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Vinyl Polymerization Promoted by VO(acac)₂ - TEMPO Complexes

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ABSTRACT

Vanadium (IV) oxyacetylacetonate or vanadium (IV) oxyacetylacetonate-2,2,6,6-tetramethylpiperidiny-1-oxy (TEMPO) complexes activated with diethyl aluminium bromide as catalysts were employed for the polymerization of methyl methacrylate in benzene at 40°C. The catalysts were compared based on various parameters such as Al/V ratio, reaction time, catalyst, monomer concentration and temperature on the rate of polymerization and yield. The rate of polymerization increased linearly with increasing monomer concentration with first order dependence. Polymer yield was maximum when the Al/V ratios were 2.2 and 1.4 and the activation energies were 8.9 and 9.1 kcal.mol⁻¹, respectively for the catalysts VO(acac)₂ / AlEt₂Br and VO(acac)₂ / AlEt₂Br / TEMPO. Inclusion of TEMPO to the catalyst system VO(acac)₂ / AlEt₂Br shows increased catalytic activity. The catalyst systems have resulted in syndiotactic rich PMMA's having M_n values in the range of 12000–23000. PMMA's of narrow molecular weight distributions in the range of 1.2-1.7 could be obtained under mild conditions in benzene solvent at 40°C.

Key Words:

vanadium (IV) oxyacetylacetonate;
MMA polymerization;
diethyl aluminium bromide;
TEMPO.

INTRODUCTION

A number of polymerizations catalyzed with Ziegler-Natta catalyst based on transition metals, have been reported in the literature. Most of the catalyst systems studied consisted of TiCl₄ or TiCl₃ along with AlEt₃ or AlEt₂Cl or Al(i-Bu)₃. After almost 50 years since the discovery of Ziegler-Natta cata-

lyst, it is still a target of continuous research in both academic and industrial sectors. The vast majority of outstanding catalysts, for instance those developed by Kaminski et al. [1], Wang et al. [2], and Tempel et al. [3], were developed as a result of experimental work. Therefore the search for new

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catalytic systems is based mainly on empirical rules. Vanadium based Ziegler-Natta catalyst has a promising potential for olefin polymerization. A good review recently published explains the characteristic of the vanadium centre in trans-metallation reactions [4]. A recent Density Functional Theory (DFT) study on Ziegler-Natta catalyst based on vanadium halides suggests that complexation and insertion energies are strongly influenced by the charge on the transition metal atom, and to some extent, by the electronegativity of the halogen atom [5].

The catalyst systems containing acetyl acetonates of various transition metals with aluminium alkyls have been used for the polymerization of several monomers. Although vanadium follows titanium in the periodic table, it has not been used as widely as titanium [6]. Studies involving polar vinyl monomers catalyzed by Ziegler-Natta catalyst based on vanadium are limited [7]. For polar vinyl monomers such as MMA, organo aluminium amides [8], organo-metallic tricomponent catalyst system such as Al (i-Bu)₃ / 2,2' bipyridine / TEMPO [9] have been reported. We have recently reported the tricomponent system AlEt₂Br / Fe(acac)₃ / TEMPO [10] for MMA polymerization. Highly crystalline polymers prepared with heterogeneous Ziegler-Natta catalyst, quite often precipitate out of the solution during polymerization. This impairs the kinetic measurements. For this reason we have chosen MMA as the monomer which is a liquid remaining soluble in benzene solvent during polymerization. While chemistry and catalytic properties of titanium complexes have been extensively studied and commercialized, much less is known about the catalytic behaviour of vanadium complexes. Kotov et al. [11] reported half-sandwich complexes of vanadium (III) with aluminium alkyls for ethylene polymerization. Cyclopentadienyl and acetyl acetonate complexes of vanadium have been reported for olefinic and diene monomers such as propylene and butadiene [12,13]. Recently Bhattacharjee et al. [14] reported the vanadium cyclopentadienyl complexes for MMA and styrene polymerization achieving high molecular weight polymers.

Hence in the absence of detailed studies on the effect of vanadium catalysts on the polymerization of polar vinyl monomers such as MMA, the present study deals with the VO(acac)₂ / AlEt₂Br and

VO(acac)₂ / AlEt₂Br / TEMPO catalyst systems for the polymerization of MMA. The investigated catalyst systems are active for MMA polymerization under mild condition in benzene yielding syndiotactic rich polymers.

EXPERIMENTAL

Chemicals

Benzene was freed from thiophene [15] by repeated stirring with conc. H₂SO₄. 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.

Acetylacetone [L.R E Mark, India] was distilled [bp139°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 Complex

Vanadium (IV) oxyacetylacetonate was prepared according to the reported procedure [16]. The crude product was recrystallized from chloroform.

Diethyl aluminium bromide was prepared according to our earlier report [17], and twice distilled under reduced pressure before the preparation of stock solution.

Polymerization

Polymerization reactions were carried out in a specially designed 50 mL Erlenmeyer 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.

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 AlEt₂Br (stock solution in benzene) was finally added and after the addition of reagents the flask was stoppered and immersed in a thermostat at 40±10°C.

After specified reaction time, the polymerization was stoppered and excess acidified ethanol was added and the polymer was precipitated. The catalyst was dissolved in the reaction mixture and only the polymer was precipitated. The precipitated polymer was collected on a sintered crucible, washed with pure methanol and dried in a vacuum to a constant weight. The kinetics was studied through standard gravimetric techniques.

Characterization

¹H NMR spectra of the polymers were recorded in CDCl₃ solvent employing a Varian Em XLAA 300 instrument and by using TMS as internal standard. The chemical shifts were expressed in ppm. A cutting-weighting method was used for calculating the intensity of the syndiotactic, heterotactic and isotactic peaks based on α-methyl resonance of PMMA.

Average molecular weights were measured by size-exclusion chromatography (SEC) with a HP1100 apparatus equipped with a set of four columns (10⁵, 10⁴, 10³, and 10² Å: polymer standards service) with chloroform as an eluent. Polystyrene samples were used as standards to construct the calibration curve.

RESULTS AND DISCUSSION

Addition of AlEt₂Br to VO(acac)₂ has resulted in brown precipitate formation and the colour has not changed during polymerization, thus confirming the heterogeneous nature of the catalyst system. Individual components such as VO(acac)₂, TEMPO and AlEt₂Br when examined at 40°C in benzene were found to be completely inert for the MMA polymerization. The initiator system AlEt₂Br-TEMPO was found to initiate a very fast and exothermic polymerization of styrene [18]. With MMA monomer, such an

exothermic reaction was not noticed but it showed low catalytic activity at 40°C. Hence it was decided to study the effect of addition of TEMPO to the catalyst system VO(acac)₂-AlEt₂Br for MMA polymerization.

The effects of various parameters such as Al/V ratio, reaction time, [monomer], [VO(acac)₂] and temperature were studied. By keeping [VO(acac)₂] at 3.7 × 10⁻⁴ mol, [AlEt₂Br] was varied from 4.0 × 10⁻⁴ mol to 10.45 × 10⁻⁴ mol so as to have an Al/V ratio of 1.08 to 2.80. It has been observed by many authors that the activity of the catalyst depends on the ratio between the catalyst and cocatalyst. In the present study, with the catalyst VO(acac)₂-AlEt₂Br, the percentage yield of PMMA increased initially with increasing the Al/V ratio, reached the maximum value at an Al/V of 2.2 and then decreased. Similarly in the case of catalyst system VO(acac)₂-AlEt₂Br-TEMPO, the Al/V ratio was varied from 0.472 to 3.795 and the maximum conversions were observed at Al/V ratio of 1.4 (Figure 1).

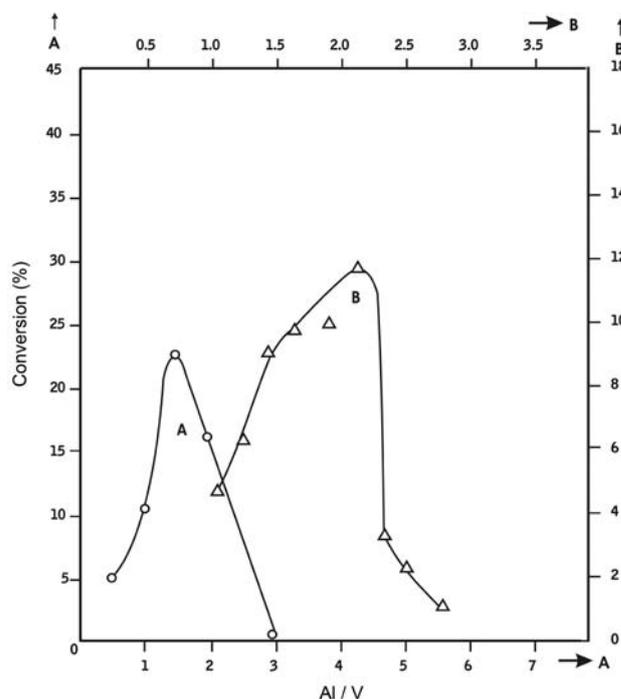


Figure 1. Effect of Al/V ratio on the percentage polymerization of MMA. A: VO(acac)₂-AlEt₂Br-TEMPO, [MMA] = 1.8697 mol.L⁻¹, [TEMPO] = 0.005 mol.L⁻¹, [VO(acac)₂] = 5.656 × 10⁻⁴ mol, reaction time = 240 min, temperature = 40°C. B: VO(acac)₂-AlEt₂Br, [MMA] = 1.8697 mol.L⁻¹, [VO(acac)₂] = 3.7 × 10⁻⁴ mol, reaction time = 240 min, temperature = 40°C.

The decrease in the activity of the catalysts at higher ratio of Al/V is probably due to over reduction of vanadium from V³⁺ → V²⁺. It was established that with organometallic system AlEt₂Br-VO(acac)₂, the maximum catalytic activity was observed when Al/V = 2 for acetylene polymerization [19]. For the catalyst system of VO(acac)₂-AlEt₂Cl in polymerization of ethylene, it was reported that vanadium forms an active species both as V(III) and V(II). However, vanadium (III) based catalyst was reported to be more active towards polymerization reactions [20,21]. Lehr et al. [22] with the catalyst system VCl₄-AlEt₂Cl, proved with ESR measurements that VCl₄ is reduced by AlEt₂Cl even at low temperatures and the active species was an alkylvanadium (III) complex. The stability of such catalyst system depends on the ratio of Al/M (M = transition metal). In the present case, variation of the Al/V ratio suggests that vanadium forms an active species as V(III) under optimum conditions. At higher Al/V ratios, the reduction in the catalytic activity is probably due to the formation of less active V(II) species.

The polymerization time was varied from 1-6 h by keeping the Al/V ratio at 2.1 and 1.4 for the catalyst system VO(acac)₂ / AlEt₂Br and VO(acac)₂ / AlEt₂Br / TEMPO, respectively. Figure 2 shows the effect of reaction time on the percentage conversion of polymer. The percentage conversion increased slowly up to 4 h, reached a maximum and then decreased with

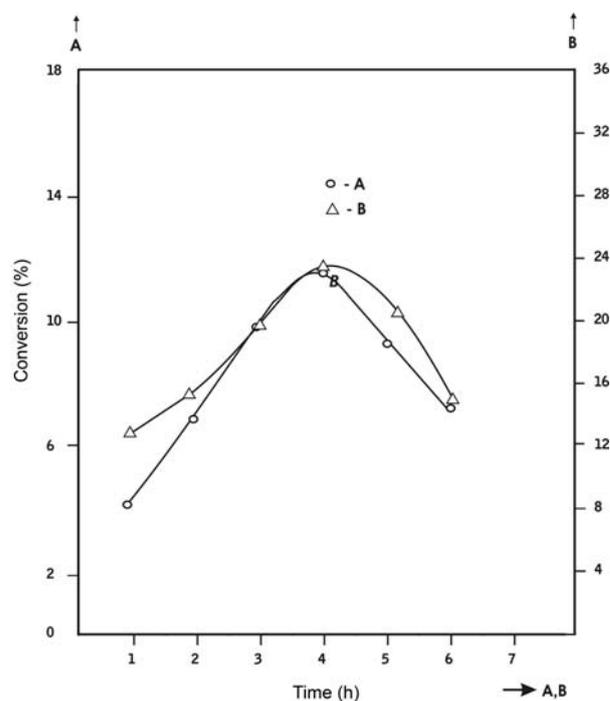


Figure 2. Effect of reaction time on the percentage polymerization of MMA. A: VO(acac)₂-AlEt₂Br-TEMPO. [MMA] = 1.8697 mol.L⁻¹, [TEMPO] = 0.005 mol.L⁻¹, Al/V = 1.4, temperature = 40°C; B: VO(acac)₂-AlEt₂Br. [MMA] = 1.8697 mol.L⁻¹, Al/V = 2.1, reaction time = 240 min, temperature = 40°C.

both the catalyst systems. However, with the addition of TEMPO to the catalyst AlEt₂Br/VO(acac)₂

Table 1. Effect of reaction time on the molecular weight and PDI.

Reaction time (h)	Catalyst ¹ AlEt ₂ Br-VO(acac) ₂			Catalyst ² AlEt ₂ Br-VO(acac) ₂ -TEMPO		
	Sample number	M _n	PDI	Sample number	M _n	PDI
1	3	17318	1.5	8	16873	1.5
2	4	16868	1.6	9	18429	1.5
3	5	12518	1.5	10	16328	1.5
4	6	17635	1.6	11	19458	1.6
5	7	15580	1.6	12	21136	1.6
6	-	23918	1.7	13	18357	1.7
4	1*	15863	1.2	-	-	-
4	2#	21427	1.4	-	-	-

1. Al/V = 2.2, temperature = 40°C; 2. Al/V = 1.4, temperature = 40°C; *. Al/V = 1.08, temperature = 40°C; #. Al/V = 1.52, temperature = 40°C.

percentage yield of polymer was nearly doubled. The decrease in the polymer yield after reaching a maximum value may be attributed to the decrease in monomer concentration at longer polymerization time and also due to the deactivation of the active sites presumably due to the detachment of ligands at longer periods of polymerization. Vanadium complexes in combination with methylalumoxane as organovanadium complexes is reported to be deactivated during polymerization process [11] due to the dissociation of ligands attached to vanadium. For MMA polymerization such a decrease in catalytic activity over longer periods of time with Cr and V based catalysts have recently been reported [14].

Effect of polymerization time on M_n and molecular weight distribution for both the catalyst systems are given in Table 1. The GPC curves of poly(methyl methacrylate)s are shown in Figures 3-5 and all the curves are monomodal. Narrow molecular weight distribution polymers are those which possess a molecular weight distribution, as defined by M_w/M_n value of approximately 1.01-1.6 which are possible through living free radical polymerization [23]. Bhattacharjee et al. [14] investigated the vanadium cyclopentadienyl complexes for MMA and styrene polymerization and reported the polydispersity values in the range of 1.2-1.9. With Cr complexes, Alipour

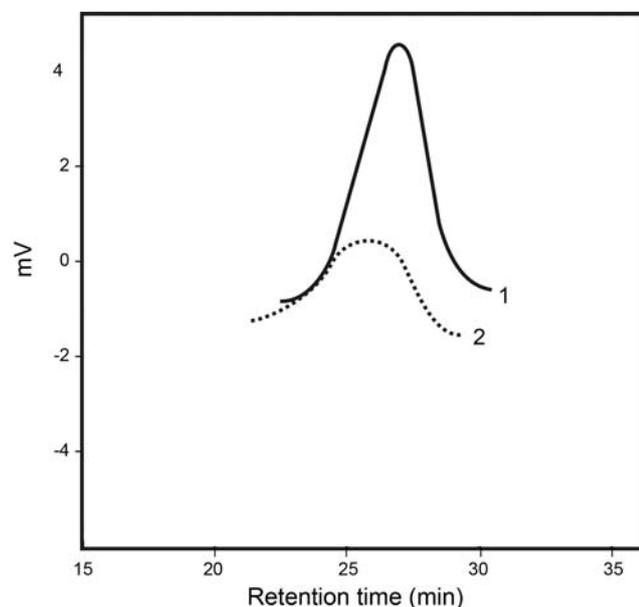


Figure 3. GPC curves of poly(methyl methacrylate)s (samples 1 & 2 in Table 1).

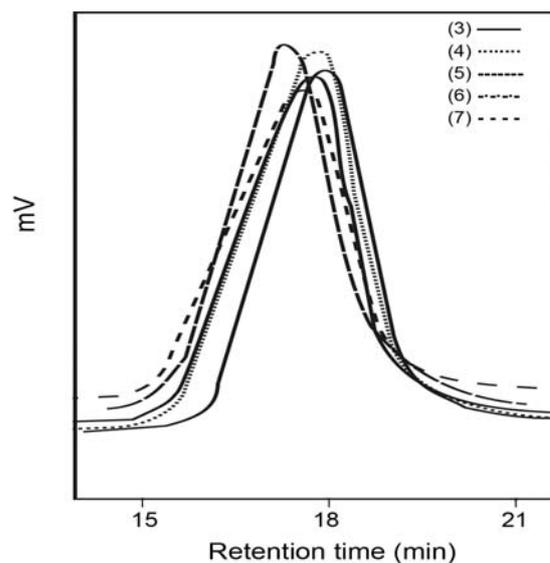


Figure 4. GPC curves of poly(methyl methacrylate)s (samples 3-7 in Table 1).

et al. [24] reported the M_w/M_n values in the range of 1.26-1.4 for vinyl monomers. With ruthenium complexes catalyzed polymerization of MMA the M_w/M_n values were found to be in the range of 1.10-1.7 [25]. With the catalyst system involving TEMPO such as Al (*i*-Bu)₃ / 2,2' bipyridine / TEMPO [9] at room temperature the M_w/M_n values were in the range of 1.45-2.17 in toluene solvent. It is observed from Table 1 that the M_w/M_n values are in the range of 1.5-1.7

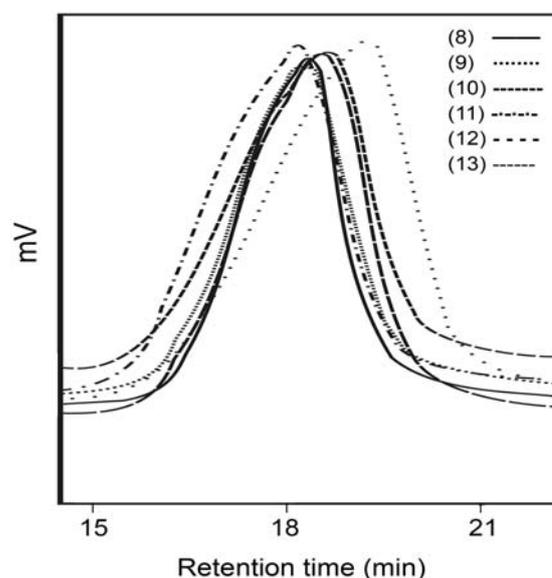
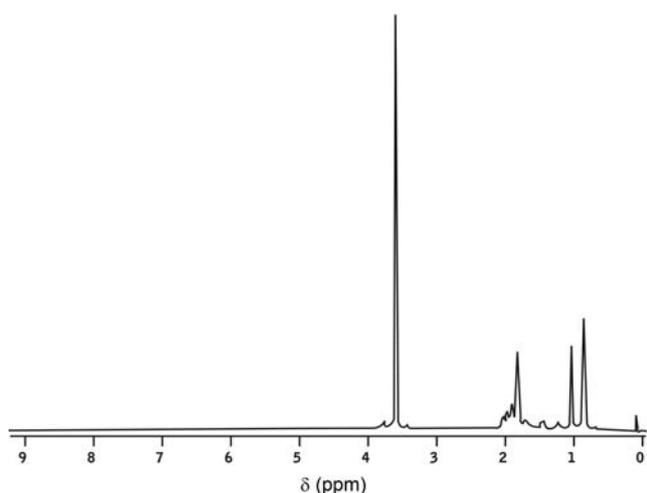


Figure 5. GPC curves of poly(methyl methacrylate)s (samples 8-13 in Table 1).

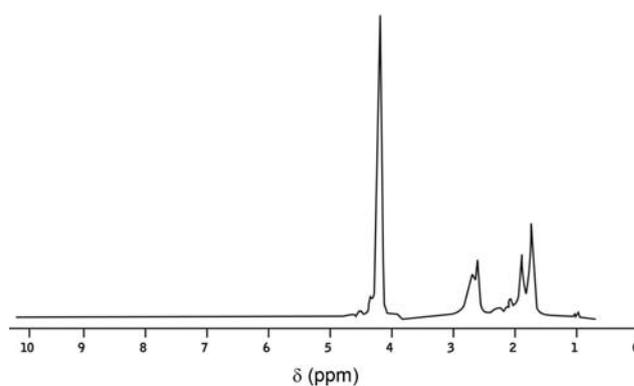
Table 2. NMR Analysis of different PMMA samples.

Sample no	Polymerization conditions	Content of different units			Reference
		rr	mr	mm	
1	AlEt ₂ Br-VO(acac) ₂ Al/V = 2.2	54.5	39.6	5.9	Present study
2	AlEt ₂ Br-VO(acac) ₂ -TEMPO Al/V = 1.4	54.9	38.2	6.7	Present study
3	AlEt ₂ Br-M _n (acac) ₃ Al/M _n = 2	63.1	31.2	5.7	Ravikumar et al.[17]
4	Al(i-C ₄ H ₉) ₃ -Cr(acac) ₃ Al/Cr = 12	63.0	31.0	6.0	Deshpande et al.[27]
5	ZnEt ₂ -Co(acac) ₃ Zn/Co = 2	61.0	35.0	4.0	Ravikumar et al.[28]
6	Al(i-Bu) ₃ /2,2' bipyridine/ TEMPO in toluene at -78°C	80.0	20.0	0.0	Matyjaszewski et al.[9]

suggesting that both the catalyst systems under study yield a narrow molecular weight distributed PMMAs. It is also of interest to note that with the catalyst system VO(acac)₂/AlEt₂Br, the M_w/M_n values are around 1.5-1.7 (at an Al/V ratio of 2.2), reaching a minimum of 1.2 at an Al/V ratio of 1.08. However, work is under progress to reach a better understanding on the effect of Al/V ratio on the PDI values of polymers.

**Figure 6.** ¹H NMR spectrum of PMMA (sample 1) (Table 2).

In recent times, for MMA polymerization the anionic coordination mechanism and free radical mechanisms are more clearly distinguished by ¹H NMR triad tacticity analysis [26-28] of the formed PMMAs. More detailed stereochemical information can be obtained from the α -methyl resonances of PMMAs. The mm, mr, and rr values from α -methyl resonances appear at δ values of 0.83, 1.0, and 1.2 ppm, respectively. The percentage of mm, mr, and rr is calculated from the measured relative intensities. The tacticity values of two PMMA samples (samples

**Figure 7.** ¹H NMR spectrum of PMMA (sample 2) (Table 2).

no 1 and 2 in Table 2) obtained under optimum conditions are shown in Figures 6 and 7. The rr, mm, and mr values coincide with typical free radically initiated PMMAs and also those of the PMMAs obtained from Ziegler-type catalysts having pronounced free radical characteristics. The catalyst system Al (i-Bu)₃ / 2,2' bipyridine / TEMPO at -78°C shows higher rr values wherein an anionic mechanism was suggested (Table 2, sample 6). However, at room temperature with the same catalyst system a radical mechanism was suggested. The observed triad distribution of PMMA, which is similar to the typical stereo-structure of PMMA obtained with Ziegler-type catalysts having pronounced free radical characteristics, allowed us to believe that, in the present case a bound free radical with the vanadium active site is in operation for MMA polymerization.

The order of a reaction with respect to monomer concentration was found to be 1 for both catalyst systems (Figure 8) $R_p V_s [M]$ is a straight-line plot passing through the origin. The order with respect to the catalyst concentration was found to be one for the

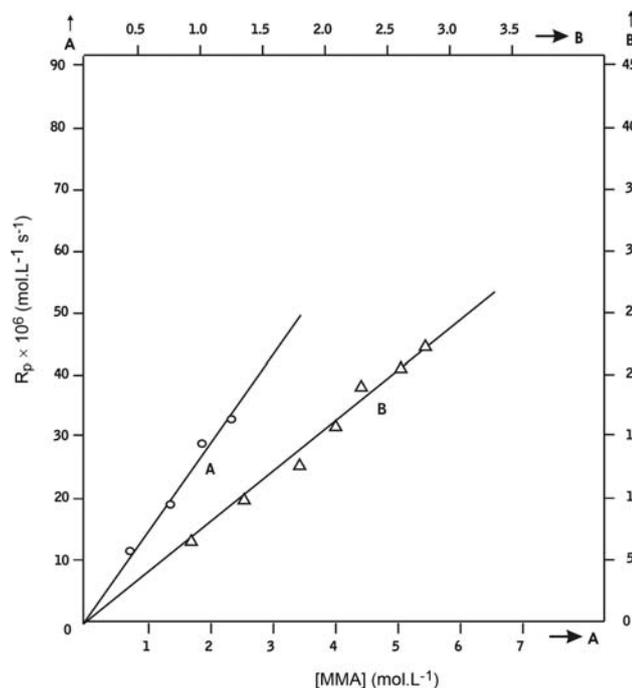


Figure 8. Effect of monomer concentration on rate of polymerization. A: VO(acac)₂-AlEt₂Br-TEMPO. [TEMPO] = 0.005 mol.L⁻¹, reaction time = 240 min, Al/V = 1.4, temperature = 40°C. B: VO(acac)₂-AlEt₂Br. Al/V = 2.1, reaction time = 240 min, temperature = 40°C.

catalyst VO(acac)₂ / AlEt₂Br and half for the catalyst VO(acac)₂ / AlEt₂Br / TEMPO system, respectively (Figure 9). The catalyst system containing acetylacetonates of various transition metals with aluminium alkyls has been reported to have a first order dependence on monomer concentration of either a first or a half dependence on catalyst concentration for vinyl polymerization [29-32]. A majority of these catalyst systems have been reported to proceed through radical mechanisms.

The effect of temperature on the rate of polymerization was studied in the temperature range of 35-50°C. The concentrations of the catalyst and monomer were kept constant during temperature variation. From the slope of the Arrhenius plot (Figure 10), the overall activation energies of polymerization were calculated and were found to be 8.9 kcal.mol⁻¹ and 9.1 kcal.mol⁻¹ for the catalyst systems VO(acac)₂ / AlEt₂Br and VO(acac)₂ / AlEt₂Br / TEMPO, respectively. These values are closer to the values reported by other authors [28, 30-32] for the polymerization of vinyl monomers with Ziegler-type catalysts show

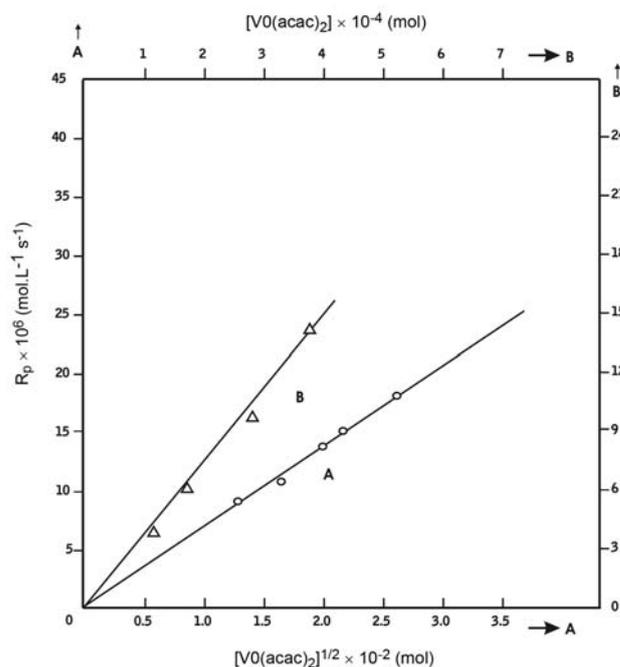


Figure 9. Effect of [VO(acac)₂] on rate of polymerization of MMA. A: VO(acac)₂-AlEt₂Br-TEMPO. [MMA] = 1.8697 mol.L⁻¹, [TEMPO] = 0.005 mol.L⁻¹, reaction time = 240 min, temperature = 40°C. B: VO(acac)₂-AlEt₂Br. [MMA] = 1.8697 mol.L⁻¹, reaction time = 240 min, temperature = 40°C.

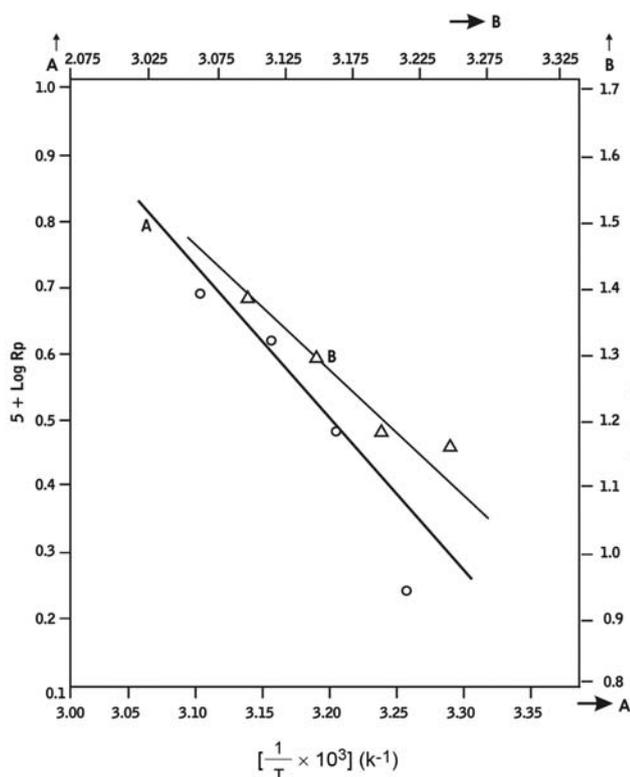


Figure 10. Arrhenius plots for the polymerization of MMA with the catalyst systems VO(acac)₂-AlEt₂Br-TEMPO (A), VO(acac)₂-AlEt₂Br (B).

radical mechanisms. TEMPO is an efficient free radical scavenger for the polymerization of styrene below 100°C [33]. However, at higher temperatures (>100°C), it acts as a mediator in nitroxide mediated polymerizations. TEMPO as a mediator in nitroxide-mediated polymerizations had limitations such as its inability to polymerize monomers other than styrenes and polymerization reactions require higher temperatures (>100°C) to obtain a sufficient concentration of propagating radicals for monomer insertion [34,35]. Arsalani et al. [36] recently reported the use of TEMPO-ended polystyrene as a macro initiator for the copolymerization of styrene and *N*-vinyl pyrrolidone. M_n and PDI values of the copolymers obtained at 125°C were in the range 11842 and 1.59, respectively. However, in the present case the catalyst system VO(acac)₂ / AlEt₂Br / TEMPO is active for polar vinyl monomer MMA in benzene under mild conditions. Inclusion of TEMPO to the catalyst VO(acac)₂ / AlEt₂Br under similar conditions, the polymer yield has increased by two fold but without any significant

change in the M_w/M_n values.

CONCLUSION

Vanadium (IV) oxyacetylacetonate complex activated with diethyl aluminium bromide displays moderate catalytic activity for MMA polymerization. Addition of TEMPO to this catalyst has resulted in increased polymer yield without any change in the tacticity of the polymer. The reported catalysts systems produce syndiotactic rich PMMAs with narrow molecular weight distributions in the range of 1.2-1.7 under mild conditions.

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