STUDIES ON THE KINETICS OF COPOLYMERIZATION OF METHACRYLATE (MA) AND FULLERENE USING BISMUTHONIUM YLIDE-MERCURIC CHLORIDE COMPLEX AS INITIATOR

Kavita Srivastava, Ravindra Singh and Deepak Srivastava

ABSTRACT

Fullerenes, which have the interesting physical and chemical properties, have attracted the attention of many workers. Various efforts have been made to include fullerene units in polymeric structures. The direct copolymerization of fullerene with vinyl monomers is an attractive approach to synthesize polymeric fullerene materials by the use of conventional initiators. Copolymerization of methylacrylate (MA) with fullerene (C_{60}) has been studied in the presence of bismuthonium ylide-mercuric chloride complex as initiator, in dioxane, at $60^{\circ}C$. The rate of polymerization (*Rp*) may be represented as $Rp \propto [\text{ylide} - \text{complex}]^{0.5} [\text{MA}]^1 [\text{Full}]^{-0.5}$, indicating that fullerene acts as inhibitor for the copolymerization. The energy of activation for the copolymerization was found to be 51.2 kJmol^{-1}. The copolymer has been characterized by FTIR spectroscopic method.

Keywords : Methylacrylate, fullerene, ylide, copolymerization, kinetics.

INTRODUCTION

Fullerene, the third allotrope of carbon, is obtained by the electric arc discharge of graphite at high temperature and pressure. Due to its unique properties, fullerene finds applications in different fields such as pharmaceuticals, automobiles, preparation of fullerene-based polymers and co-polymers [1, 2]. Fullerene-containing polymeric materials have novel

1. **Kavita Srivastava,** Department of Chemistry, V. S. S. D. College, Kanpur – 208 002 (U.P.), India.
2. **Ravindra Singh,** School of Chemical Technology, Department of Plastic Technology
   H. B. Technical University, Kanpur – 208 002 (U.P.), India
3. **Deepak Srivastava,** School of Chemical Technology, Department of Plastic Technology
   H. B. Technical University, Kanpur – 208 002 (U.P.), India.
   Corresponding author: dsri92@gmail.com

optical and electro active properties and have been used in organic solar cells. There are a number of methods by which fullerene can be inserted into the polymer backbone of common vinyl monomers viz. methyl acrylate, methyl methacrylate, styrene, etc.

Various efforts have been made to include fullerene units in polymeric structures. The direct copolymerization of fullerene with vinyl monomers is an attractive approach to synthesize polymeric fullerene materials by the use of conventional initiators [3, 4]. However, these initiators requires a larger time for effective copolymerization. Some new initiators viz. ylides [5, 6] and (ylide – complex) [7], which are effective initiators, have been found to give stereo specific polymers. However, due to their synthetic problems these initiators have not been examined for the synthesis of fullerene – copolymers. In the present communication, the synthesis of (Bismthonium ylide – Mercuric chloride) complex and its use as an initiator in copolymerization of methylacrylate (MA) and fullerene (C_{60}) is reported. The kinetics of the copolymerization have been investigated in detail.

MATERIASL AND METHODS

Materials

Fullerene (C_{60}) (Lancaster), tetraphenyl cyclopentadiene (Across), and *p*-toluene sulphonyl hydrazide (Aldrich) were used as such during the synthesis with Cu (II) bishexafluoroacetyl acetanato (Merck) as catalyst. Methylacrylate (Merck) was purified with 4% NaOH followed by repeated washing with conductivity water and drying over fused $CaCl_2$. Then it was distilled in an atmosphere of nitrogen and, finally dried over silica gel for 24 h. The solvents were purified before use. Conductivity water was prepared by redistilling distilled water in presence of alkaline $KMnO_4$ in all - glass pyrex unit.

Methods

Synthesis of triphenyl bismuthonium 1, 2, 3, 4- tetraphenyl cyclopentadiene ylide

The triphenyl bismuthonium 1,2,3,4 tetraphenyl cyclopentadiene ylide was synthesized according to the method of Lloyd [8]. A solution of 2.19×10^{-4} moles of 1, 2, 3, 4-tetraphenylcyclopentadiene, 7.46×10^{-4} moles of p-toluene sulphonylhydrazide in 6.3 ml diethyl amine was kept at $0^{\circ}C$ for 10 days. It was then followed by addition of 3.5 ml water, 5 ml ether and dried over anhydrous silica gel, when yellow crystals of diazo compound were obtained. It

was washed with methanol. A solution containing 2.64×10^{-4} moles of diazo compound, 7.35×10^{-5} moles of catalyst and 4.95×10^{-5} moles of triphenyl bismuth (Merck) in 10 ml benzene was refluxed for 2 hrs. The evaporation of the solvent in vacuum resulted bismuthonium ylide with 19% yield.

Synthesis of triphenyl bismuthonium 1, 2, 3, 4- tetraphenyl cyclopentadiene {ylide – mercuric chloride} complex

The triphenyl bismuthonium 1, 2, 3, 4- tetraphenyl cyclopentadiene {ylide-mercuric chloride} complex was synthesized according to the method as adopted by Srivastava *et al* [9] used for the synthesis of phenacydimethyl sulphonium ylide- mercuric chloride complex.

Ylide-complex was prepared from the prepared ylide by the reaction of 1.0 mol of mercuric chloride, in 25 mL methanol, with drop-wise addition of 2.0 mol of triphenylbismuthonium 1, 2, 3, 4- tetraphenylcyclopentadien ylide, in 20 mL methanol. The solution was stirred for 2 h at 25°C. The final reaction mixture was suction filtered and dried after repeated washings with water. The{ ylide-mercuric chloride}was characterized by Fourier-transform infrared (FTIR) spectrophotometer.
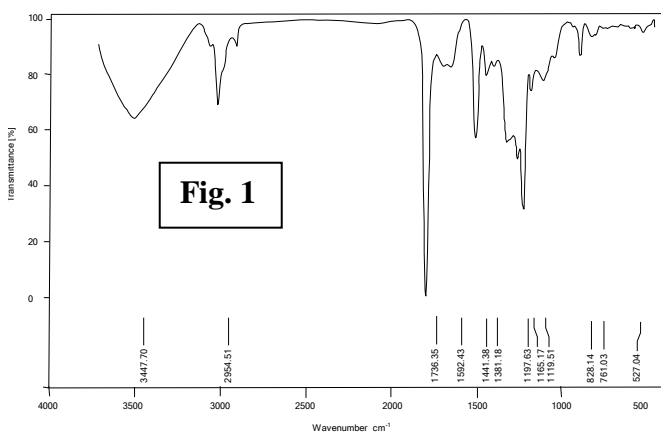
Copolymerization

The purified monomer (MA) and C_{60} were radically copolymerized in presence of metal – ylide complex in a modified dilatometer apparatus (capillary 2mm diameter) at 60±0.1°C for 3h in inert atmosphere. At different time intervals, the copolymer was precipitated with acidified methanol and dried to constant weight. Then it was refluxed with cyclohexane to remove homopolymers of methyl acrylate only, as fullerene does not undergo homopolymerization at low temperature up to 80°C. A separate experiment was made for the study of homopolymerization of C_{60} under the experimental conditions at 60°C. It was observed that fullerene does not undergo homopolymerization at low temperature up to 80°C.

Kinetics of Polymerization

The progress of reaction was followed by monitoring the meniscus movement with the help of a cathetometer. For calculating the rate of polymerization, a master graph was plotted between percent conversion and volume contraction. With the help of this master graph, a plot was made between percent conversion and time. The rate of polymerization (*Rp*) was then evaluated from the graphical slope of the plot of percent conversion versus time.

RESULTS AND DISCUSSION

The IR spectra of copolymer has been shown in Fig. 1. The figure clearly evidenced that there appeared peaks near 2954 cm^{-1} due to C-H stretching in methyl group, 1736 cm^{-1} due to C=O stretching, near 1441 and 1381 cm^{-1} due to C=C stretching in aromatic, at 828 and 761 cm^{-1} due to C-C deformation and at 527 cm^{-1} due to {Fullerene – Co – Methylacrylate} copolymer.
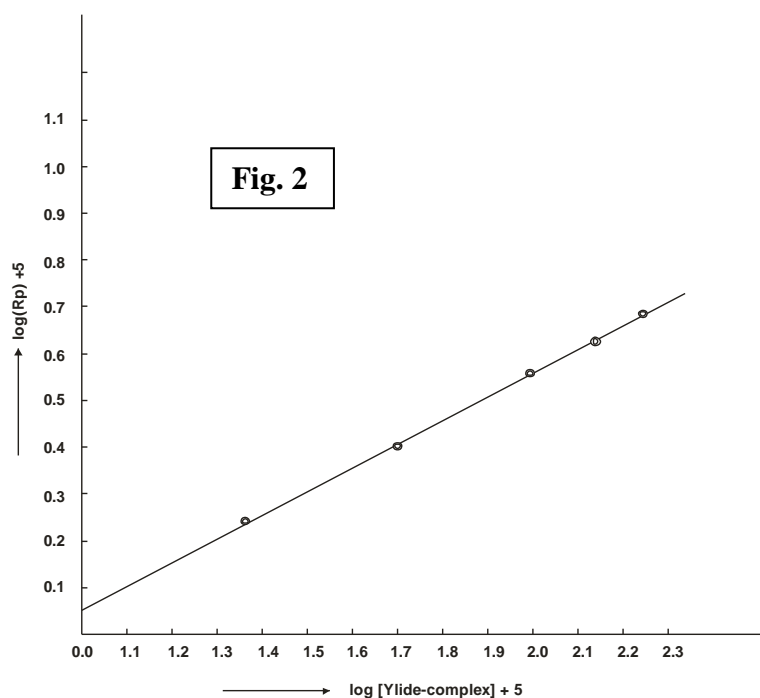

Fig. 1

Kinetic Study

The effect of {ylide – complex} on polymerization was studied by varying its concentration from 2.3 x10^{-4} mol dm^{-3} to 18.4 x10^{-4} mol dm^{-3} at 60°C and at constant concentration of fullerene and methylacrylate. The (Rp) increased as the concentration of {ylide – complex} increases (Table 1). The initiator exponent value for {ylide – complex} was calculated from the slope of the plot of log Rp versus log {ylide – complex} (Fig. 2) was 0.55±.01.
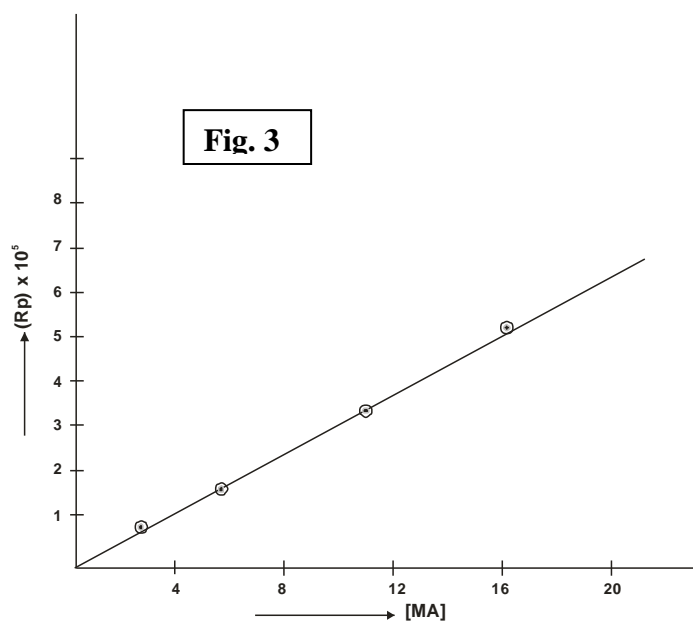
The effect of methylacrylate [MA] on Rp was studied by varying the concentration from 2.7 to 16.8 mol dm^{-3} at 60°C keeping initiator (9.2x10^{-4} mol dm^{-3}) and fullerene (3.5.0x10^{-4} mol dm^{-3}) at constant concentrations. The percentage conversion and (Rp) were found to increase with an increase in [MA].

Table 1

S. No.	[ylide-complex]x10^4 (mol dm^{-3})	[Methylacrylate] (mol dm^{-3})	[Fullerene] x10^4 (mol dm^{-3})	(R_P)x10^5 (mol dm^{-3}s^{-1})
1.	2.3	11.2	3.5	1.8
2.	4.6	11.2	3.5	2.5
3.	9.2	11.2	3.5	3.5
4.	13.8	11.2	3.5	4.2
5.	18.4	11.2	3.5	4.9
6.	9.2	2.8	3.5	0.9
7.	9.2	5.6	3.5	1.6
8.	9.2	16.8	3.5	4.6
9.	9.2	11.2	7.0	2.7
10.	9.2	11.2	14.0	2.3
11.	9.2	11.2	21.0	1.5
12.	9.2	11.2	28.0	1.3

Fig. 2

A plot of *Rp* versus [MA] at 60°C was found to be linear passing through the origin (Fig. 3) suggesting that the rate of copolymerization is directly proportional to [MA].


Fig. 3

The effect of fullerene (C_{60}) on R_P was studied by varying [Fullerene] from 3.5 to 28.0 x 10^{-4} mol dm^{-3} at 60°C and keeping initiator and methylacrylate at constant concentrations as given in (Fig. 4). It is clear from Fig. 4 that R_P decreased with an increase in [Fullerene]. A plot of *log Rp* versus *log [Fullerene]* was linear with a negative slope (Fig. 4) which was found to be 0.55± 0.05. This resulted the following relationship:

$$(1/Rp) \propto [\text{Fullerene}]^{0.55 \pm .05}$$

Further evidence that C_{60} acts as an inhibitor for the MA polymerization comes from the simple dilatometry experiments. The change in reacting solution volume was monitored as a function of time for MA in 1-4 dioxane and ylide-complex as initiator, at 60°C, with and without C_{60} present. After an initial thermal expansion the solution began to contract smoothly as polymerization proceeded. The slopes of the time dependent Δv curves were similar with and without C_{60} but showed a longer induction period when C_{60} was present in the reaction solution.

The inhibition effect of fullerene in copolymerization of fullerene and styrene is also reported in the literature [10].

Fig. 4
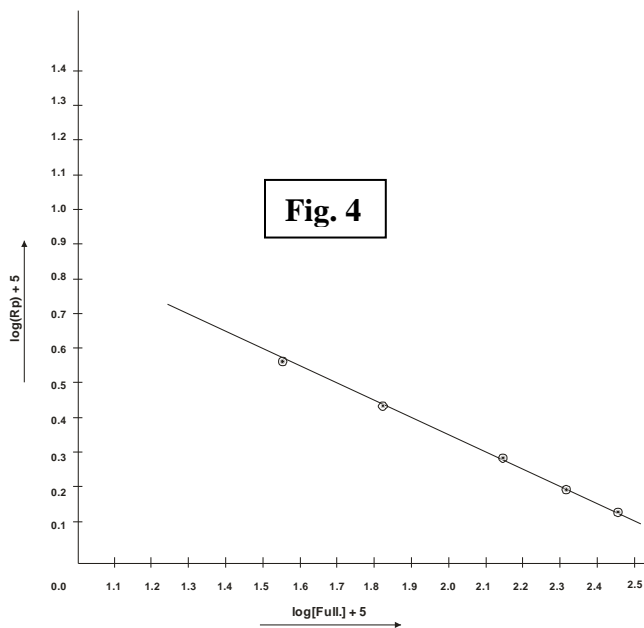
The effect of temperature on rate of copolymerization was studied by carrying out the copolymerization at 60, 65, 70 and 75°C (Table 2). The energy of activation calculated from the Arrhenius plot (Fig. 5) was obtained as 51.2 ± 0.5 kJmol^{-1}.

Table 2

S. No.	Temperature (K)	R_p x 10^5 (mol dm^{-3}s^{-1})
1.	333	3.5
2.	338	4.8
3.	343	6.3
4.	348	8.2

Fig. 5
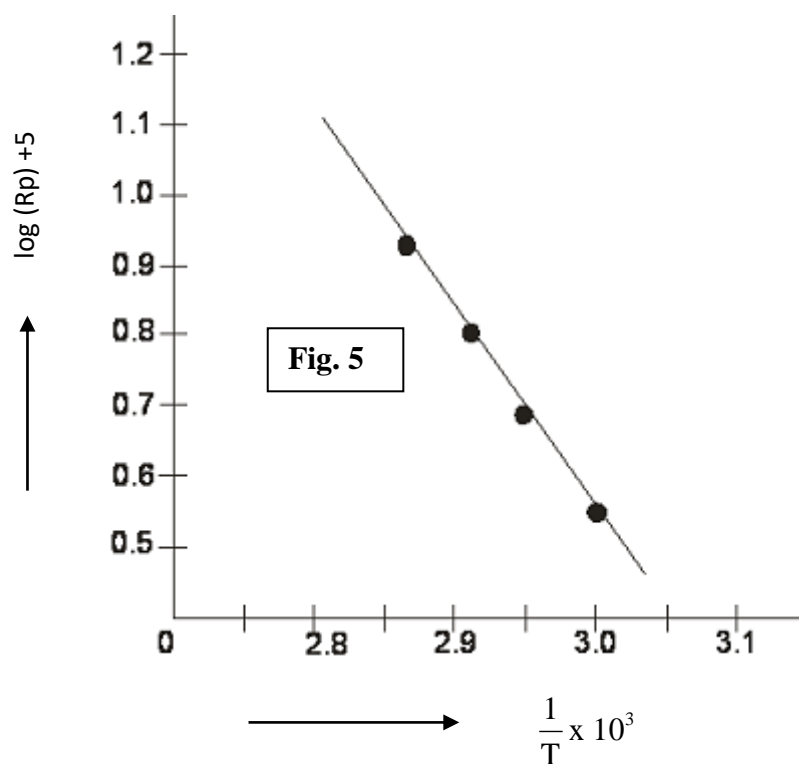
CONCLUSIONS

The rate of copolymerization (Rp) has been represented by $Rp \propto$ [ylide – complex]$^{0.5}$ [MA]^1 [Full]$^{-0.5}$, indicating that fullerene acted as inhibitor for the copolymerization. The energy of activation for the copolymerization was found to be 51.2 kJmol^{-1}. The copolymer has been characterized by FTIR spectroscopic method.

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