Effect of Co and V Complexes on Polymerization of Methyl Methacrylate Initiated by AlEt₂Br-TEMPO Catalyst

Lingam Ravikumar, Raju Thevi

Department of Chemistry, CBM College, Coimbatore 641 042, India

ABSTRACT: 2,2,6,6-Tetramethyl piperidinoxy (TEMPO) activated with diethyl aluminum bromide was employed as an initiator system for methyl methacrylate polymerization. Effect of addition of $Co(acac)_3$ and $VO(acac)_2$ complexes to the initiators system on methyl methacrylate polymerization were studied in benzene solvent. Various reaction parameters such as Al/TEMPO, monomer concentration, reaction temperature and time applied to the polymerization were investigated. The polymer yields, molecular weight and molecular weight distributions can be controlled with the addition of $Co(acac)_3$ to the initiator system. PMMA's of molecular weight distributions, as low as 1.10 was obtained under relatively mild conditions, in the temperature range 40–60°C in benzene solvent. However, Co and V complexes did not influence the micro structure of the PMMA's formed. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3932–3938, 2009

Key words: diethyl aluminum bromide; TEMPO; methyl methacrylate; cobalt (III) acetylacetonate; vanadium oxy acetylacetonate; molecular weight distribution

INTRODUCTION

Organometallic compounds[1] and organoaluminum derivatives[2] have been reported to yield living radical polymerizations via reversible deactivation. Organoaluminum amides are known as initiators for well controlled polymerization of methyl methacrylate.[3] 2,2,6,6-Tetramethyl piperidinoxy (TEMPO) is the most commonly used stable radicals in nitroxide mediated polymerization.[4] However, it has many disadvantages such as its inability to polymerize other than styrenes due to the stability of the dormant alkoxyamine it forms. Moreover, high temperatures and bulk solutions are also required for the polymerization. Benzoyl peroxide with excess TEMPO[5] or even the simple mixtures of TEMPO and styrene when heated to a temperature around 125–130°C should form living polymerization in which the thermal initiation occurs by the Mayo mechanism.[6] With stable free radical polymerization of styrene in dispersed media, TEMPO finds extensive use where in polymerization temperatures are usually above 125°C.[4] Organoaluminum compounds/benzoyl peroxide initiator systems were reported for the free radical polymerization of vinyl monomers.[7] A US Patent[8] discloses, a free radical polymerization process with a narrow molecular weight distributions using the catalyst system organoaluminum compounds/dimethylglyoxime/TEMPO and Al(i Bu)₃/dipiridine/galvinoxyl for vinyl monomers.

It is of interest to note that when aluminum alkyls are complexed with TEMPO, they initiate a very fast and exothermic polymerization of styrene.[9] Polymer yields of up to 98% could be achieved at short polymerization times under relatively mild conditions in benzene solvent. There are only few reports describing the aluminum alkyl/TEMPO system as efficient initiators for polar vinyl monomers such as methyl methacrylate. Al(i Bu)₃/2,2′- bipyridine/TEMPO initiating system have been reported for methyl methacrylate and vinyl acetate polymerization.[10] At room temperature this initiating system failed to confirm the living radical mechanism. However, at −78°C, it showed some living characterists. In multimetallic catalyst systems involving aluminum alkyls, third component such as PCl₃ or Co(acac)₃ has been reported to influence the isotacticity and polymer yield for the styrene monomer.[11] Apart from the combinations of organic ligands with TEMPO activated by aluminum alkyls, there are no reports on the combinations of TEMPO with transition metal complexes. In this contribution we report the initiator systems AlEt₂Br-TEMPO, AlEt₂Br-TEMPO–Co(acac)₃, and AlEt₂Br-TEMPO–VO(acac)₂ for methyl

methacrylate polymerization in benzene solvent in the temperature range 40-60°C.

EXPERIMENTAL

Chemicals

Benzene

Benzene was freed from thiophene[12] by repeated stirring with Conc. H_2SO_4. It was then washed with distilled water and sodium carbonate solution and dried over anhydrous calcium chloride. Benzene was then decanted and refluxed for several hours with sodium shavings. Finally, it was distilled and stored over sodium wire.

Methanol and ethanol were purified by refluxing over calcium oxide for 6 h and distilled before use.

Acetyl acetone (L.R E.Merck, India) was distilled (B.P. 139°C) before use.

Purification of monomer

MMA (AR. E. Merck) was freed from inhibitor by treating with 5% NaOH solution, washed with distilled water and dried over anhydrous calcium chloride. It was then distilled under reduced pressure in nitrogen atmosphere and stored in a refrigerator. TEMPO (Lancaster) was used as received without further purification.

Preparation of transition metal complexes

Cobalt(III) acetylacetonate was prepared according to the standard procedure[13] and recrystallized from benzene/petroleum ether.

Vanadium(III) oxy acetylacetonate was prepared according to the reported procedure.[14] The crude product was recrystallised from chloroform.

Diethyl aluminum bromide was prepared according to our earlier report,[15] and twice distilled under reduced pressure before the preparation of stock solution.

Polymerization

Polymerization reactions were carried out in a specially designed 50 mL Erlen–Meyer flask with B-19 cone joint fitted with B-19 ground joint. Reagents were transferred using an all glass hypodermic syringe fitted with a stainless steel needle. Transfer of reagents to the flask was done inside a glove box which was continuously flushed with oxygen-free dry nitrogen.

Initiator system AlEt$_2$ Br/TEMPO

This forms a homogeneous system and the addition of reagents are described as follows. To a fixed volume of benzene, TEMPO (stock solution in benzene), monomer and finally AlEt$_2$Br (stock solution in benzene), were added in that order. After the addition of reagent the flask was stoppered and immersed in a thermostat at 40°C.

Initiator system AlEt$_2$ Br/TEMPO/Co(acac)$_3$

This initiator system is also a homogeneous one. The order of addition is described as follows. To a fixed volume of benzene, TEMPO (stock solution in benzene), Co(acac)$_3$ (stock solution in benzene), monomer and finally AlEt$_2$Br (stock solution in benzene), were added in that order. After the addition of reagent the flask was stoppered and immersed in a thermostat at 60°C.

Initiator system AlEt$_2$ Br/TEMPO/VO(acac)$_2$

This initiator system is a heterogeneous one since VO(acac)$_2$ is sparingly soluble in benzene. To a fixed volume of benzene, weighed quantities of VO(acac)$_2$ crystals were added followed by TEMPO (stock solution in benzene) and monomer. The AlEt$_2$Br (stock solution in benzene), was finally added and after the addition of reagent the flask was stoppered and immersed in a thermostat at 40°C.

After specified reaction time, the polymerization was stopped and precipitated by the addition of excess of acidified ethanol. In the case of initiator system involving VO(acac)$_2$, addition of acidified ethanol dissolves the reaction mixture and polymer alone gets precipitated. With Co(acac)$_3$ system after the polymerization time, addition of excess of acidified ethanol causes precipitation of only PMMA and after filtration there is no traces of the metal complexes. However, for the spectral analysis PMMA's were twice precipitated from acetone/methanol system. The precipitated polymer was collected on a sintered crucible, washed with pure methanol and dried in vacuum to constant weight.

CHARACTERIZATION

FTIR analysis of the catalysts were recorded using Perkin–Elmer 1760 system with KBr pellets.^{1}H-NMR Spectra of the polymers were recorded in CDCl$_3$ solvent employing a Varian Em XLAA 300 instrument and by using TMS as internal standard. The chemical shifts were expressed in ppm.

Average molecular weights were measured by size-exclusion chromatography (SEC) with a HP1100 apparatus equipped with a set of four columns
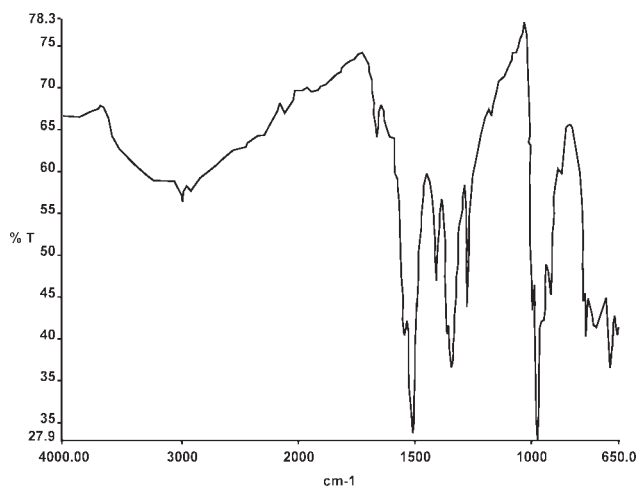
Figure 1 IR-spectrum of VO(acac)$_2$.

$(10^5$, 10^4, 10^3, and 10^2 A¢^{a}: polymer standards service) with chloroform as an eluent. Polystyrene samples were used as standards to construct the calibration curve.

RESULT AND DISCUSSIONS

IR spectra of VO(acac)$_2$ and Co(acac)$_3$ are shown in Figures 1 and 2 respectively. The characteristic V-O stretch of the oxycation appears at 995 cm^{-1} for VO(acac)$_2$ and for Co(acac)$_3$ the fundamental carbonyl stretching absorptions around 1600 and 2900 cm^{-1} are similar to the reported values.[16] Preliminary experiments indicated that the single component TEMPO, Co(acac)$_3$, and VO(acac)$_2$ were completely inert to MMA olymerization in benzene at 40°C. AlEt$_2$Br also showed no catalytic activity in benzene at 40°C for MMA. When AlEt$_2$Br-TEMPO is used as an initiator system, it initiates a very fast and exothermic polymerization of styrene. However, methyl methacrylate as monomer, there was no exothermic reaction and the initiator system was found to be active at 40°C in benzene solvent. Investigations where also carried out with the initiator systems AlEt$_2$Br-TEMPO–Co(acac)$_3$ and AlEt$_2$Br-TEMPO–VO(acac)$_2$ on MMA polymerization in benzene medium in the temperature range 40–60°C. AlEt$_2$Br-TEMPO (**1a**) and AlEt$_2$Br-TEMPO–Co(acac)$_3$ (**1b**) forms a homogeneous system in benzene while the initiator system AlEt$_2$Br-TEMPO–VO (acac)$_2$ (**1c**) is a heterogeneous one for MMA polymerization.

The effect of various parameters such as Al/TEMPO ratio, reaction time, and monomer concentration and polymerization temperature were studied for the three initiator systems. With the catalyst (**1a**), by keeping the concentration of TEMPO and MMA at 6.25×10^{-3} mol L^{-1} and 1.8697 mol L^{-1} respectively, the concentration of AlEt$_2$Br was increased from 5.9×10^{-2} mol L^{-1} to 12.06×10^{-2}
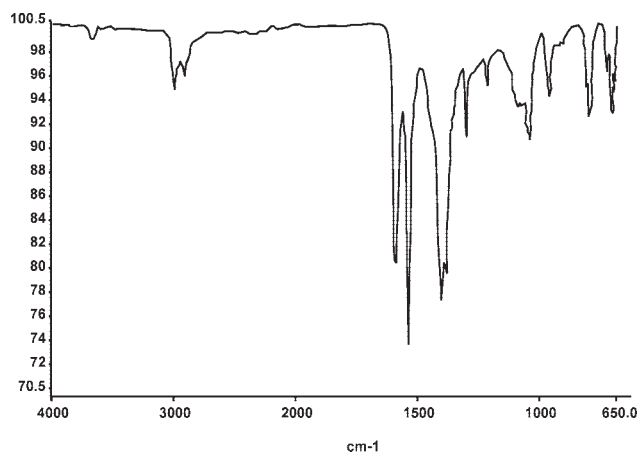

Figure 2 IR-spectrum of Co(acac)$_3$.

mol L^{-1}, so that Al/TEMPO ratio was kept in the range 9.5–19.3. Similarly with the catalyst (**1b**) and (**1c**) the Al/TEMPO ratio was varied from 4.2 to 21.4 and 6.2 – 18.6 respectively. The effect of Al/TEMPO ratios on the polymer yield with the catalyst systems investigated is shown in Figure 3. It is seen from Figure 3 that variation of the molar ratio of organoaluminium/TEMPO, which is expressed here as Al/TEMPO ratio, showed considerable effects on the polymerization of MMA. Polymer yields increase first and then decreases with the increase of Al/TEMPO ratio. With the catalysts **1a**, **1b**, and **1c** the highest yields of PMMA's were obtained when Al/TEMPO ratios were about 17.2, 17.2, and 9.3 respectively.

Among the three initiator systems **1a** without any third component displayed low catalytic activity for
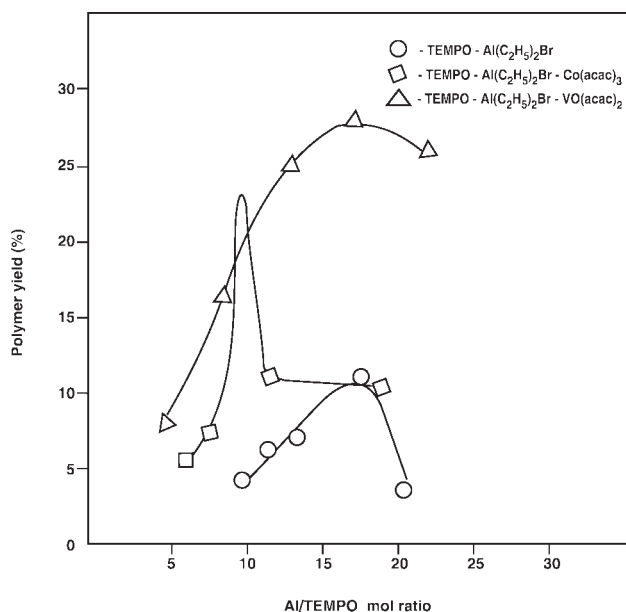

Figure 3 Dependence of monomer conversion versus Al/TEMPO ratio.

TABLE I
Polymerization of Methyl Methacrylate (Initiator System: AlEt₂Br-TEMPO)

S. No	Polymerization time (h)	Yield %	M_n	M_w/M_n
1	2	5.9	27,296	1.54
2	3	9.8	29,395	1.61
3	4	10.2	31,245	1.54
4	5	10.4	32,561	1.55

TABLE III
Polymerization of Methyl Methacrylate Initiator System: AlEt₂Br–TEMPO–VO(acac)₂

S. No	Polymerization time(h)	Yield (%)	M_n	M_w/M_n
1	1	8.4	16,873	1.46
2	2	13.7	18,429	1.51
3	3	19.9	16,328	1.52
4	4	23.3	19,458	1.59
5	5	18.5	21,136	1.64
6	6	14.6	18,357	1.71

the polymerization of MMA. At the optimum Al/ TEMPO ratios addition of a third component Co(acac)₃ (Catalyst **1b**) and VO (acac)₂ (Catalyst **1c**) showed higher catalytic activity and the yields of PMMA's has more than doubled when compared to the PPMA yield obtained with catalyst **1a**. Catalyst **1b** displayed highest catalytic activity for the polymerization of MMA. Addition Co(acac)₃ or VO (acac)₂ to the initiator system AlEt₂Br-TEMPO might have resulted in the stabilization of the initiating species which in turn increases the polymer yields. Catalytic activity seems to be dependent on the nature of the transition metal and homogeneity of the systems.

At this optimum Al/TEMPO ratio polymerization time was increased from 1 to 6 h with all the three initiator systems for MMA polymerization. Polymer yields, M_n and molecular weight distributions (M_w/M_n values) with increasing polymerization time are given in Tables I–III (Fig. 4).

Narrow molecular weight distribution polymers are those which possess a molecular weight distribution, as defined by M_w/M_n value of ~1.01 to 1.6. Wide polydisperisities of 2.4 or more are typical for free radical homopolymerization of styrene.[17] Stable free radical polymerization processes with proxyl nitroxides enable polydispersities of between 1.60 and about 2.2 for styrene polymerization.[18] However, Moad et al.[19] reported the use of TEMPO as an

inhibitor for free radical polymerization of styrene performed at low temperatures (below 100°C). Little is known as concerning the reaction of TEMPO with aluminum alkyls in the presence of either organic ligand such as bipyridine or transition metal complexes such as Co(acac)₃. Matyjaszewski and co-workers.[10] reported the initiator system A1(i-Bu)₃/ 2,2'-bipyridine/TEMPO for MMA polymerization at room temperature in which the M_w/M_n values are in the range 4.9–5.9 with multimodal distributions. However, at −78°C the initiator system has resulted in PMMA's of M_w/M_n = 1.1. At −78°C it was suggested that complex A1(i-Bu)₃, 2,2'-bipyridine is responsible for the MMA polymerization and TEMPO remains as an inert compound. At room temperature the reactions between the combinations of Al(i-Bu)₃ 2,2'-bipyridine /TEMPO has been speculated to follow the alkoxyamine mediated polymerization.

With the initiator combinations A1(i-Bu)₃/2,2'-bipyridine/TEMPO and Al(i-Bu)₃/2,2'-bipyridine/galvinoxyl for MMA polymerization M_n and M_w/M_n values were reported in the range 12,460–13,480 and

TABLE II
Polymerization of Methyl Methacrylate Initiator system: AlEt₂Br-TEMPO–Co(acac)₃

| S. No	Polymerization time(h)	Yield %	M_n	M_w/M_n
1	2	15.0	10,956	1.34
2	3	22.2	11,480	1.30
3	4	27.5	14,514	1.15
4	5	27.5	15,998	1.16
5	6	27.8	13,143	1.10
6	4 (Reaction Temp. 90°C)	27.2	12,049	1.09
7	4 (Reaction Temp. 55°C)	27.8	18,950	1.08
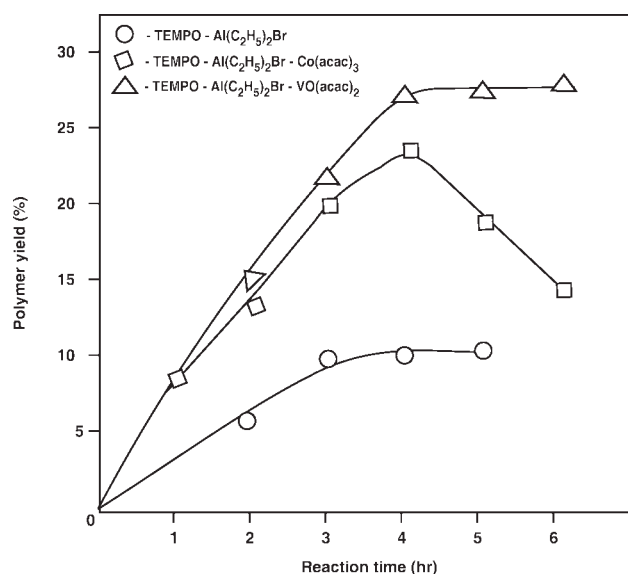
Figure 4 Effect of reaction time on polymer yield.
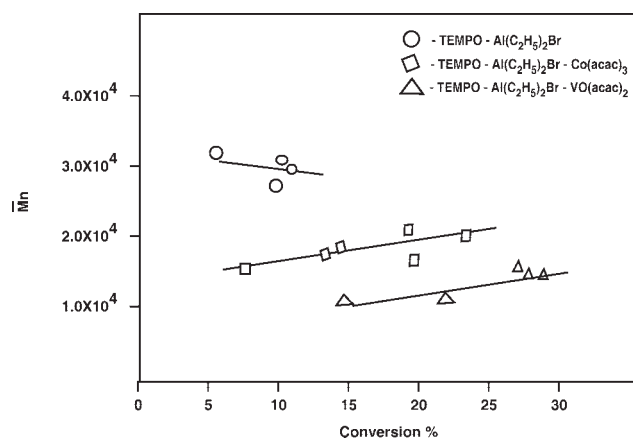
Figure 5 Dependence of M_n on the monomer conversion for the MMA polymerization.

1.24–1.37 respectively.[7] For MMA polymerization methyl aluminoxane was reported as a catalyst in which the polymers exhibit low to moderate molar mass with broad distributions.[20] Considering the above mentioned facts the molar mass and M_w/M_n values obtained with initiator system AlEt$_2$Br–TEMPO/Co(acac)$_3$ clearly indicates that this system is an effective one for MMA polymerization under mild conditions in benzene solvent. M_n against % conversion for the polymerization of MMA in the presence of the initiators **1a**, **1b**, and **1c** is shown in Figure 5. With the catalyst **1a** the M_n Vs % conversion decreases which is typical of a radical catalyst.
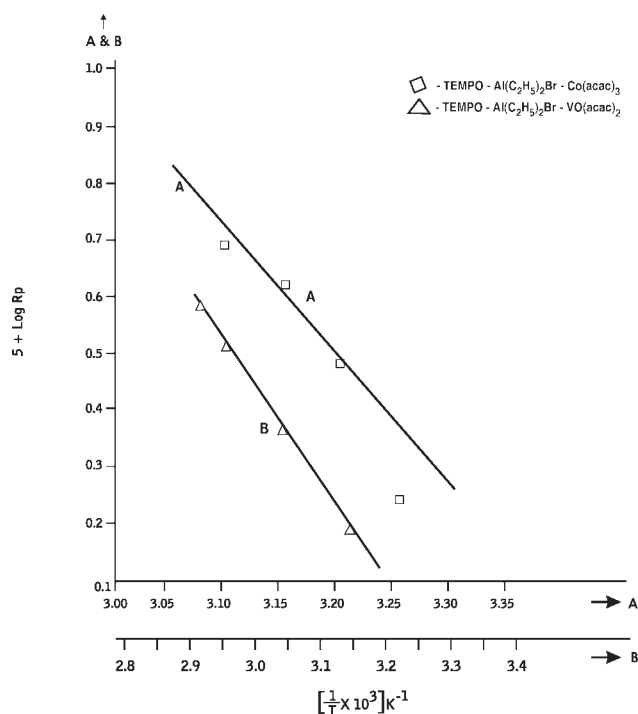

Figure 6 Arrhenius plots: (A) AlEt$_2$Br-TEMPO–Co(acac)$_3$ (B) AlEt$_2$Br-TEMPO/VO(acac)$_2$.

TABLE IV
Tacticity Value of PMMA Samples

S. No	Initiator systems/ polymerization condition	rr	mr	mm	Ref.
1	VO(acac)$_2$/ AlEt$_2$Br/TEMPO Al/TEMPO = 9.3 in benzene at 40°C	54. 9	38.2	6.7	Present study
2	Co(acac)$_3$/AlEt$_2$Br/ TEMPO Al/ TEMPO = 17.2 in benzene at 60°C	56.5	35.4	8.2	Present study
3	Co(acac)$_3$/AlEt$_2$Br/ TEMPO Al/ TEMPO = 12.9 in benzene at 60°C	54.4	39.8	5.8	Present study
4	Co(acac)$_3$/AlEt$_2$Br/ TEMPO Al/ TEMPO = 21.5 in benzene at 60°C	57.1	34.1	8.7	Present study
5	AlEt$_2$Br/TEMPO Al/TEMPO = 17.2 in benzene at 40°C	54.2	38.3	7.4	Present study
6	Al(i –Bu)$_3$/Bipy/ TEMPO at −78°C in toluene	79.0	20.0	1.0	10
7	Benzoyl peroxide in benzene at 40°C.	61.9	33.7	4.4	23

However, with **1b** and **1c** M_n Vs % conversion increases which resembles with that of controlled free-radical polymerization technique. The water and oxygen plays a vital role in aluminum alkyls – TEMPO initiated systems for vinyl polymerization. With small amount of oxygen and water, polymerization reaction were significantly accelerated when compared to the reactions with nearly complete exclusion of water and oxygen.[21] In the temperature range 40–60°C the initiator systems examined do not strictly confirm to the controlled radical polymerization. It is possible that the impurities such as oxygen and water might affect the course of the reaction and the process is considerably more complicated. However, with the initiator system AlEt$_2$Br–
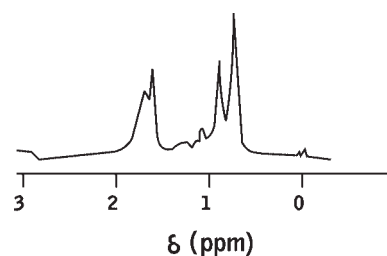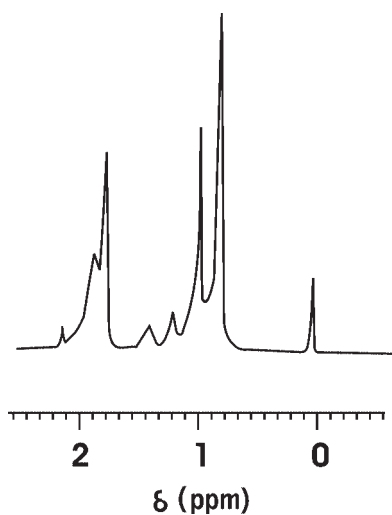

Figure 7 ^{1}H-NMR of polymer sample 1 (Table IV).

Figure 8 ^{1}H-NMR of polymer sample 2 (Table IV).

Figure 10 ^{1}H-NMR of polymer sample 4 (Table IV)

TEMPO–Co(acac)$_3$ it is possible to obtain PMMA's of molar mass in the range 10,000 to 18,000 with the polydispersity as narrow as 1.08. In the absence of a clear cut evidence of the mechanism of polymerization we have decided to examine the activation energy and the microstructure of PMMA's obtained from the initiator systems employed.

The E_a values calculated from the Arrhenius plots (Fig. 6) for the initiator systems AlEt$_2$Br – TEMPO–Co(acac)$_3$ and AlEt$_2$Br-TEMPO/VO(acac)$_2$ were found to be 9.1 and 6.9 k cal mol L^{-1} respectively. These values are in close proximity to these values reported for the catalyst system A1 (i-Bu)$_3$/2,2'-bipyridine/TEMPO.[2] The E_a values obtained for the present initiators is also found to be close to those values obtained from Ziegler – type catalyst for MMA polymerization involving a bound radical mechanism.[22]
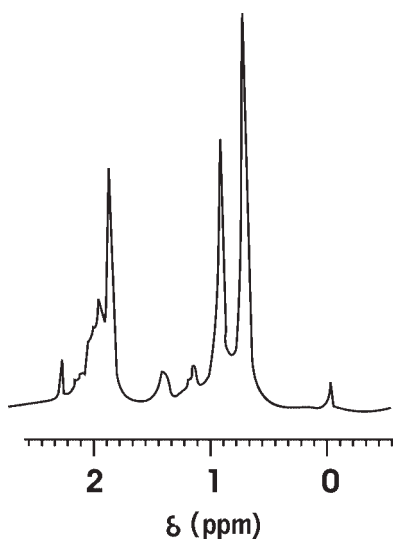
Further the micro structure of PMMA's obtained with the investigated initiator systems using ^{1}H-NMR spectra of the PMMA samples based on α-methyl resonance[24] are given in Table IV (Figs. 7–11). It is seen from Table IV that PMMA's obtained form the present initiator systems shows the rr, mr, and mm values that coincides to those values of PMMA's obtained from benzoyl peroxide. The observed triad distribution of PMMA's, which is similar to the typical stereo-structure of radical PMMA led us to suggest that the initiator systems **1a, 1b, 1c** shows radical characteristics. The rr, mr, and mm values of PMMA obtained from the initiator systems A1(i-Bu)$_3$/2,2'-bipyridine/TEMPO in toluene at −78°C shows higher rr values (Table IV entry 6) which is typical of an anionic process. The initiator system has resulted narrow polydispersity under relatively mild conditions for MMA polymerization.

CONCLUSION

TEMPO/AlEt$_2$Br along with Co(acac)$_3$ and VO(acac)$_2$ complexes display moderate catalytic activity
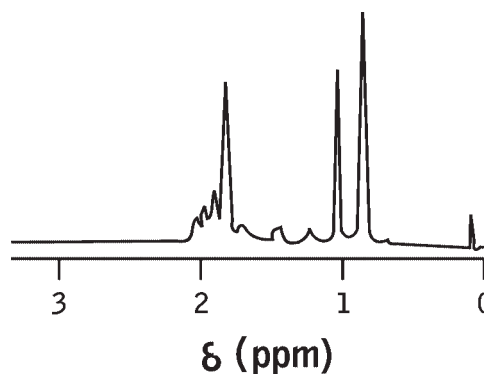

Figure 9 ^{1}H-NMR of polymer sample 3 (Table IV).

Figure 11 ^{1}H-NMR of polymer sample 5 (Table IV).

for the polymerization of MMA, producing PMMA's with narrow molecular weight distributions under mild conditions. The polymer yield, catalytic activities and molecular weight distributions can be controlled with initiator **1b**.The stereo-structure of the PMMA was not affected by the addition of Co and V complexes.

References

1. Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. J Am Chem Soc 1994, 116, 7943.
2. Mardare, D.; Matyjaszewski, K. Macromolecules 1994, 27, 645.
3. Mardare, D.; Matyjaszewski, K.; Coca, S. Macromol Rapid Commun 1993, 15, 37.
4. Entezami, A. A.; Abbasian, M. Iranian Polym J Iranian Polym J 2006, 15, 583.
5. Veregin, R.; Georges, M.; Hamer, G.; Kazmaier, P. Macromolecules 1993, 26, 2987.
6. Mayo, F. J Am Chem Soc 1968, 90, 1289.
7. Mardare, D.; Matyjaszewski, K. U.S. Pat. 5,312,871, 1994.
8. Florjanczyk, Z.; Sivdakiewicz, M. J Polym Sci Part A: Polym Chem 1986, 24, 1849.
9. Thevi, R. Ph.D. Thesis, Bharathiar University, 2007.
10. Gravel, C.; Jerome, R.; Greszta, D.; Matyjaszewski, K. Macromolecules 1993, 26, 2987.
11. Sun, Q.; Fan, Y.; Liao, S.; Liu, J.; Wan, F.; Xu, J. Polymer 2001, 42, 4087.
12. Furniss, B. S.; Hannford, A. J.; Smith, P. W. G.; Tatchell, A. R. Vogel's Text Book of Practical Organic Chemistry, 4th ed.; ELBS: Singapore, 1983; p 266.
13. Bryant, B. E.; Femelius, N. C. Inorganic Synthesis, Mc Graw-Hill: New York, 1975; Vol. 5, p 30.
14. Bryant, B. E.; Femelius, W. C.; Busch, D. H.; Stoufer, R. C.; Startton, W. Inorganic Synthesis; Mc Graw-Hill Book Co., Inc.: New York, 1957, Vol. 5, p 114.
15. Ravikumar, L.; Ramarajan, K. Eur Polym J 1998, 34, 509.
16. Selbin, J.; Holms, L. H.; Mcglynn, S. P. J Inorg Nucl Chem 1963, 25, 1359.
17. Odian, G. Principles of Polymerization; 2nd ed.; Wiley: New York, 1981; 280.
18. ACS Symposium series 854. Advances in Controlled/Living Radical Polymerization, Chapter 32, p 452.
19. Moad, G.; Rizzardo, E.; Soloman, D. H. Polym Bull 1982, 6, 589.
20. Po, R.; Fiocca, L.; Cardi, N.; Simone, F.; Cardaci, M. A.; Spera, S.; Salvalaggio, M. Polym Bull 2006, 56, 101.
21. White, D.; Matyjaszewski, K. J Macromol Sci Pure Appl Chem 1997, 34, 221.
22. Deshpande, A. B.; Kale, S. M.; Kapur, S. L. J Polym Sci 1973, 11, 1307.
23. Ravikumar, L.; Ramarajan, K.; Venkatarao, K. J Polym Sci: Part A Polym Chem 1995, 33, 2113.
24. Bovey, F. A.; Tiers, G. V. D. J Polym Sci 1960, 44, 173.