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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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Copolymerization of Fullerene (C₆₀) and Methyl Methacrylate (MMA) using Triphenylbismuthonium Ylide as a Novel Initiator and Characterization of the Copolymers (C₆₀-MMA)

Rashmi Katiyar^a; Dibyendu S. Bag^b; Indira Nigam^a

^a Department of Plastic Technology, H.B. Technological Institute, Kanpur, India ^b Defense Materials and Stores Research and Development Establishment (DMSRDE), Kanpur, India

Online publication date: 05 April 2010

To cite this Article Katiyar, Rashmi , Bag, Dibyendu S. and Nigam, Indira(2010) 'Copolymerization of Fullerene (C₆₀) and Methyl Methacrylate (MMA) using Triphenylbismuthonium Ylide as a Novel Initiator and Characterization of the Copolymers (C₆₀-MMA)', Journal of Macromolecular Science, Part A, 47: 5, 468 – 477

To link to this Article: DOI: 10.1080/10601321003659762

URL: <http://dx.doi.org/10.1080/10601321003659762>

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Copolymerization of Fullerene (C₆₀) and Methyl Methacrylate (MMA) using Triphenylbismuthonium Ylide as a Novel Initiator and Characterization of the Copolymers (C₆₀-MMA)

RASHMI KATIYAR¹, DIBYENDU S. BAG^{2,*} and INDIRA NIGAM^{1,**}

¹Department of Plastic Technology, H.B. Technological Institute, Kanpur, India

²Defense Materials and Stores Research and Development Establishment (DMSRDE), Kanpur, India

Received June 2009, Accepted November 2009

Copolymerization of fullerene (C₆₀) with methyl methacrylate (MMA) was carried out using triphenylbismuthonium ylide (abbreviated as Ylide) as a novel initiator in dioxan at 60°C for 4 h in a dilatometer under a nitrogen atmosphere. The reaction follows ideal kinetics: $R_p \propto [\text{Ylide}]^{0.5}[\text{C}_{60}]^{-1.0}[\text{MMA}]^{1.0}$. The rate of polymerization increases with an increase in concentration of initiator and MMA. However, it decreases with increasing concentration of fullerene due to the radical scavenging effect of fullerene. The overall activation energy of copolymerization was estimated to be 57 KJ mol⁻¹. The fullerene-MMA copolymers (C₆₀-MMA) were characterized by FTIR, UV-Vis, NMR and GPC analyses.

Keywords: Fullerene (C₆₀) containing polymers, copolymerization, methyl methacrylate (MMA), triphenylbismuthonium ylide

1 Introduction

Fullerenes are now a well-established subject of research in many areas since their discovery (1). The novel and unique properties of the fullerenes have been of great interest in the field of nanotechnology, supramolecular chemistry and materials chemistry (2,3). One of the most promising territories of investigation involves modification of the fullerene cage (C₆₀) and/or its attachment into polymeric matrices to improve and/or enhance its qualities for various applicative purposes (4). Fullerene-containing polymeric materials have received special attention for their potential technological applications in the field of optical and electroactive materials (5–12). The fullerene containing polymers can be classified into three categories (i) polyfullerenes, which are all carbon polymers formed by covalently linking fullerene molecules (13–15), (ii) polymers with pendant fullerenes, in which fullerene

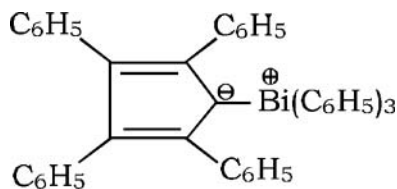
molecules are attached to groups or branches on polymer chains (so called ‘bucky ball fishing’ (16)) and (iii) copolymers of fullerene and vinyl monomers such as styrene, MMA, vinyl acetate, acrylonitrile, N-vinyl pyrrolidone, etc. (17–22).

Copolymerization is an effective method to incorporate a large number of fullerene molecules into polymeric structures. This approach potentially enables better processing of fullerene based materials into various shaped objects and thin films. Copolymerization of fullerenes with vinyl monomers using conventional initiators like 2,2'-azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), etc. have already been reported in the literature (23–25). These initiators require high temperature and more time for effective copolymerization.

In this paper, we report a comprehensive experimental investigation of copolymerization of fullerene with MMA using triphenylbismuthonium ylide as an effective initiator. Hence, copolymerization was carried out with various molar concentrations of fullerene and MMA as well as initiator concentrations. The structural characterization of the C₆₀-MMA copolymers was carried out using FTIR, UV-VIS, ¹H-NMR, ¹³C-NMR and Gel Permeation Chromatography (GPC). The mechanism of copolymerization of fullerene and MMA is also discussed.

*Address correspondence to: Dibyendu S. Bag, Defense Materials and Stores Research and Development Establishment (DMSRDE), Kanpur 208013, India. E-mail: ds_bag@rediffmail.com

**Indira Nigam, H.B. Technological Institute, Kanpur 208002, India. E-mail: indiranigam@rediffmail.com



Sch. 1. Chemical structure of 1,2,3,4-tetraphenylcyclopentadiene triphenylbismuthonium ylide (Ylide).

2 Experimental

2.1 Materials

Methyl methacrylate (Merck) was purified by the standard method (26). Solvents (toluene and dioxan) were distilled before use. Tetraphenylcyclopentadiene (Acros), p-toluenesulphonyl hydrazide (Aldrich), fullerene 99.9+% (Lancaster) were used as received. Bismuthonium ylide was prepared by the method of Lloyd (27) (Scheme 1).

2.2 Copolymerization

The copolymerization of fullerene and MMA was carried out in a dilatometer under the inert atmosphere of nitrogen for 4 h in dioxan using bismuthonium ylide as the initiator. The effect of variation of initiator concentration, molar ratio of fullerene and MMA as well as temperature on copoly-

merization was studied. The progress of the reaction was monitored by observing the movement of meniscus in the dilatometer with the help of a cathetometer. The copolymer thus formed in each case was precipitated by using acidified methanol and then dried to constant weight. The copolymer samples were purified by precipitating twice from THF into hexane and then dried under vacuum at 60°C.

2.3 Determination of Rate of Polymerization

Initially the percentage conversion was calculated gravimetrically. Then, a master graph was plotted between percentage conversion and volume contraction (in cm) data from the movement of meniscus in dilatometer (Fig. 1) The rate of polymerization in each set of experiments was estimated from the volume contraction in the dilatometer and with the help of the master graph. The energy of activation was calculated by carrying out copolymerization at different temperatures in the range 60°C to 90°C.

2.4 Characterization

The C₆₀-MMA copolymers were characterized by FTIR and NMR analyses. FTIR spectra of the samples were measured in KBr pellets in a Perkin-Elmer 599 B spectrophotometer. The NMR spectra of the copolymers

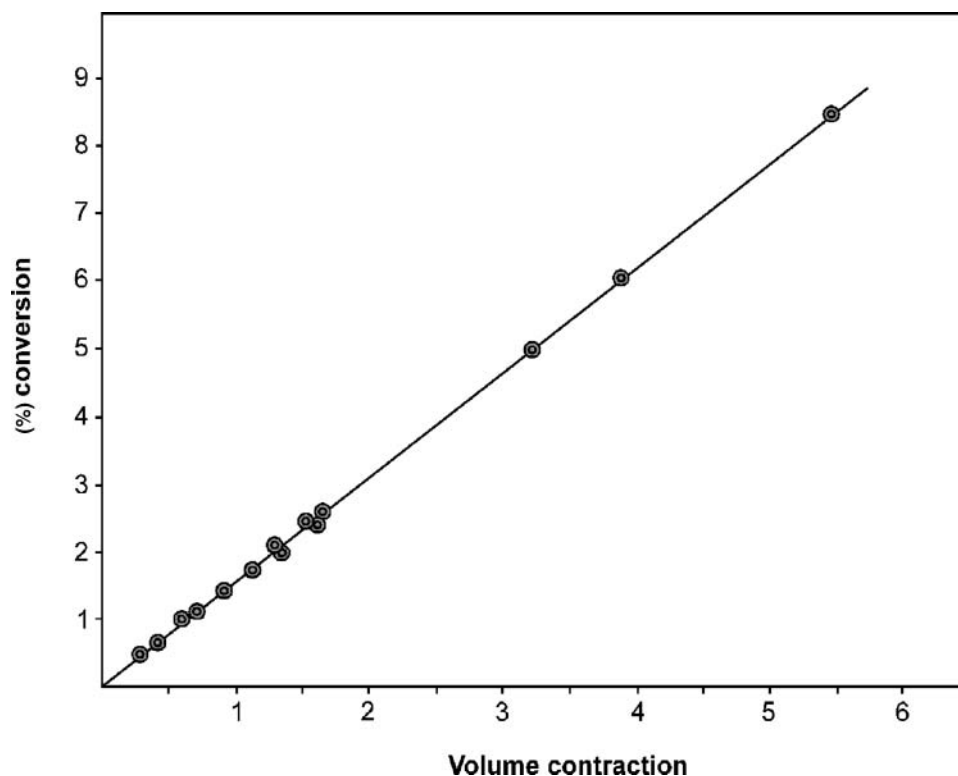


Fig. 1. Master graph (plot of % conversion vs. volume contraction in dilatometer) {each point is average of three measurements having variation of $\pm 2\%$ }.

Table 1. Effect of initiator (ylide) concentration on the rate of copolymerization of MMA and fullerene

Sl. No.	$[Ylide] \times 10^5 \text{ mol l}^{-1}$	$R_p \times 10^7 \text{ mol l}^{-1} \text{ s}^{-1}$
1	1.547	3.270
2	3.094	5.450
3	4.641	7.089
4	5.414	8.177

$[Fullerene] = 2.32 \times 10^{-4} \text{ mol l}^{-1}$, $[MMA] = 1.1773 \text{ mol l}^{-1}$, Time = 4 h, Temperature = 60°C .

were recorded on a 400 MHz BRUKER FT-NMR spectrometer by dissolving the samples in CDCl_3 . The UV-Vis spectra were recorded on a Varian CARY 500 UV-Vis-NIR spectrophotometer using a solution of the samples in dichloromethane.

The molecular weights of the polymers were measured by using a GPC equipped with a Waters 2414 RI detector, a Waters 1515 Isocratic HPLC pump and Waters 717 Plus Auto sampler in HSP RT MB-H, HSP RT 6.0 [Graft, linear, 500 Å, 100 Å] columns using THF as a mobile phase. The column was calibrated with PS standards.

3 Results and Discussion

The copolymerization of fullerene with MMA was studied by varying the concentrations of initiator (ylide), ratio of MMA and fullerene and temperature. The rate of polymerization, order of reaction and overall activation energy were estimated. The rate of polymerization was calculated from the graph plot of variation of % conversion with time at different initiator and monomer concentrations, while the order of reaction was determined with the help of a log plot of rate of polymerization (R_p) vs. concentrations of initiator and monomers. The energy of activation was calculated from the plot of logarithm of rate of polymerization vs. inverse temperature.

3.1 Effect of Initiator Concentration

The effect of initiator (ylide) on the rate of polymerization (R_p) was studied by varying its concentration from $1.547 \times 10^{-5} \text{ mol l}^{-1}$ to $5.414 \times 10^{-5} \text{ mol l}^{-1}$ while the concentration of fullerene and MMA were kept constant (Table 1). The time and temperature of polymerization were 4 h and 60°C , respectively. At each concentration of initiator, the percentage conversion increases with the time of polymerization (Fig. 2). The rate of polymerization (R_p) in each case of initiator concentration was calculated from the plot (Fig. 2). The log plot of rate of polymerization (R_p) vs. initiator concentration is shown in Figure.3. It indicates the effect of initiator concentration on the rate of polymerization. As the initiator concentration increases, the rate of polymerization increases. The initiator exponent value was

Table 2. Effect of [MMA] on the rate of copolymerization of MMA and fullerene

Sl. No.	$[MMA] \text{ mol l}^{-1}$	$R_p \times 10^7 \text{ mol l}^{-1} \text{ s}^{-1}$
1	0.7064	0.245
2	1.1773	0.545
3	1.8837	1.264
4	2.3546	1.635

$[Ylide] = 3.094 \times 10^{-5} \text{ mol l}^{-1}$, $[Fullerene] = 2.32 \times 10^{-4} \text{ mol l}^{-1}$, Time = 4 h, Temperature = 60°C .

calculated from the slope of log plot of R_p versus initiator concentration to be 0.5 ± 0.01 which is the value expected (0.50) for ideal kinetics (28).

3.2 Effect of MMA Concentration

The effect of MMA concentration on the rate of polymerization (R_p) was studied by varying it from 0.7064 to $2.3540 \text{ mol l}^{-1}$ while the concentration of initiator (ylide) and fullerene were kept constant (Table 2). The time and temperature of polymerization were 4 h and $60 \pm 1^\circ\text{C}$, respectively. At each concentration of MMA, the percentage conversion increases with the time of polymerization (Fig. 4). The rate of polymerization in each case of MMA concentration was calculated from the plot. The log plot

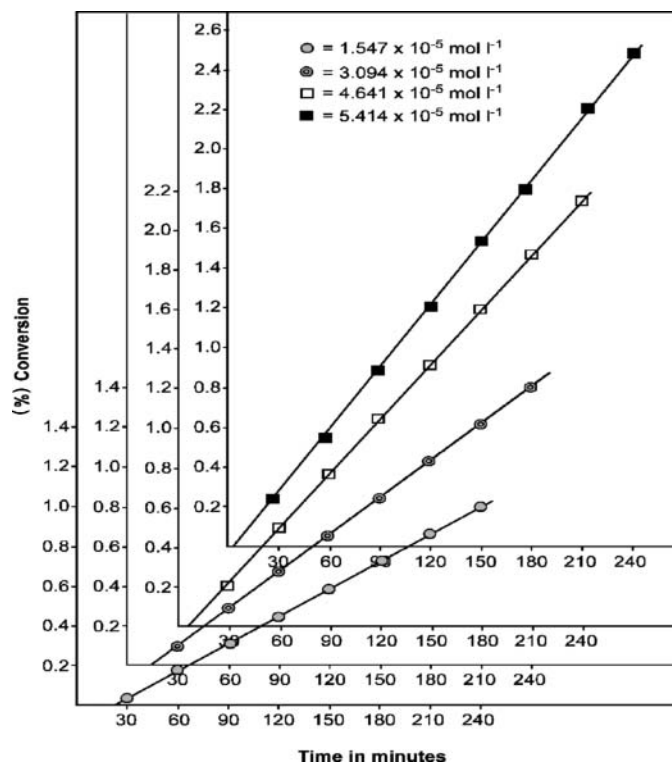


Fig. 2. Variation of % conversion with time at different initiator concentrations {each point is average of three measurements having variation of $\pm 2\%$ }.

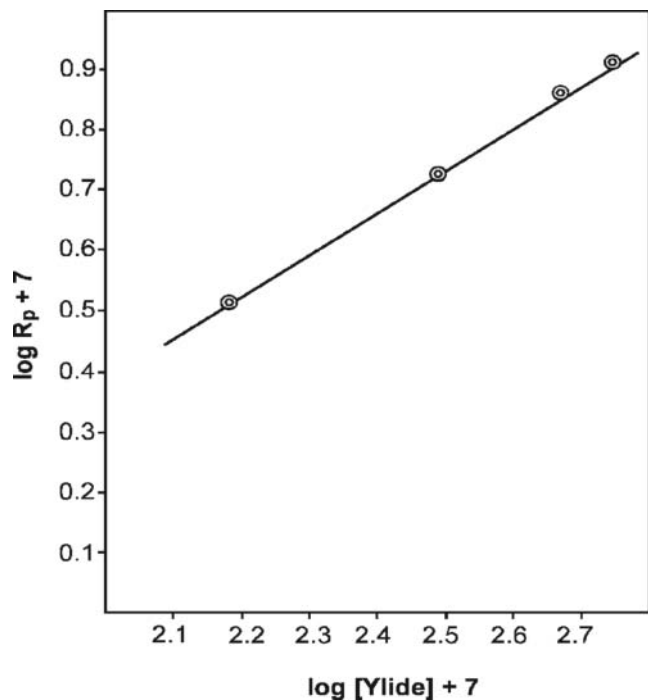


Fig. 3. Log plot of rate of polymerization (R_p) vs. initiator concentration {each point is average of three measurements having variation of $\pm 2\%$ }.

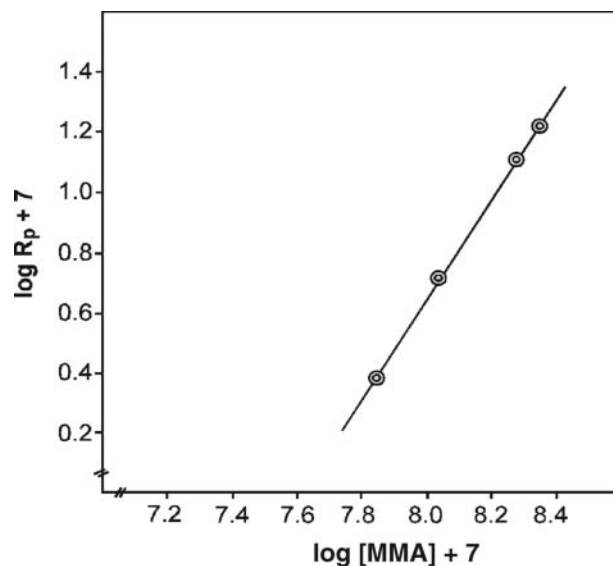


Fig. 5. Log plot of rate of polymerization (R_p) vs. concentration of MMA {each point is an average of three measurements having variation of $\pm 2\%$ }.

of rate of polymerization (R_p) vs MMA concentration indicates the effect of MMA on the rate of polymerization (Fig. 5). The rate of polymerization increases with increasing MMA concentration. The exponent value for MMA calculated from the slope of log plot of R_p vs. MMA concentration is estimated to be 1.03, which is close to the value expected (1.0) for ideal kinetics (28).

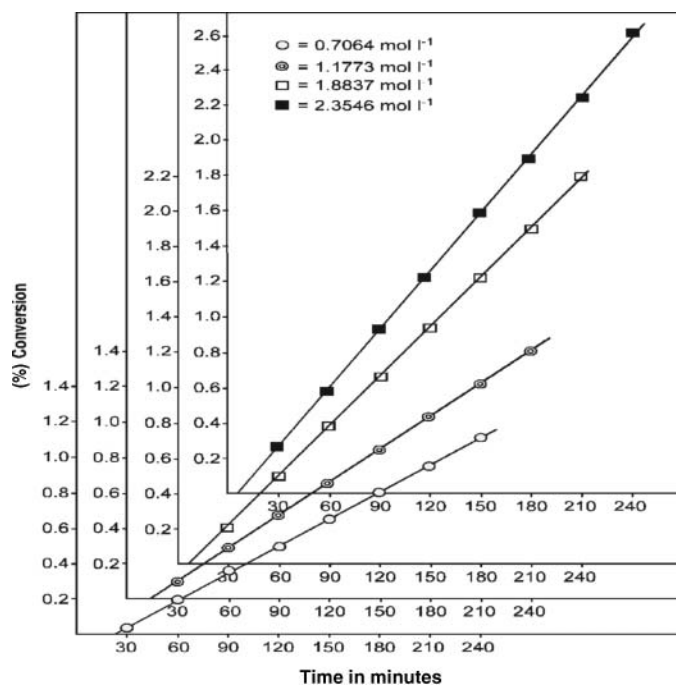


Fig. 4. Variation of % conversion with time at different concentrations of MMA {each point is average of three measurements having variation of $\pm 2\%$ }.

3.3 Effect of Fullerene

The effect of fullerene concentration on the rate of polymerization (R_p) was studied by varying it from $1.17 \times 10^{-4} \text{ mol l}^{-1}$ to $6.945 \times 10^{-4} \text{ mol l}^{-1}$, while the concentration of initiator (ylide) and MMA were kept constant (Table 3). The time and temperature of polymerization were kept fixed at 4 h and 60°C , respectively. At each concentration of fullerene the percentage conversion increases with the increase in time of polymerization (Fig. 6). The rate of polymerization in each case was calculated from the plot (Fig. 6). The log plot of rate of polymerization (R_p) with

Table 3. Effect of fullerene on the rate of copolymerization of MMA and fullerene

Sl. No.	Sample Code	$[\text{Fullerene}] \times 10^4$ mol l^{-1}	$R_p \times 10^7$ $\text{mol l}^{-1}\text{s}^{-1}$
1	FMMA-1	1.17	5.990
2	FMMA-2	2.32	5.450
3	FMMA-3	3.47	3.546
4	FMMA-4	5.79	3.270
5	FMMA-5	6.949	1.637

$[\text{Ylide}] = 3.094 \times 10^{-5} \text{ mol l}^{-1}$, $[\text{MMA}] = 1.1773 \text{ mol l}^{-1}$, Time = 4 h, Temperature = $60 \pm 1^\circ\text{C}$.

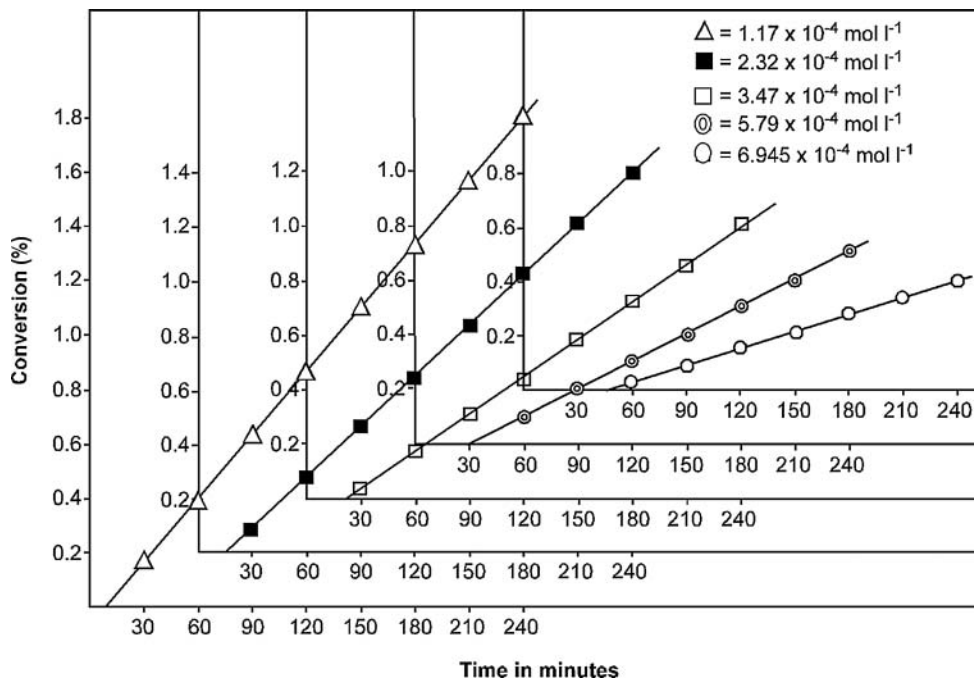


Fig. 6. Variation of % conversion with time at different concentrations of fullerene {each point is average of three measurements having variation of $\pm 2\%$ }.

fullerene concentration is shown in Fig. 7. The R_p is an inverse function of fullerene concentration. The rate of polymerization decreases with the increase in concentration of fullerene, which is due to the radical scavenging effect of fullerene. The log plot is linear and the exponent value is estimated to be -1.02 . That is of the order of unity (28).

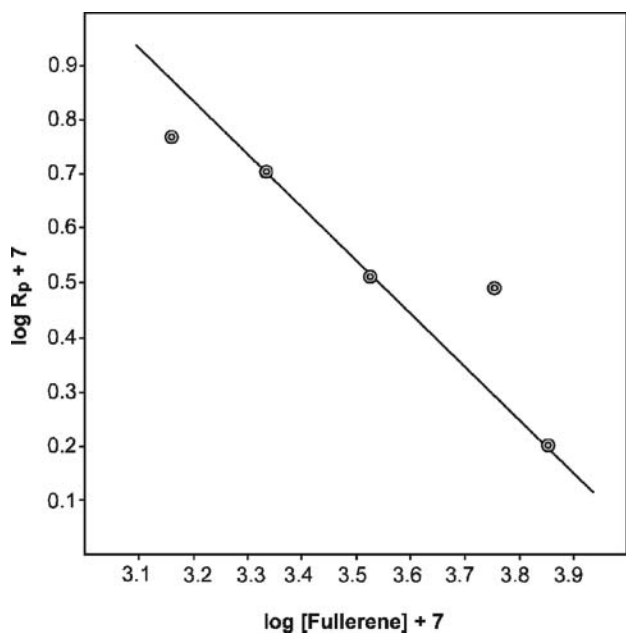


Fig. 7. Log plot of rate of polymerization vs. concentration of fullerene {each point is average of three measurements having variation of $\pm 2\%$ }.

From Table 3 as well as Figure 7, it is concluded that the rate of polymerization (R_p) decreases on increasing the concentration of fullerene (C_{60}) in the copolymerization system, thereby indicating the inhibiting nature of fullerene. Further evidence that C_{60} acts as an inhibitor for the MMA polymerization is observed from the comparison of the slope of time dependent percentage conversion with and without C_{60} (Fig. 8). The slopes are very similar to each other. But a longer induction period was observed when C_{60} was present. Therefore, we conclude that C_{60} reacts with initiator free radicals much faster than MMA, such that MMA polymerization occurs only after sufficient C_{60} is consumed to permit the reaction of initiator radical with MMA to compete. The inhibition action of fullerene is now well established. Cao and Webber also observed that fullerene acts as an inhibitor for fullerene-styrene copolymerization (23).

3.4 Effect of Temperature

The polymerization reactions were also carried out at different temperatures (60–90°C) for 4 h at fixed concentration of MMA, fullerene and initiator: $[MMA] = 1.1773 \text{ mol l}^{-1}$, $[Fullerene] = 2.32 \times 10^{-4} \text{ mol l}^{-1}$ and initiator, $[Ylide] = 3.094 \times 10^{-5} \text{ mol l}^{-1}$. The rate of polymerization increases with increasing temperature. The energy of activation is thus calculated as 57 kJ mol^{-1} from the plot of $\log R_p$ vs $1/T$ (Fig. 9).

In order to compare the activation energy for MMA polymerization in the presence of fullerene with that in

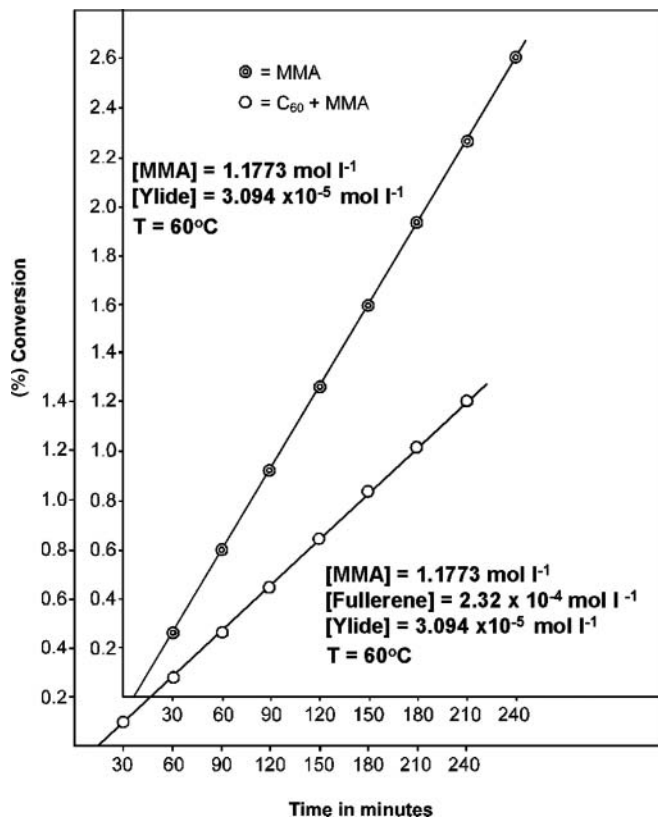


Fig. 8. Variation of % conversion of MMA with time in presence and absence of fullerene (C₆₀) {each point is average of three measurements having variation of ±2%}.

the absence of fullerene, the polymerization of MMA was carried out at different temperatures (60–80°C) for 4 h at fixed concentration of [MMA] = 1.1773 mol l⁻¹ and initiator (Ylide) = 3.094 × 10⁻⁵ mol l⁻¹. The rate of polymerization increases with the increase in temperature which is quite obvious. The plot of log R_p vs. 1/T is shown in Figure 10 and the energy of activation of MMA polymerization is

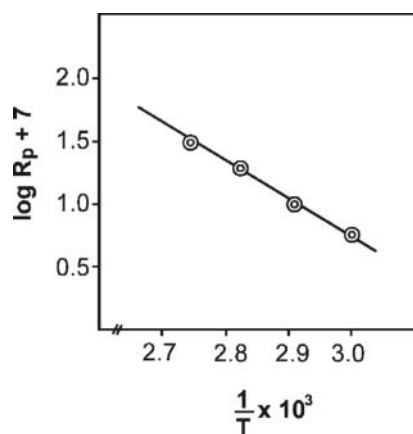


Fig. 9. Plot of log R_p vs. 1/T (MMA polymerization with C₆₀) {each point is average of three measurements having variation of ±3%}.

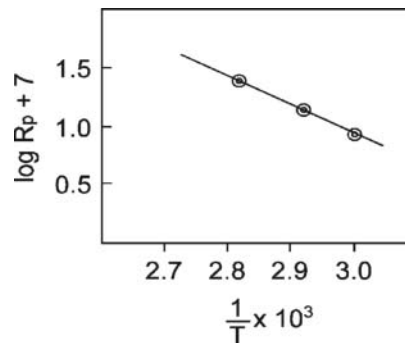


Fig. 10. Plot of log R_p vs. 1/T (MMA polymerization without C₆₀) {each point is average of three measurements having variation of ±3%}.

thus calculated as 44.8 kJ mol⁻¹. Hence, the energy of activation is lower when polymerization of MMA is carried out in the absence of C₆₀. It thereby indicates the inhibitory action of C₆₀ to the polymerization reaction.

3.5 Structural Characterization of Fullerene (C₆₀)-MMA Copolymers

3.5.1. FTIR Analysis

The C₆₀-MMA copolymers were characterized by FTIR analysis (Fig. 11). The distinct peak at 527 cm⁻¹ due to functionalized C₆₀ cages is identified in the copolymer samples (29). The sharp peak at 1740 cm⁻¹ is due to the C=O group of ester of MMA comonomer. A peak at 1148 cm⁻¹ is due to the presence of methoxy group (-OCH₃) of MMA unit. These evidences indicate the formation of a copolymer of fullerene and MMA. The C-H stretching of methyl (-CH₃) and alkyl chain (-CH₂-) appears at 2900–3000 cm⁻¹. Again the characteristic peak of C₆₀ cage is more prominent in the copolymer sample FMMA-5 than FMMA-2, which is obvious because of more fullerene content in the sample.

3.5.2. NMR Analysis

¹H-NMR and ¹³C-NMR spectra of C₆₀-MMA copolymers are shown in Figures 12 and 13. The proton NMR shows a peak at 0.84 ppm and 1.68 ppm indicating the presence of methyl (CH₃) and methylene (CH₂) protons, respectively. The highly intense peak at 3.60 ppm occurs due to the presence of methoxy protons (-OCH₃) of MMA comonomer in the copolymer. However, no characteristic peak is observed for the presence of fullerene in the copolymer due to the absence of protons in the fullerene molecule.

The ¹³C-NMR spectrum shows a very small peak in the range of 135–160 ppm, which indicates the presence of functionalized fullerene (C₆₀) cage (24). However, it was not observed in the copolymer prepared at lower concentration of fullerene. The spectrum also shows a peak at 18.89 ppm indicating the presence of methyl carbon (-CH₃) in the copolymer due to the MMA unit. A peak at 44.75 ppm is

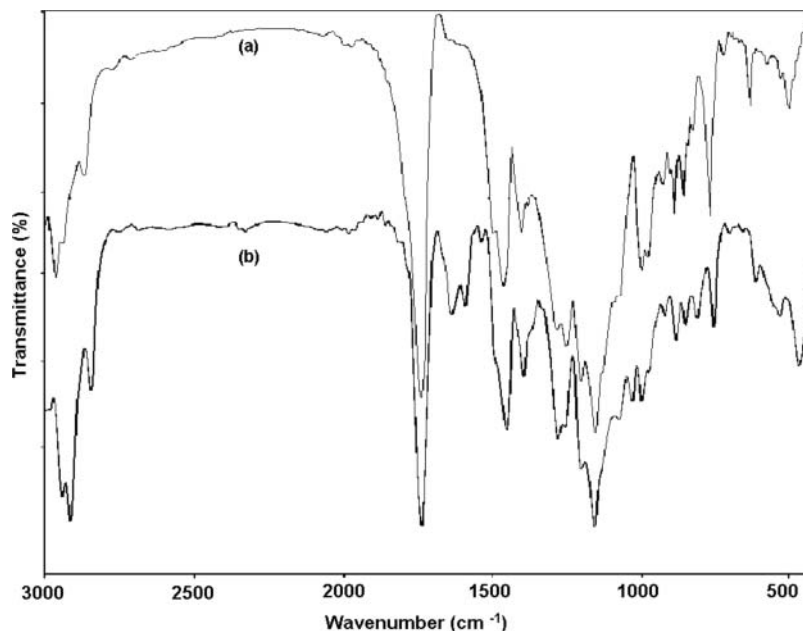


Fig. 11. FTIR spectra of C_{60} -MMA copolymers: (a) FMMA-2 and (b) FMMA-5.

due to quaternary carbon resonance while methylene carbon appears at 66.49 ppm. The methoxy carbon (OCH_3) appears at and 51.25 ppm. In addition, a peak at 178.07 pm indicates the presence of $-C=O$ group of MMA unit in the copolymer.

3.5.3. UV-Vis Analysis

As reported in the literature, the UV-Vis spectrum of pure fullerene (C_{60}) usually exhibits three absorption peaks at 340, 250 and 210 nm (18). In this study, we observe a prominent UV-Vis absorption of C_{60} -MMA copolymer samples in dichloromethane at 257 nm. Typical UV-Vis spectra of two copolymer samples are shown in Figure 14. In order to understand the concentration of fullerene in the C_{60} -MMA copolymer samples, first a calibration curve is

prepared from the UV-Vis study of pure fullerene sample in dichloromethane. The plot of absorption vs. concentration of fullerene is shown in Figure 15. The plot is linear. Now, from the UV-Vis absorbance values of the C_{60} -MMA copolymer samples (obtained at 257 nm), the concentration of fullerene in the copolymer is calculated with the help of the calibration curve (Fig. 15). The C_{60} content in the copolymers like FMMA-2, FMMA-3 and FMMA-5 are found to be 3.2, 6.2 and 8.4 wt%, respectively.

3.5.4. GPC Analysis

GPC measurements were carried out to understand the molecular weight of the fullerene containing polymers. Although fullerene is completely insoluble in pure THF, the C_{60} -MMA copolymers were soluble in THF. GPC analysis

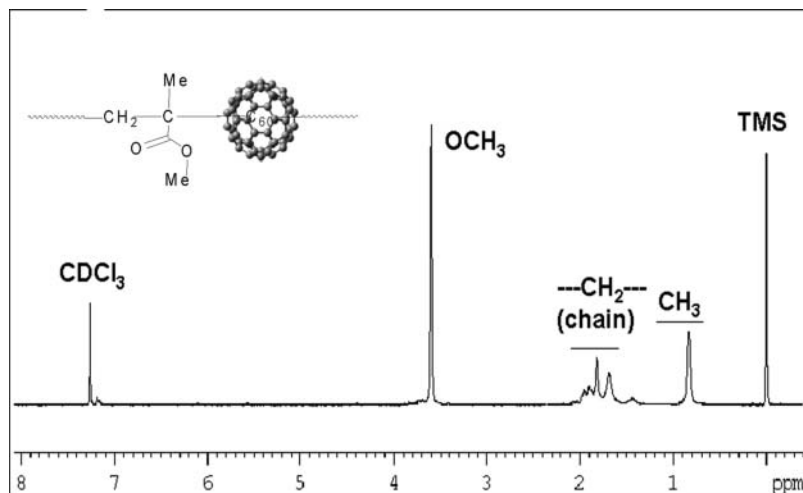


Fig. 12. Proton NMR spectrum of C_{60} -MMA copolymer (FMMA-2).

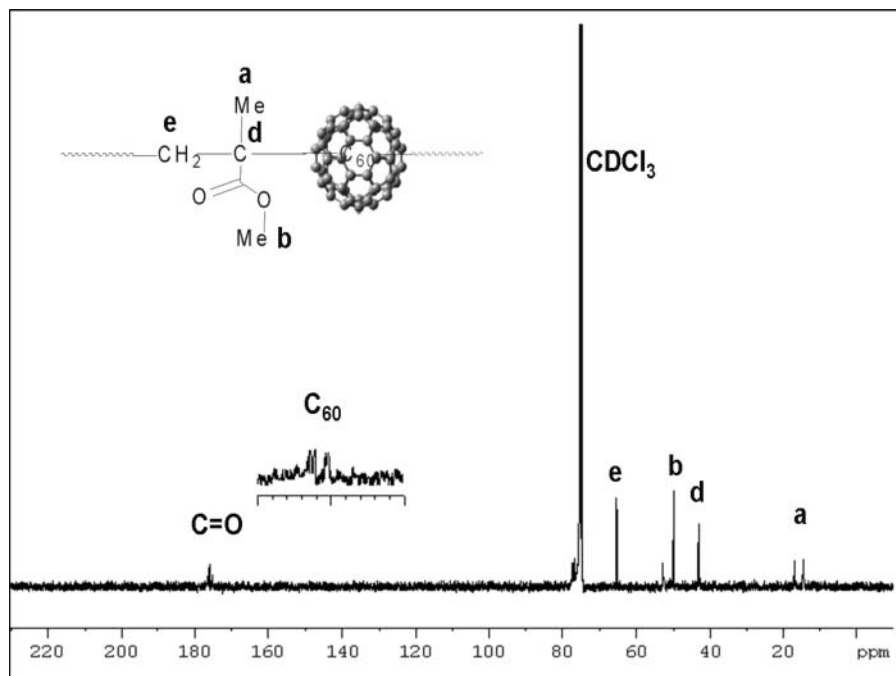


Fig. 13. ^{13}C -NMR spectrum of C_{60} -MMA copolymer (FMMA-5).

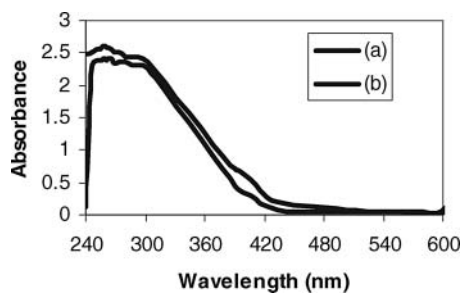


Fig. 14. UV-Vis absorption spectra of (a) FMMA-5 and (b) FMMA-2 in dichloromethane (2.5 mg/mL).

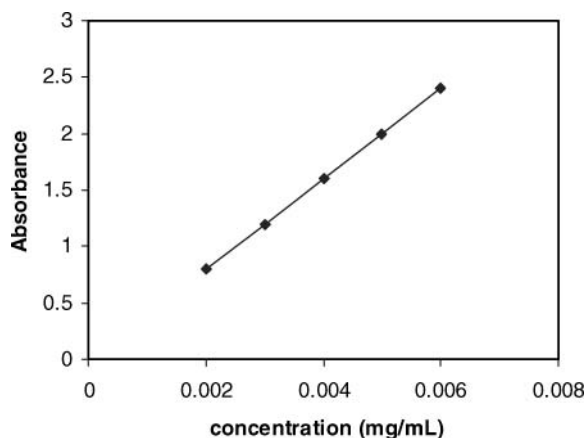


Fig. 15. UV-Vis absorption vs concentration of fullerene.

was therefore performed with an RI detector using THF solvent. Figure 16 shows the GPC chromatograms and results are also shown inside.

As the fullerene concentration increases in the copolymerization, the molecular weight of the fullerene containing polymer i.e., the C_{60} -MMA copolymer increases. Since fullerene acts as a radical scavenger in the copolymerization system, some of the generated initiator radicals are scavenged. Hence the available number of initiator radicals for polymerization is diminished more in the case where the concentration of fullerene is high. The molecular weight of the polymers thus obtained in the system having a higher concentration of fullerene is more than that of the system

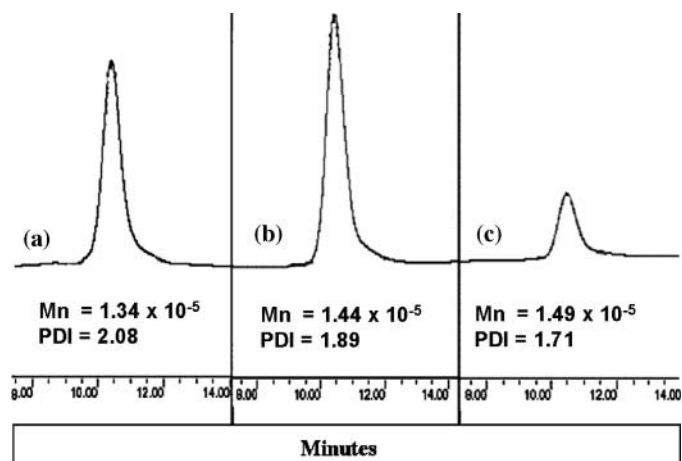


Fig. 16. GPC chromatograms of C_{60} -MMA copolymers (a) FMMA-1, (b) FMMA-2 and (c) FMMA-5.

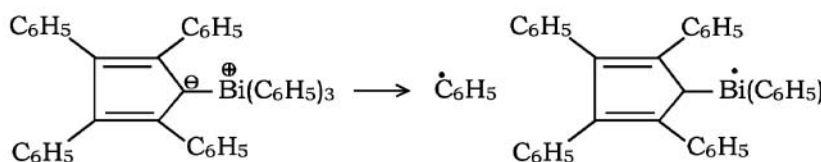
containing lower concentration of fullerene (Fig. 16). On the other hand, the polydispersity index (PDI) decreases in the same order.

3.6 Mechanism

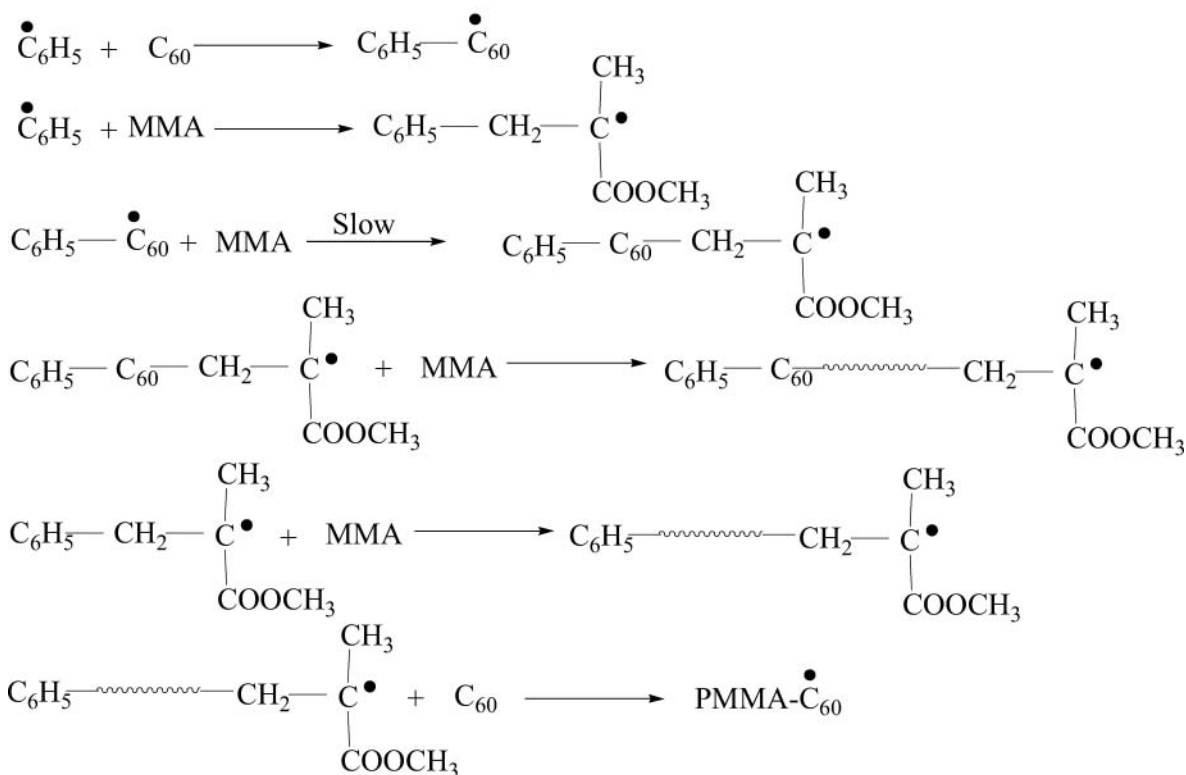
The mechanism of initiation of polymerization by triphenylbismuthonium ylide has been reported in the litera-

ture (30). Triphenylbismuthonium ylide dissociates giving rise to a phenyl free radical. The phenyl radical in subsequent steps propagates the polymerization. The possibility of termination by disproportionation is ruled out as the system follows ideal kinetics. The most plausible mechanism of fullerene-MMA copolymerization (C_{60} -MMA) is thus given below:

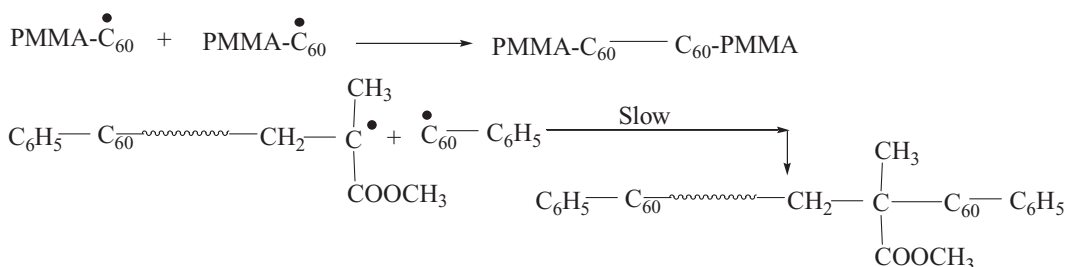
Initiation:

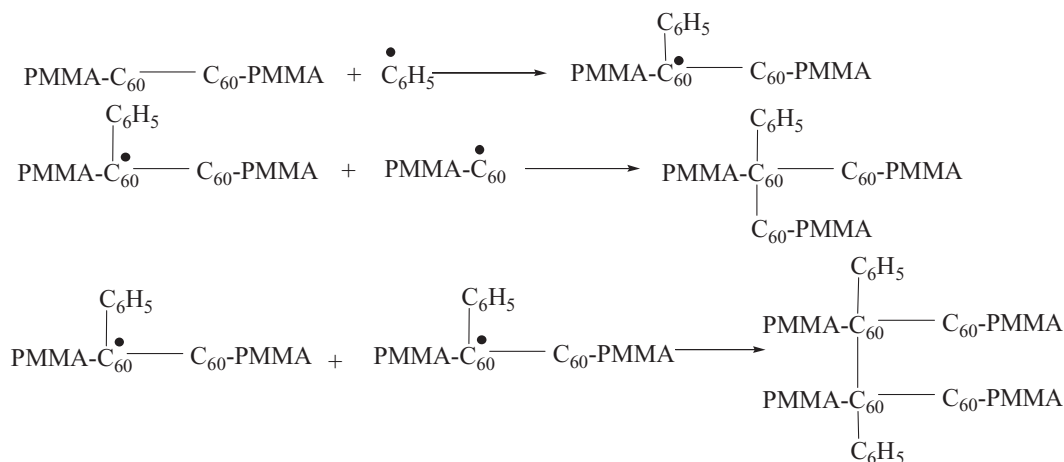


Propagation:



Termination:



Branching/Crosslinking:**4 Conclusion**

The copolymerization reaction of fullerene (C₆₀) with MMA follows ideal kinetics. The rate of polymerization (R_p) increases with increase in the concentration of initiator and MMA. However, it is observed to decrease on increasing the concentration of fullerene because of the radical scavenging action of fullerene. But the molecular weight of the polymer increases with the increase of fullerene concentration. The structure of the C₆₀-MMA copolymers was investigated using FTIR, UV-Vis ¹H- and ¹³C-NMR spectroscopy.

Acknowledgement

The authors are thankful to the Director of H.B.T.I. Kanpur, and the Director of DMSRDE Kanpur for providing the necessary facilities and support required to carry out the research work.

References

- Kroto, H.W., Heath, J.R., O'Brien, S.C., Curl, R.F. and Smalley, R.E. (1985) *Nature*, 318, 162.
- Langa, F. and Nierengarten, J-F (Eds.) *Fullerenes: Principles and Applications*, RSC Publishing: Cambridge, U.K., 2007.
- Wang, Y., Geckeler, K.E. *Nanostructures Based on Fullerenes*. In *Functional Nanomaterials*, Geckeler, K.E., Rosenberg, Eds. American Scientific Publishers: California, 2006.
- Wanga, C., Guob, Z.-X., Fua, S., Wub, W. and Zhub, D. (2004) *Prog. Polym. Sci.* 29, 1079.
- Dresselhaus, M.S.; Dresselhaus, G.; and Eklund, P.C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, 1996, 320.
- Prato, M.J. (1997) *Mater. Chem.*, 7, 1097.
- Chen, Y., Huang, Z.E., Cai, R.F. and Yu, B.C. (1998) *Eur. Polym. J.*, 34, 137.
- Tan, Z., Hou, J.H., He, Y.J., Zhou, E., Yang, C. and Li, Y. (2007) *Macromolecules*, 40 (6), 1868.
- Chu, C.C., Ho, T.I. and Wang, L. (2007) *Macromol. Rapid. Com.*, 28 (2), 200.
- Yu, H.Z. and Peng, J.B. (2008) *Organic Electronics*, 9 (6), 1022.
- Sevim, A.O. and Mutlu, S. (2009) *Organic Electronics*, 10(1), 18.
- Rao, A.M., Zhou, P., Wang, K.-A., Hager, G.T., Holden, J.M., Wang, Y., Lee, W.T., Bi, X.-X., Eklund, P.C., Cornett, D.S., Duncan, M.A. and Amster, I.J. (1993) *Science*, 259, 955.
- Iwasa, Y., Arima, T., Fleming, R.M., Siegrist, T., Zhou, O., Haddon, R.C., Rothberg, L.J., Lyons, K.B., Carter, H.L., Jr, Hebard, A.F., Tycko, R., Dabbagh, G., Krjewski, J.J., Thomas, G.A. and Yagi, T. (1994) *Science*, 264, 1570.
- Sun, Y.P., Ma, B., Bunker, C.E. and Liu, B. (1995) *J. Am. Chem. Soc.*, 117, 12705.
- Pekker, S., Janossy, A., Milhaly, L., Chauvet, O., Carrad, M. and Forro, L. (1994) *Science*, 265, 1077.
- Hawker, C.J. (1994) *Macromolecules*, 27, 4836.
- Weis, C., Friedrich, C., Mulhaupt, R. and Frey, H. (1995) *Macromolecules*, 28, 405.
- Cao, T. and Webber, S.E. (1995) *Macromolecules*, 28, 3741.
- Bunker, C.E., Lawson, G.E. and Sun, Y.P. (1995) *Macromolecules*, 28, 3744.
- Camp, A.G., Lary, A. and Ford, W.T. (1995) *Macromolecules*, 28, 7959.
- Ford, W.T., Nishioka, T. and Mc Cleskey, S.C. (2000) *Macromolecules*, 33, 2413.
- Mehrotra, S., Nigam, A. and Malhotra, R. (1997) *Chem. Commun.*, 463.
- Cao, T. and Webber, S.E. (1996) *Macromolecules*, 29, 3826.
- Sun, Y.P., Lawson, G.E., Bunker, C.E., Johnson, R.A., Ma, B., Farmer, C., Riggs, J.E. and Kitaygorodskiy, A. (1996) *Macromolecules*, 29, 8441.
- Yuan, X., Lu, J., Xu, Q. and Wang, L. (2005) *Polymer*, 46 (21), 9186.
- Vogel, A.I., *A Text Book of Practical Organic Chemistry*, 5th Edn. (Longman: London), 1989, 397.
- Lloyd, D. and Glidewell, C. (1988) *Synthesis*, 319.
- (a) Odian, G. *Principles of Polymerization*, 3rd Edn., 1991 (b) Sharma, S., Srivastava, A.K. (2003) *J. Macromol. Sci. Pure. and Appl. Chem.*, A40, 593.
- Atwood, J.L., Koutsantonis, G.A. and Ratson, C.L. (1994) *Nature*, 368, 229.
- Bajpai, R. and Srivastava, A.K. (2001) *Ind. J. Chem. Tech.*, 8, 301.