Metal-catalysed organic transformations in water: From bromination to polymerisation

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Abstract.   Reaction of α,β-unsaturated aromatic carboxylic acids with KBr and H_2O_2 in the presence of $Na_2MoO_4 \cdot 2H_2O$ in aqueous medium affords β-bromo alkenes in high yields. Metallocene dichlorides, Cp_2MCl_2 (M = Ti, Zr, or V) catalyse polymerisation of olefins in aqueous medium to afford high molecular weight polymers with low molecular weight distribution.

Keywords.   Aqueous medium; bromination; polymerisation; titanium; zirconium; vanadium.

1. Introduction

Water as a reaction medium has attracted a great deal of attention in recent years. This is because water as a solvent has high heat capacity, high polarity, and is not-miscible with most organic solvents. These properties make water a unique solvent. Due to increasing environmental concerns aqueous phase reactions are becoming more and more popular.[1] In recent years, a large number of reports have appeared on metal catalysed polymerisation in aqueous medium.[2] These reports involve mainly late transition metal catalysts.[2] One of the major problems in the use of late transition metal catalysts is the ease of β-hydride elimination, which typically competes with chain growth and affords low molecular weight polymers.[2a] The use of early transition metal catalysts is expected to afford high molecular weight polymers. However, owing to their extreme moisture sensitivity, the use of early transition metal organometallic compounds as polymerisation catalysts in aqueous medium still poses a challenge.

As a part of our exploration of transition metal catalysed aqueous medium organic transformations, we have been exploring transition metal-catalysed electrophilic bromination of organic substrates[3] and polymerisation of olefins in aqueous medium.[4] In this paper we present the results of our studies on early transition metal catalysed aqueous polymerisations of olefins and electrophilic bromination of organic substrates.

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2. Results and discussion

2.1 *Sodium molybdate catalysed aqueous Hunsdiecker reaction*

The classical Hunsdiecker reaction and its later modifications are efficient in the syntheses of organic halides.[5] However, these reactions have major limitations, such as toxicity and hazards involving the use of elemental bromine, salts of Hg(II), Tl(I), Pb(IV), Ag(I). Apart from this, very poor yields of the products are obtained in the cases of α,β-unsaturated aromatic carboxylic acids. Recently, some of these difficulties have been overcome by the use of lithium acetate as the catalyst and N-bromosuccinimide as the bromine source, the reaction medium being aqueous acetonitrile.[6] However, low yields were obtained in the cases of α,β-unsaturated aromatic carboxylic acids bearing electron-withdrawing groups in the aromatic ring.

Transition metal peroxo compounds have been shown to be efficient oxidizing agents for various organic substrates.[7] Some marine organismsuse vanadium-dependent enzyme, bromoperoxi-dase, for the bromination of organic compounds using inorganic bromides and hydrogen peroxide.[8] We have been investigating bromination of organic compounds using vanadium (V) or molybdenum(VI), potassium bromide, and hydrogen peroxide in aqueous medium.[3] It was observed that transition metal peroxo complexes can oxidize inorganic bromide and produce Br_3^- species which is in equilibrium with HOBr and Br_2. We thought that this biomimetic system can be utilized as an alternative route to the Hunsdiecker reaction.

Thus, when α,β-unsaturated aromatic carboxylic acid is stirred with KBr and Na$_2$MoO$_4$·2H$_2$O in water and H$_2$O$_2$ is added dropwise, rapid reaction takes place and after 20 min of stirring, the corresponding β-bromo-styrene is obtained in good yield (scheme 1).[9]

It has been shown earlier that MoO$_4^{2-}$ forms a number of peroxo species in solution in the presence of H$_2$O$_2$. The pH of the solution of Na$_2$MoO$_4$ (0·001 mol) in H$_2$O$_2$ (15 cm^3) is basic in nature, pH being around 8. We have noted that, below this pH, the yield of the product is not very good. Thus it is clear that for the reaction a basic medium is required. The ^{95}Mo NMR spectra of a solution of Na$_2$MoO$_4$ (0·001 M) in H$_2$O$_2$ (15 cm^3) shows a major signal at -336 ppm and a relatively low intensity signal at -509 ppm. These are due to the formation of [MoO(O$_2$)$_3$]$^{2-}$ and [Mo(O$_2$)$_4$]$^{2-}$ species, respectively.[10] Upon addition of Br$^-$ both the signals at -509 and -336 ppm disappear and two signals appear at -222 and -37 ppm. The signal at -222 ppm can be assigned to [MoO(O$_2$)$_2$]$^{2-}$.[10] The signal at -37 ppm may be assigned to a molybdate species coordinated to bromide. The slight shift in the observed ^{95}Mo NMR spectra from those of reported ones[10] may be due to the effect of pH as well as extent of hydration.

A blank reaction, that is a similar reaction without adding Na$_2$MoO$_4$, did not afford the brominated products. Thus, it is clear that, bromide is oxidized by the peroxomolybdate species formed in solution.

The electronic spectrum of a solution (10^{-3} M) of Na$_2$MoO$_4$ in H$_2$O$_2$ (2×10^{-2} M) shows bands at 445 ($\varepsilon = 162$) and at 293 nm ($\varepsilon = 1620$). These are due to the tetraperoxo and triperoxomolybdate species.[10] When KBr is added to this solution an absorbance increase is observed in the region 700 to 290 nm. However, no new band appears. The molar extinction coefficient of the 445 nm band increases to 320 and the band at 293 nm shifts to 298 nm with increase in the molar extinction coefficient ($\varepsilon = 1833$). It may be noted that the oxidized bromide species, Br$_2$, Br$_3^-$ and OBr$^-$, absorb in the region, 450 to 300 nm. It is clear that the peroxomolybdate generated from the
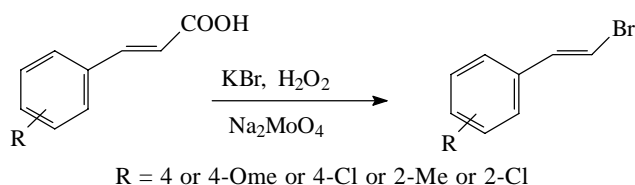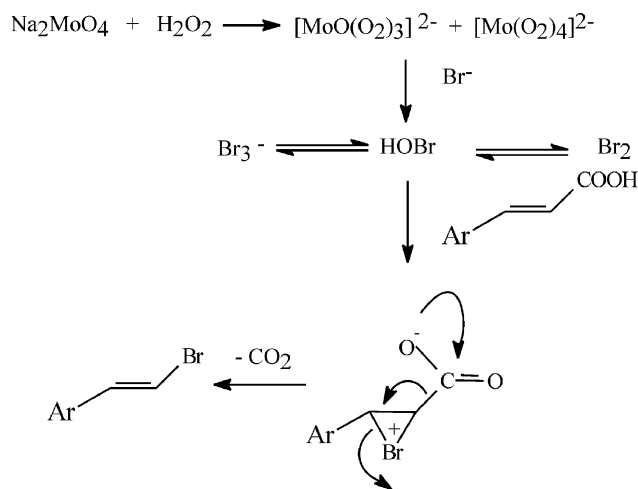
reaction of H$_2$O$_2$ and MoO$_4^{2-}$ reacts with Br$^-$ to produce an equilibrium mixture of Br$_2$, Br$_3^-$, and OBr$^-$, which then react with the unsaturated acid to give bromo-alkene (scheme 2).

2.2 *Cp$_2$TiCl$_2$ and Cp$_2$ZrCl$_2$ catalysed homo-polymerisation of styrene and methylmethacrylate*

Aqueous catalytic polymerisation seems like a contradiction at first sight because of the high moisture sensitivity of the Ziegler–Natta catalysts. However, there is a strong commercial and environmental driving force to develop aqueous routes to polyolefin with the desired property.[11] Free radical initiated emulsion polymerisation of olefins is well known. A large numbers of reports have appeared on the catalytic systems capable of polymerisation in aqueous medium involving mainly late transition metal catalysts.[2] A recent report deals with syndiospecific polymerisation of styrene in water–toluene biphasic medium using [(C$_5$Me$_5$)Ti(OMe)$_3$] catalyst along with a borate and an alkylaluminium compound as activators and cationic or neutral surfactant as emulsifier.[2e] Development of an early transition metal based catalyst system for polymerisation of olefin in aqueous medium without using any organic solvent or any activator such as MAO or other alkyl aluminum compounds or borate still remains a challenge.

It has already been shown that, in the homogeneous Ziegler–Natta catalyst, [Cp$_2$MMe]$^+$ (M = Ti or Zr) is responsible for stereospecific polymerisation.[12] It is also well known that, Cp$_2$MCl$_2$ when dissolved in water, gives [Cp$_2$M(H$_2$O)Cl]$^+$, [Cp$_2$M(H$_2$O)$_2$]$^{2+}$,

$$Na_2MoO_4 + H_2O_2 \longrightarrow [MoO(O_2)_3]^{2-} + [Mo(O_2)_4]^{2-}$$

Scheme 2.

R = 4 or 4-Ome or 4-Cl or 2-Me or 2-Cl

Scheme 1.

and $[Cp_2M(OH)]^+$ in solution as major products.[13] Our general synthetic approach is *in situ* formation of $[Cp_2M(OH)]^+$ from aqueous solution of Cp_2MCl_2 and stabilization of this cation by large, soft and non-coordinating anion, *n*-dodecyl sulphate, and utilization of $[Cp_2Ti(OH)]^+$ as polymerisation catalyst. Sodium *n*-dodecyl sulphate (SDS) is expected to play the dual role of stabilizer of the cation as well as an emulsifying agent for the monomer.

Accordingly, homo-polymerisation of styrene[4a,4c] and methylmethacrylate (MMA)[4b,4c] was carried out in aqueous medium in the presence of SDS and one mole percent of catalysts, Cp_2MCl_2 (M = Ti[4a,4b] or Zr[4c]). The details of the results are given in tables 1 and 2. The average molecular weights of the polystyrene (PS) and poly(methylmethacrylate) (PMMA), measured by GPC (against standard polystyrene.) lies in the range 690,000 to 540,000 and 739,000 to 514,000, respectively. On an average M_w/M_n ratio is found to be 1·7 and 1·6, respectively, which is fairly narrow and is indicative of a single site catalyst.[14] The molecular weights are much higher then the ordinary commercially available PS or PMMA. The homo-polymers obtained were characterized by dif-ferential scanning calorimetry (DSC), ^1H, and ^{13}C NMR, and IR spectroscopy. The DSC measurements, ^1H, and ^{13}C NMR of PS clearly established the atactic nature of the polymer. The relative ratio of the triads [*rr*], [*mr*], [*mm*] in PMMA was found to be 60 : 38 : 2 from ^1H NMR spectra, which is similar to that obtained from radical polymerisation of MMA.

It has been found that the conversion is both temperature and time dependent. In the case of Cp_2TiCl_2 catalysed polymerisation of MMA, up to 40°C we could not detect any product. The conversion is negligible at 50°C. The highest conversion was observed at 70°C, and the conversion drops dramatically at the temperature 90°C. Up to 9 h of reaction time we could observe only little polymerisation. After 9 h of reaction time the yield increases steadily rises to a maximum at the reaction time of 11 h. In the case of Cp_2TiCl_2 catalysed styrene polymerisation, maximum conversion is observed at the reaction time of 6 h and up to 30°C no polymerisation takes place. At 50°C, the conversion is found to be highest and the conversion drops with further increase in tempe ra ture. Similarly, in Cp_2ZrCl_2 catalysed polymerisations, up to 40°C we could not detect any product.

Table 1. Polymerisation of MMA and styrene with Cp_2TiCl_2 at different temperature using different surfactant[a].

Cp_2TiCl_2 (mol)	MMA (mol)	Styrene (mol)	Surfactant ($\times 10^{-3}$ mol)	T (°C)	M_w	M_n	M_w/M_n	Yield (%)
0·0005	0·05		SDS (1·6)	70	514,000	321,250	1·6	70[b]
0·0005	0·05		SDS (1·6)	90	739,000	461,875	1·6	20[b]
0·0005		0·05	SDS (1·6)	50	540,000	300,000	1·8	73[c]
0·0005		0·05	SDS (1·6)	70	688,000	404,705	1·7	46·2[c]
0·0005		0·05	SDS (1·6)	90	690,000	405,880	1·7	5·8[c]
0·0005		0·05	CTAB (1·6)	70	–	–	–	–
0·0005		0·05	–	70	–	–	–	–
–		0·05	SDS (1·6)	70	–	–	–	–

[a]T = polymerisation temperature; M_w = molecular weight (GPC); MMA/styrene concentration = 0·5 mol/l [Ti] = 0·005 mol/l. [b]Reaction time = 11 h. [c]Reaction time = 6 h

Table 2. Polymerisation of MMA and styrene with Cp_2ZrCl_2 at different temperature using SDS[a].

| Cp_2TiCl_2 (mol)	MMA (mol)	Styrene (mol)	Surfactant ($\times 10^{-3}$ mol)	T (°C)	M_w	M_n	M_w/M_n	Yield (%)
0·0005	0·05		SDS (1·6)	70	781200	564300	1·4	20·0[b]
0·0005	0·05		SDS (1·6)	90	581000	462000	1·3	49·0[b]
0·0005		0·05	SDS (1·6)	70	840700	582800	1·4	33·5[c]
0·0005		0·05	SDS (1·6)	90	525600	269400	1·9	84[c]

[a]T = polymerisation temperature; M_w = molecular weight (GPC); MMA/styrene concentration = 0·5 mol/l [Zr] = 0·005 mol/l. [b]Reaction time = 12 h. [c]Reaction time = 15 h

The conversion is negligible at 50°C. The highest conversion is observed at 90°C, and the conversion drops dramatically at temperatures above 90°C. The conversion is also found to be dependent on polymerisation time (table 3). Up to 3 h of reaction time we could observe only slight polymerisation. After 3 h of reaction time the yield increases steadily rises to a maximum at reaction time of 15 h in the case of styrene, whereas, in MMA polymerisation, maximum yield is obtained at 12 h of reaction time. The plot of polymer yield versus time (figure 1) clearly indicates that the active species is stable up to 12 to 15 h. The plot of number-averaged molecular weight (M_n) versus percentage yield (figure 2) clearly shows that the polymerisation is not natural.

Table 3. Time-dependence polymerisation of styrene and methylmethacrylate[a].

Monomer	Time (h)	Yield (%)	M_n	M_w/M_n
Styrene	3	5	b	
	5	27·26	247000	1·72
	10	64·07	238000	1·78
	15	84	269400	1·9
	20	81·9	198000	1·8
MMA	10	3·5	b	
	12	49	462999	1·25
	15	25·64	401000	1·26
	20	34·8	562900	1·8
	25	36·48	484000	1·2

[a]Polymerisation temperature = 90°C, MMA/styrene concentration = 0·5 mol/l [Zr] = 0·005mol/l; b = not determined
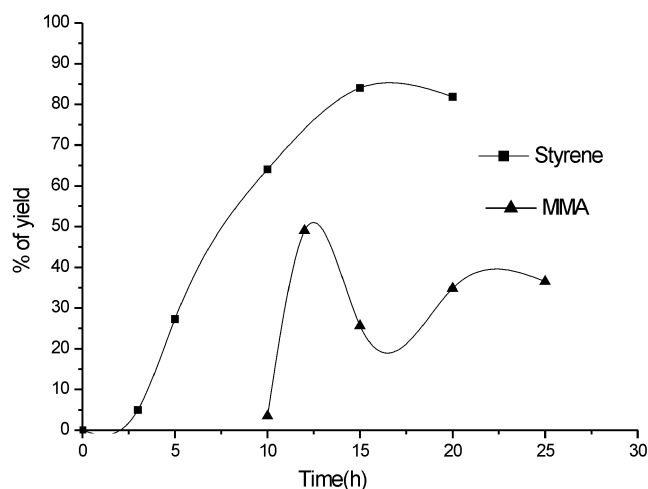
Figure 1. Plot of polymer yield versus polymerisation time (■ styrene, ▲ MMA).

The observed atactic nature of the polystyrene and the observed triad distribution of PMMA, which is similar to the typical stereo-structure of free radical PMMA led us to believe that, in the present case a free radical polymerisation may be in operation, though, a large number of Ziegler–Natta catalytic systems are known to afford atactic polymers. Attempted polymerisation without the addition of Cp_2MCl_2 failed. This clearly shows that Cp_2MCl_2 catalyses the polymerisation reactions and that the polymerisation is not spontaneous. Dioxygen is a strong inhibitor for radical polymerisation of styrene[15] and is known to increase the induction time and decrease the molecular weight of the polymer.[15] We have carried out polymerisation reactions in the presence of dioxygen and we could neither observe any increase in the induction period, nor observe any major difference in the molecular weight of the polystyrene. Also, we have carried out polymerisation reactions using styrene or methylmethacrylate (MMA) without removing stabilizer (4-tert-butyl-catechol and hydroquinone, respectively) and could polymerise both the monomers successfully. However, addition of potassium fluoride or chloride (Zr : F⁻/Cl⁻ ratio was maintained at 1 : 2) completely inhibits polymerisation. This may be explained by the fact that fluoride/chloride ions destroy the cation and thus inhibit polymerisation. Although, radical mechanism cannot be ruled out completely, all the results are indicative of an insertion mechanism.

2.3 *Cp_2TiCl_2-catalysed co-polymerisation of styrene and methylmethacrylate*

In order to further probe the mechanism of polymerisation, Cp_2TiCl_2-catalysed copolymerisation of MMA and styrene has been carried out[4d] and the microstructure of the copolymer has been determined from ^{1}H NMR spectroscopy. Also, the reactivite ratios of the monomers have been determined. The details of the results of co-polymerisation are presented in table 4.

It is observed that at MMA : styrene ratio 1 : 4, molecular weight of the copolymer is highest and M_w/M_n is lowest. As the concentration of MMA is increased in the monomer feed, the incorporation of MMA in the copolymer increases. The ideal feed ratio was determined to be 1 : 1, as in this feed ratio molecular weight of the copolymer was 250, 245 with lowest M_w/M_n ratio (1 : 1), and higher yields.

Table 4. Cp$_2$TiCl$_2$-catalysed copolymerisation of styrene and methylmethacrylate.

Cp$_2$TiCl$_2$ (mol)	Feed ratio MMA/ styrene (mol/mol)	Surfactant ($\times 10^{-3}$ mol)	Copolymer composition (MMA : styrene)[b]	M_w[c]	M_w/M_n[c]	Yield (%)[d]
0·0005	2·125 : 1	SDS (1·6)	1 : 0·35	195, 200	1·5	35
0·0005	1 : 1	SDS (1·6)	1 : 0·57	250, 200	1·1	32
0·0005	0·56 : 1	SDS (1·6)	1 : 1·02	215, 400	1·3	31
0·0005	0·25 : 1	SDS (1·6)	1 : 2	254, 800	1·2	9

[a]Reaction time = 16 h. Reaction temperature = 70°C. Total monomer concentration (MMA + styrene) = 0·5 mol/l [Ti] = 0·005 mol/l. [b]Composition of extracted copolymer obtained from ^{1}H NMR; In mole [c]M_w = molecular weight (GPC). [d]Obtained from total monomer feed and extracted copolymer
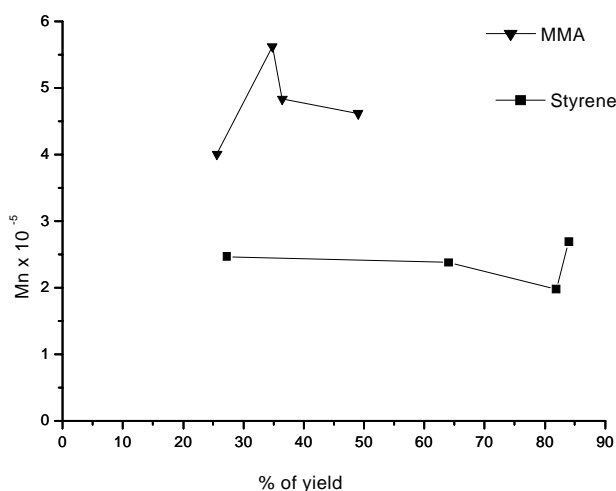
Figure 2. Plot of numbers averaged molecular weight (M_n) versus polymer yield (▲ MMA, ■ styrene).

A temperature-dependent copolymerisation was done and it was found that up to 50°C no polymerisation could be observed the optimum temperature was found to be 70°C. Similarly, time-dependent copolymerisation study was conducted and optimum time was determined to be 16 h.

The ^{13}C and ^{1}H NMR spectra of the copolymers confirm the random nature of the copolymer.[16] The FT–IR spectra matches well with those of reported random copolymers. The ^{1}H NMR spectra of the copolymer show signals for the methoxy (–OCH$_3$) protons of the enchained MMA units in the region δ 2·2 to δ 3·6 ppm with the most intense peak at δ 3·6 ppm, integrating as ~ 70% of the δ 2·2–3·6 ppm region. The 3·6 ppm signal is due to cosyndiotactic MMA units. Thus, the ^{1}H NMR studies show clearly that the copolymer contains atactic polystyrene with cosyndiospecifically enchained MMA units and thus is completely different from radical styrene and MMA copolymerisations that usually afford non-stereoregular random copolymers.[16]

For the determination of reactivity ratio, a set of four copolymerisation reactions were conducted using different monomer feed ratios under identical experimental condition, while conversion was restricted to below 10%. The composition of the copolymers was determined from the ^{1}H NMR spectra. The monomer reactivity ratio was determined using the Finemann–Ross method[17], and found to be $r_1 = 0·385$ and $r_2 = 1·19$. The reactivity ratios are completely different from free radical co-polymerisation.[18]

Reactivity ratios of the monomers as well as the inhibition experiments clearly show that the polymerisation reactions do not proceed by radical mechanism. Also, the low polydispersities of the polymers and copolymers obtained indicates that the catalysts are single-site catalysts. All these results indicate that an insertion mechanism is operative in these cases.

2.4 *Cp$_2$VCl$_2$-catalysed polymerisation of styrene and methylmethacrylate and dramatic effect of dioxygen on the molecular weights and yields of the polymers*

Transition metal complexes have been used for activation of dioxygen and hydrogen peroxide and subsequent oxidation of various substrates.[3,7,9,19] For example, vanadium (IV) compounds have been shown to transfer electron to exogenous O$_2$.[20] Also, it has been shown that [Cp$_2$V(acac)]$^+$ cation can initiate O$_2$ dependent peroxidation of lipid, wherein a radical mechanism has been proposed.[21] We were interested in exploring activation of dioxygen by Cp$_2$VCl$_2$, for aqueous emulsion polymerisation.

Thus, polymerisation was initiated by the addition of an aqueous solution of Cp$_2$VCl$_2$ to aqueous emulsified monomer under aerobic condition. The details of the results of polymerisation are given in table 5.[22]

Table 5. Polymerisation of MMA and styrene with Cp_2VCl_2 at different temperature using SDS under argon and aerobic atomsphere[a].

Cp_2VCl_2 (mol)	Styrene (mol)	MMA (mol)	T (°C)	Reaction Atmosphere	M_w (M_w/M_n)	Yield (%)
0·0005	0·05		70	Argon	33,000 (2·6)	[b]14·4
0·0005	0·05		70	Air	2,59,800 (2·0)	[b]42·3
0·0005	0·05		90	Air	2,70,200 (1·95)	[b]38·4
0·0005		0·05	70	Air	2,54,000 (1·8)	[c]62·2
0·0005		0·05	90	Air	1,32,700 (1·6)	[c]43·6

[a]T = polymerisation temperature, M_w = molecular weight (GPC, against standard polystyrene), SDS concentration = $1·6 \times 10^{-2}$ mol/l, MMA/styrene concentration = 0·5 mol/l, [V] = 0·005 mol/l. [b]Reaction time = 3 h. [c]Reaction time = 15 h
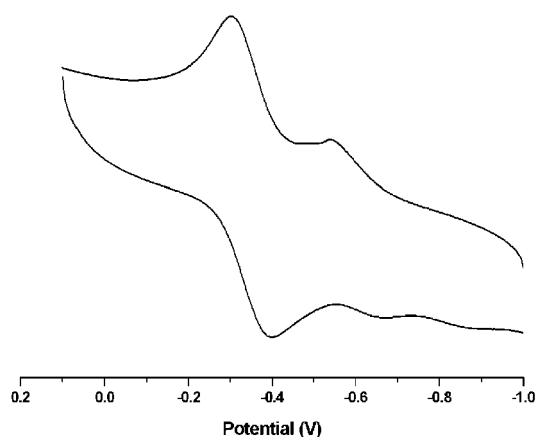
Figure 3. Cyclic voltammogram of the V^{IV}/V^V couple in water of Cp_2VCl_2 in the presence of SDS with Ag/AgCl reference electrode, glassy carbon working electrode and a platinum wire auxiliary electrode. Scan rate = 0·2 V/s.

The average molecular weights of PMMA, measured by GPC, are high and lie in the range 132,000 to 254,000. Similarly, the average molecular weights of PS lie in the range 259,000 to 270,600. The M_w/M_n ratios are found to lie in the range 1·6 to 2·0 and clearly show low molecular weight distribution and indicate a single-site catalytic system.[14]

It has been shown that in aqueous solution Cp_2VCl_2 is converted to a cationic species $[Cp_2V(H_2O)_2]^{2+}$ which undergoes subsequent hydrolysis to $[Cp_2V(OH)(H_2O)]^+$ and $[Cp_2V(OH)_2]$.[13] Thus, it is anticipated that an aqueous solution of Cp_2VCl_2 would afford cationic vanadium species, which could react with dioxygen of air to produce radical species that would act as an initiator for polymerisation.

Accordingly, polymerisation reactions of styrene and MMA were carried out in air and we could isolate PS and PMMA with high molecular weights and low molecular weight distribution (table 5). In order to elucidate the effect of dioxygen we have carried out polymerisation of styrene in argon atmosphere and isolated PS in poor yield (14·4%) with much lower molecular weight ($M_w = 33,000$) and higher molecular weight distribution ($M_w/M_n = 2·6$). Dioxygen has been shown to increase induction time and reduce molecular weight of the polymer and thus acts as an inhibitor.[18] However, the observed results clearly show that presence of dioxygen increases molecular weight and decreases molecular weight distribution dramatically. Polymerization reactions are completely inhibited by 4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy free radical (4-hydroxy-TEMO) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) indicating that the polymerisation proceeds through a radical mechanism.

The cyclic voltammetry of the oxidative scan (figure 3) of an aqueous solution of Cp_2VCl_2 containing SDS shows a quasi-reversible oxidative couple at $E_{1/2} = -0·603$ V and a nearly reversible oxidative couple at $E_{1/2} = -0·350$ V under argon atmosphere. These oxidative couples can be assigned to V^V/V^{IV} couples of two V(IV) species generated in solution. It has been reported that cyclic voltammetry of an aqueous solution of Cp_2VCl_2 in the presence of KCl shows a quasi-reversible V^{IV}/V^{III} reductive couple at $E_{1/2} = -0·472$ V.[21] Thus, it is clear that, in the presence of SDS, the electrochemical behaviour of Cp_2VCl_2 completely changes and oxidation of V^{IV} to V^V is feasible.

The ESR spectral change observed for an aqueous solution of Cp_2VCl_2 containing SDS is shown in figure 4. The spectral feature of a freshly prepared solution of Cp_2VCl_2, under argon atmosphere, can be explained as a superposition of 8 hyperfine ($A_{av} = 76$ G and 109 G) peaks (figure 4a) of two species, $[Cp_2V(H_2O)_2]^{2+}$ and $[Cp_2V(OH)(H_2O)]^+$ respectively.

Figure 4. X-band ESR spectra of Cp_2VCl_2. (a) Spectrum of Cp_2VCl_2 taken in aqueous SDS solution under argon atmosphere within 5 min. (b) Spectrum of (a) taken after 45 min under argon atmosphere. General conditions: temperature = 298 K, microwave frequency = 9·85 GHz, microwave power = 0·64 mW, modulation frequency = 50 kHz, modulation amplitude = 4 G, receiver gain = 1·59 × 10^5. Sweep width = 1000 G. Time constant = 81·92 ms. Conversion time = 655·36 ms.

Figure 5. X-band ESR spectrum of Cp_2VCl_2 taken in aqueous SDS solution in the presence of DMPO after exposure to air for 1 h. General conditions: temperature = 298 K, microwave frequency = 9·85 GHz, microwave power = 0·64 mW, modulation frequency = 50 kHz, modulation amplitude = 0·5 G, receiver gain = 8·93 × 104. Sweep width = 100 G. Time constant = 55·36 ms. Conversion time = 163·84 ms.

Scheme 3.

The solution on standing for about an hour shows an 8 line spectrum (A_{av} = 109 G) which may be due to $[Cp_2V(OH)(H_2O)]^+$ (figure 4b). The ESR experiments with DMPO as the spin trap were done to examine the formation of radical species during aerial oxidation of the aqueous solution of Cp_2VCl_2. When aerial oxidation of the aqueous solution of Cp_2VCl_2 was done in presence of DMPO, a typical 6-line spectrum (A_N = 15·34 G, A_H^β = 9·30 G, A_H^α = 6·06 G) (figure 5) of a DMPO trapped radical appeared.

A similar kind of ESR spectrum of DMPO trapped $^\bullet$OMe radical has been reported recently.[23] It is clear that the generated radical is neither OH$^\bullet$ nor superoxide radical, as spin-trapped DMPO–OH gives a four-line spectrum and the observed values of A_H^α and A_H^β are not the same as reported for the DMPO–OOH radical.[24] Thus it is clear that a new kind of radical species is generated upon interaction of aerial oxygen with an aqueous solution of Cp_2VCl_2 and we hypothesized it to be ($^\bullet$OV^{V}Cp$_2^{2+}$). A similar kind of radical, ($^\bullet$OV^V(O$_2$)$_2^+$), has been suggested as an intermediate in the reduction of $[VO(O_2)_2]^-$ by VO^{2+}.[25] Also, It may be noted that in the oxygen-dependent $Cp_2V(acac)^+$ initiated lipid peroxidation a similar inner sphere, electron transfer between vanadium(IV) and dioxygen has been suggested.[21] Similar experiments with $VOSO_4$ did not show formation of any radical species indicating that VO^{2+} does not have any interaction with DMPO. Based on the ESR experiments, a mechanism has been formulated and is shown in scheme 3. The first step is the hydrolysis of Cp_2VCl_2 to afford $[Cp_2V(OH)(H_2O)]^+$, which coordinates dioxygen and an inner sphere electron transfer takes place to afford V(V) coordinated superoxo species, **A**, that reacts with another $[Cp_2V(OH)(H_2O)]^+$ to give μ-peroxo V(V) species, **B**. The species **B** then undergoes homolytic cleavage to afford an oxo-radical, $^\bullet$OV^{V}Cp$_2^{2+}$, **C**, which is responsible for initiating polymerisation.

3. Conclusions

Thus, an environmentally benign route to Hunsdiecker products have been developed. Also, it has been shown that in hydrolysis of Cp_2MCl_2 (M = Ti, V or Zr) commercially available early transition metal compounds, can be advantageously used as catalysts for aqueous polymerisation. Using these catalysts, high molecular weight polymers with low molecular weight distribution can be obtained. In contrast to the general notion that oxygen is an in-

hibitor in polymerisation, it has been shown for the first time that oxygen can enhance polymerisation. Comparison with the Cp_2TiCl_2 and Cp_2ZrCl_2 catalysed homo- and co-polymerisation of styrene and methyl methacrylate,[4] reported from this laboratory, shows that vanadium-catalysed polymerisation is fundamentally different. Whereas Cp_2VCl_2-catalysed polymerisation[22] proceeds via a radical mechanism, those catalysed by corresponding titanium and zirconium compounds proceed via insertion mechanism. It may be noted that time and again it has been emphasized in literature that the early transition metal organometallic compounds are highly moisture sensitive and thus, are not suitable as catalysts for aqueous polymerisation. However, it has been shown that the metal–cyclopentadienyl bond in Cp_2MCl_2 (M = V, Ti, or Zr) compounds is quite stable[15] and in aqueous solution produces cationic species of the types $[Cp_2M(H_2O)_2]^{2+}$, $[Cp_2M(HO)]^+$, and $[Cp_2M(OH)_2]$, depending upon the pH of the solution, while in lower pH the M–Cp bond remains intact for days. It has been observed that the structural integrity of Cp_2V^{2+} ion is maintained even at higher pH.[12] In the present work as well as in our earlier works the stability of these cationic species has been exploited for their catalytic activity.

4 Experimental

4.1 *Sodium molybdate catalysed aqueous Hunsdiecker reaction*

When a suspension of α,β-unsaturated aromatic carboxylic acid (0·02 mol) is stirred with KBr (0·04 mol) and $Na_2MoO_4 \cdot 2H_2O$ (0·001 mol) in water (5 cm^3) and H_2O_2 (15 cm^3, 0·13 mol) is added dropwise at room temperature (30°C), a rapid reaction takes place and the temperature rises to 80°C within 20 min. The reaction mixture is stirred for farther 20 min and the product as well as the un-reacted acid are extracted with diethyl ether. The corresponding β-bromo-styrene are separated from the starting material by column chromatography in good yield.

4.2 *Cp_2MCl_2 (M = Ti, V, or Zr) catalysed homo-polymerisation of styrene and methylmethacrylate*

All the polymerisation reactions were carried out under argon atmosphere as well as under aerobic conditions. No major difference could be observed in case of titanium and zirconium compounds. In the case of Cp_2VCl_2 catalysed polymerisation the polymerisation reactions were carried out under aerobic condition. A general procedure is described below.

Cp_2MCl_2 (0·0005 mol) was suspended in water (20 ml) and this suspension was stirred for about 1 h, whereupon a clear solution was obtained. Sodium *n*-dodecyl sulphate (SDS) ($1·6 \times 10^{-3}$ mol) was dissolved in water (80 ml). To this was added methylmethacrylate (MMA) or styrene (0·05 mol) and the whole were stirred for 1 h. To the emulsified monomer solution was then added the aqueous solution of Cp_2MCl_2. The polymerisation mixture was then placed in an oil bath maintained at the desired temperature and the reaction mixture was stirred for required time period. The reaction was quenched by the addition of the emulsion to a mixture of methanol (200 ml) and hydrochloric acid (20 ml). The precipitated polymer was then filtered, washed repeatedly with methanol and dried *in vacuo* at ambient temperature. Finally, the polymer was extracted with hot water for 3 h and filtered to remove water soluble material. PMMA was purified by dissolution in acetone and re-precipitation with the addition of excess methanol. Polystyrene was extracted with refluxing acetone for 3 h to remove low molecular weight fraction of the polymer. The polymer was finally purified by dissolving it in toluene and precipitation by the addition of methanol and finally dried *in vacuo*.

4.3 *Cp_2TiCl_2 catalysed co-polymerisation of styrene and methylmethacrylate*

A typical polymerisation procedure is described below. A sample of Cp_2TiCl_2 (0·1245 g; 0·0005 mol) was suspended in water (20 ml) and this suspension was stirred for about 1 h, where upon a yellow solution was obtained. Sodium *n*-dodecyl sulphate (SDS) ($1·6 \times 10^{-3}$ mol) was dissolved in water (80 ml). To this styrene (2·6 g; 0·025 mol) and methylmethacrylate (2·5 g; 0·025 mol) was added. The monomers were emulsified by stirring for 1 h. To the emulsified monomer solution was then added the aqueous solution of Cp_2TiCl_2. The reaction mixture was then placed in an oil bath maintained at the desired temperature and the reaction mixture was stirred for required time period. The reaction was quenched by the addition of the reaction mixture to a mixture of methanol and hydrochloric acid. The precipitated polymer was filtered, washed repeatedly with methanol and dried *in vacuo* at ambient temperature. The

crude copolymer was then extracted with cyclohexane to remove polystyrene and with acetonitrile to remove poly (methylmethacrylate) homopolymers.

To further study the copolymerisation of styrene with methylmethacrylate, a set of four experiments was conducted. Different feed ratios of styrene and methylmethacrylate were employed and the copolymerisation reactions were quenched at low yields ($< 10\%$). The copolymer composition was calculated by ^{1}H NMR and the reactivity ratio was determined by Finemann–Ross equation.

Acknowledgements

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