1.33	3.1	1.1238	1.4914	11.5	9.13	2.4	1.9604	1.3802	30.2
5.89	3.62	1.7702	1.5587	2.0	4.12	1.301	1.6149	14.1	18.2	18.2	2.2601	1.5051	42.7
7.85	4.13	1.8952	1.616	2.67	4.78	1.4265	1.6794	16.3	27.4	27.4	2.4378	1.6021	52.2
9.82	5.52	1.9921	1.8952	3.33	5.6	1.5228	1.7482	18.2	36.5	36.5	2.5623	1.6684	60.3

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

$R_p$  values in  $10^{-5}$  molL $^{-1}$ ;

$[\text{BscI}]^{0.5}$  values in  $10^{-2}(\text{mol}^{-1})^{0.5}$ ;

$[\text{DMA}]^{0.5}$  values in  $10^{-2}(\text{mol}^{-1})^{0.5}$ .

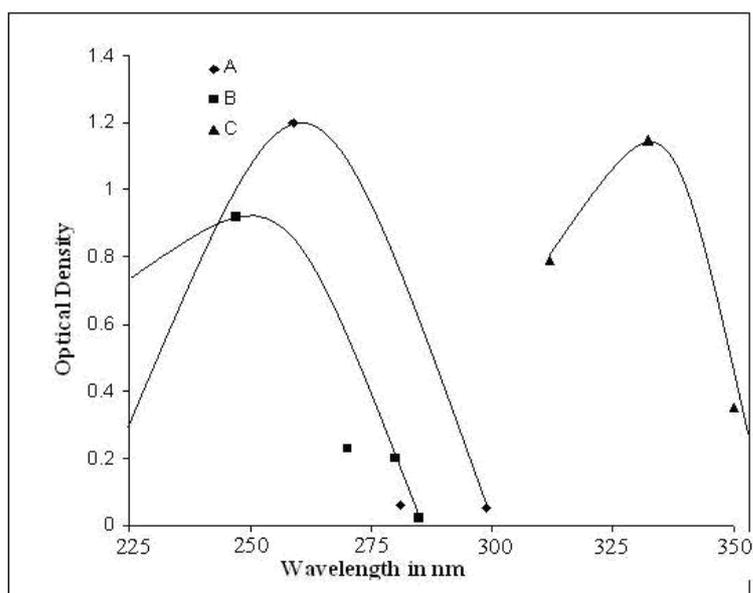


Figure 1. UV-Spectra of DMA and BscI with spectra of DMA-BscI complex. A. DMA; B. BscI; C. Mixture containing DMA and BscI

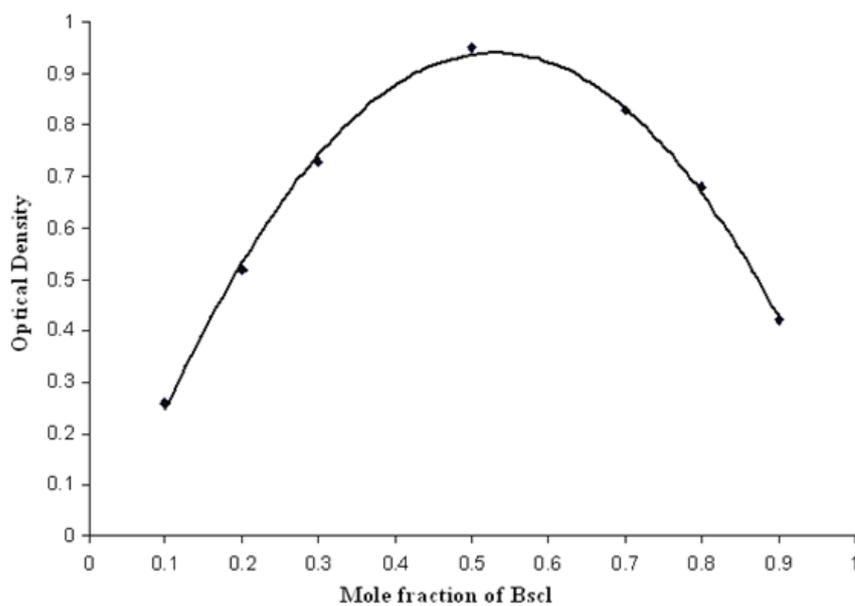


Figure 2. Jobs' method of continuous variation;  $[DMA] + [Bscl] = 0.2 \text{ mol}\cdot\text{L}^{-2}$

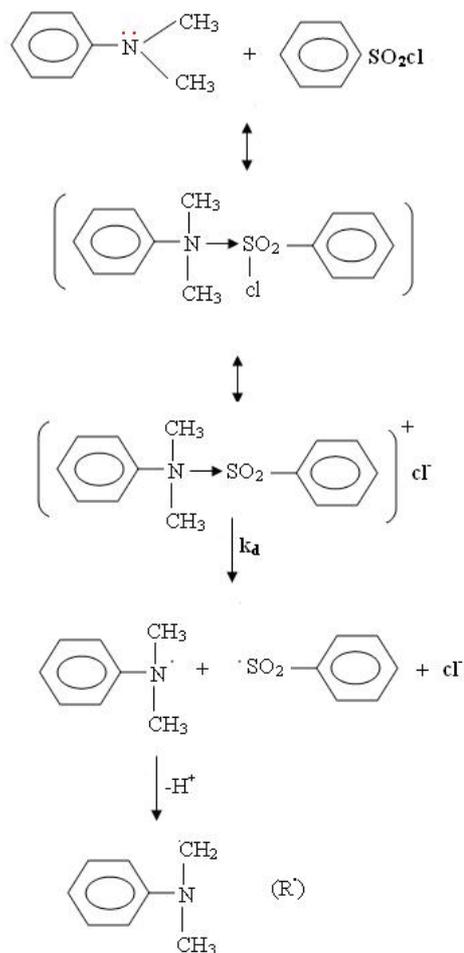


Figure 3. Formation of CT complexes and its thermal decomposition

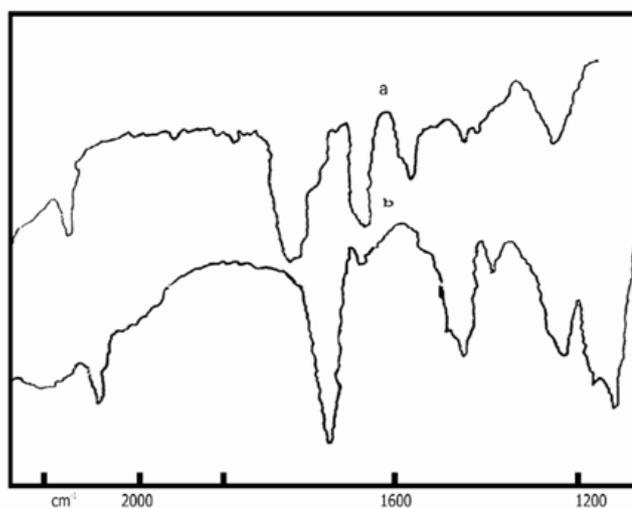


Figure 4. IR Spectra (a) Poly MBA (b) MBA

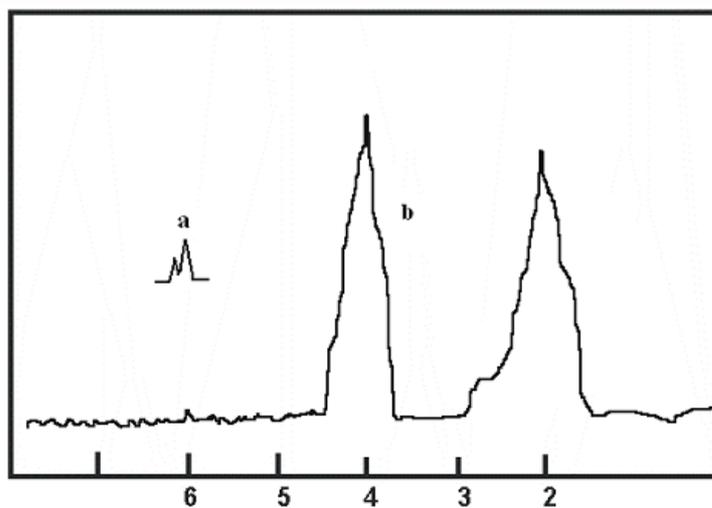


Figure 5. HNMR Spectra (b) MBA (a)  $\text{CH}_2=\text{CH}_2$  Protons in MBA Recorded in  $\text{CDCl}_3$  at 100 °C

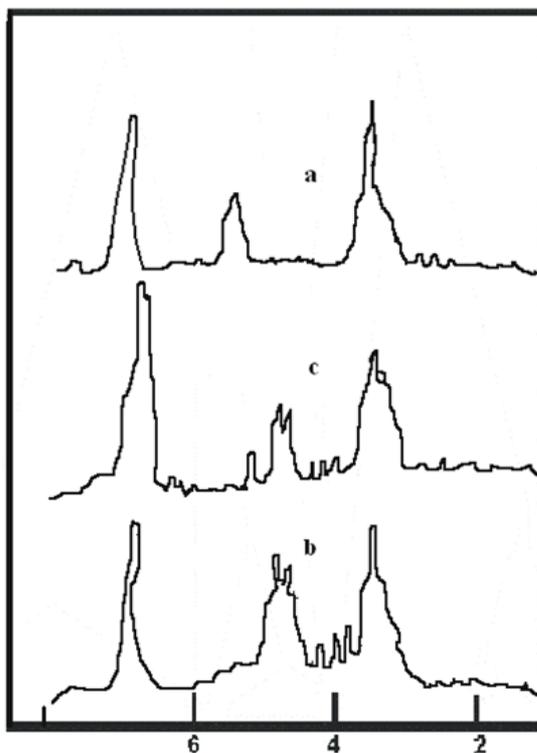


Figure 6. HNMR Spectra Model Compounds (a) for Pure HH (b) for Pure HT and (c) 30/70 HH/HT addition Propagation

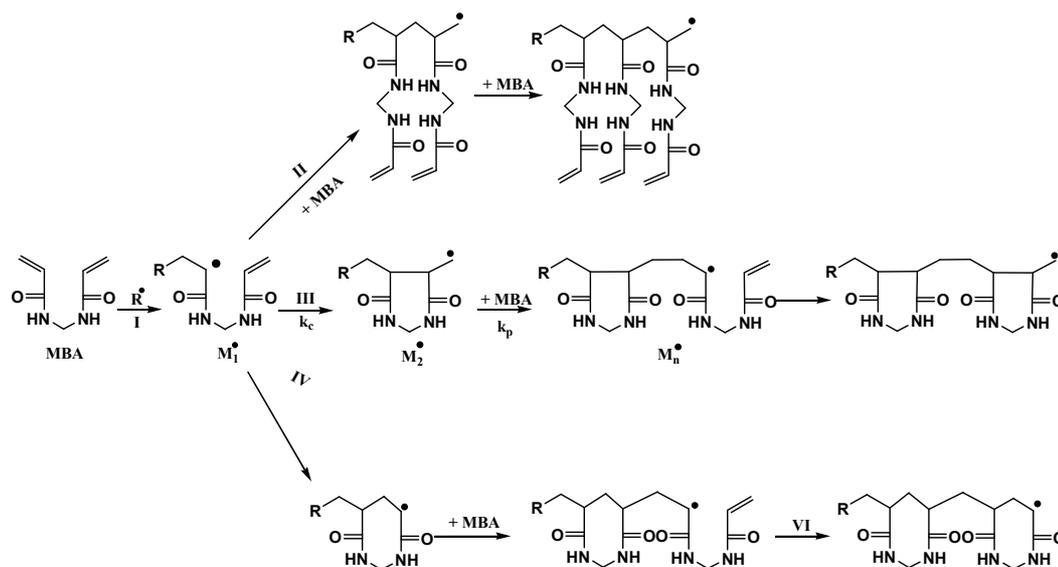


Figure 7. Propagation Sequences

**Step I:** Initiation by free radical generated by the decomposition of redox pair complex

**Step II:** Vinyl propagation by intermolecular HT addition

**Step III:** Cyclopolymerization by HH intramolecular addition giving seven membered ring unit

**Step IV:** Cyclopolymerization by HT intra and intermolecular addition propagation giving eight membered ring unit

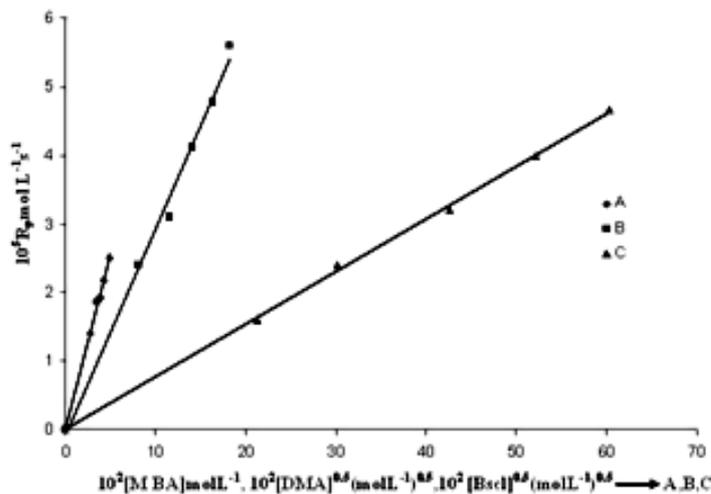


Figure 8. (A) Dependence of  $R_p$  on  $[MBA]$ ;  $[BscI]=18 \times 10^{-2}$ ,  $[DMA]=1.33 \times 10^{-2}$   
 (B) Dependence of  $R_p$  on  $[DMA]$ ;  $[BscI]=9.1 \times 10^{-2}$ ,  $[MBA]=4.9 \times 10^{-2}$   
 (C) Dependence of  $R_p$  on  $[BscI]$ ;  $[BscI]=3.33 \times 10^{-2}$ ,  $[MBA]=3.87 \times 10^{-2}$

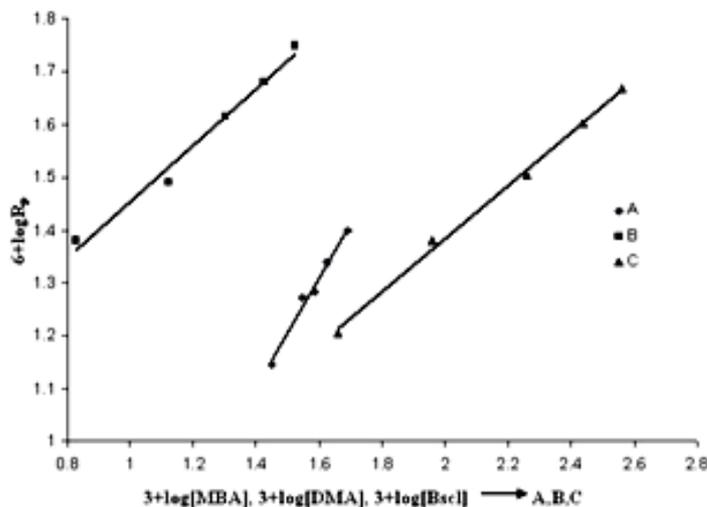


Figure 9. (A) Dependence of  $\log R_p$  on  $\log [MBA]$ ;  $[BscI]=18 \times 10^{-2}$ ,  $[DMA]=1.33 \times 10^{-2}$   
 (B) Dependence of  $\log R_p$  on  $\log [DMA]$ ;  $[BscI]=9.1 \times 10^{-2}$ ,  $[MBA]=4.9 \times 10^{-2}$   
 (C) Dependence of  $\log R_p$  on  $\log [BscI]$ ;  $[BscI]=3.33 \times 10^{-2}$ ,  $[MBA]=3.87 \times 10^{-2}$