Redox Initiated Free Radical Polymerization of 4-Methylstyrene

Anne-Cecile Mortamet,* Richard A. Pethrick

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, Scotland

ABSTRACT: Studies of the thermally initiated polymerization of 4-methylstyrene using alkylperoxide in conjunction with cobalt and tertiary amine catalysts are reported. Addition of cobalt salts leads to a facile low temperature initiation of the polymerization process. The polymerization process was investigated using differential scanning calorimetry [DSC] and vibrating probe rheological measurements. Color changes which occur when the cobalt complex and peroxide are combined were studied using UV-visible spectroscopy. The kinetics of polymerization was investigated using two different cobalt complexes. The initiation step in the polymerization is the conversion of the cobalt (II) to cobalt (III). The presence of the tertiary amine does not affect the oxidation state of the cobalt complex. The cobalt (III) complex gives a better rate of conversion than the cobalt (II) complex. The polymerization process is discussed in terms of redox reaction between the cobalt complex and the alkyperoxide. At low temperatures, the rate of conversion obeys simple Arrhenius kinetics. At higher temperatures the effects of gelation and catalysts inhibition influence the polymerization process. The polymerization process is sensitive to the level of available oxygen during the initiation step and inhibition by aldehyde is observed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1539–1547, 2012

Key words: free radical polymerization; cobalt catalysis; Haber–Weiss catalytic cycle; benzaldehyde inhibition; 4-methylstyrene; gelation
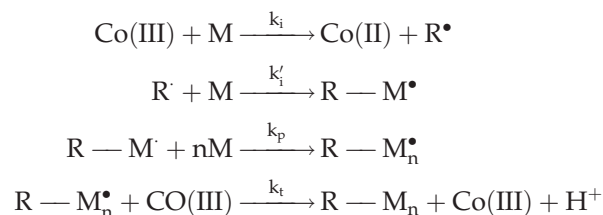
INTRODUCTION

Vinyl polymerization can be initiated using a variety of different methods.[1] In recent years, atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) and a variety of transition metal catalysts have been extensively studied as catalysts for polymerization of vinyl monomers.[2–4] In a number of industrial applications, low temperature polymerization of vinyl resins is often achieved with the aid of cobalt catalysts. Despite the wide use of these cobalt complexes in polymerization, there still remain a number of aspects of the mechanism which are not fully understood.

In the absence of oxygen and in normal atmospheric conditions, facile polymerization can be readily achieved. However, if the level of oxygen is reduced, the polymerization can become inhibited. This study investigates the kinetics of cobalt assisted free radical polymerization of 4-methylstyrene in an attempt to understand the oxygen inhibition process.

The typical low temperature polymerization catalysts package is made up of a metal complex, a peroxide and a tertiary amine. The initiation step for the polymerization process is sensitive to changes in each of these components. A number of oxidising metal ions have been used in combination with reducing agents such as ketones, aldehydes, amides and amines to participate in the redox initiation step of free radical polymerization reactions. Metal ions mainly used for this purpose are Fe(III), Cr(VI), and Co(III). Cobalt (III) is believed to polymerize vinyl monomers according to the following scheme:

$$Co(III) + M \xrightarrow{k_i} Co(II) + R^\bullet$$

$$R^\cdot + M \xrightarrow{k_i'} R\!-\!M^\bullet$$

$$R\!-\!M^\cdot + nM \xrightarrow{k_p} R\!-\!M_n^\bullet$$

$$R\!-\!M_n^\bullet + CO(III) \xrightarrow{k_t} R\!-\!M_n + Co(III) + H^+$$

In addition to the reactions shown above, termination will occur by the usual transfer and disproportionation reactions. The concentration of the metal-catalysts is a crucial parameter for the radical polymerization processes to occur.[5–7] Cobalt complexes are usually used in conjunction with peroxides and

**Present address:* Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, England.

*Correspondence to:* R. A. Pethrick (r.a.pethrick@strath.ac.uk).

tertiary amines. However, tertiary amines can also act as promoters for the dissociation of organic peroxides and aid the initiation of low temperature polymerization processes.[8,9]

Molecular oxygen can act as an initiator, inhibitor or retarder in free radical polymerization processes. In the presence of organometallic catalysts, oxygen can coordinate to the metal center. For instance, Co(II) complexes containing *N*-chelate ligands react with O_2 to form labile O_2 complexes.[10,11] The ligand coordination about the cobalt atom is essentially square planar but can also adopt an octahedral structure. Complexation of O_2 is assisted by coordination of an amine to the axial position. The formation of the oxygen complex usually involves transfer of some electron density from the metal to the O_2 ligand:

$$Co^{2+} + O_2 \rightleftharpoons Co^{3+} + O\text{----}O^-$$

The *N*-donor ligands facilitate oxygen bonding through partial electron donation and aid formation of the O_2^- species. The mechanism of the reaction Co(II) complexes with dioxygen to give the mononuclear Co(III) compound has been investigated by using nuclear magnetic resonance.[12] By monitoring the concentrations of the initially formed peroxo compounds and of the mononuclear Co(III) complexes it was concluded that the peroxo compounds are intermediates in the formation of the mononuclear Co(III) complex and suggests that reduction of the peroxo complex is achieved by the Co(II) complex.

Cobalt can act as a promoter for the homogeneous free radical polymerization initiated using alkyl hydroperoxides[13–16] as shown in the Scheme:

$$Co(II) + ROOH \longrightarrow Co(III)(OH) + RO^\bullet$$
$$Co(III) + ROOH \longrightarrow Co(II) + ROO^\bullet + H^+$$
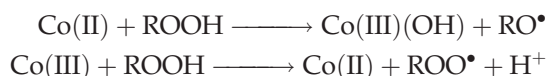
The oxidation of Co(II) takes place first via formation of a complex in which the hydroperoxide becomes a ligand on the metal center. Electron transfer from cobalt to oxygen occurs after complexation. Weakening the O—O bond favors the breakdown of the complex and formation of the unstable alkoxy radical. The second reaction reduces Co(III) and forms the more stable alkylperoxy radical. The oxidation potentials of these reactions are balanced allowing both processes to occur at the same time in solution, giving rise to the Haber–Weiss cycle.[17] The rapid shuttling of the cobalt atom between the two oxidation states, catalyzes the breakdown of ROOH into radicals and allows initiation of vinyl polymerizations. Although cobalt is an oxidation catalyst at low concentrations, at high concentrations it inhibits

oxidation by keeping radical concentrations so low that oxidation can not be initiated[18,19]:
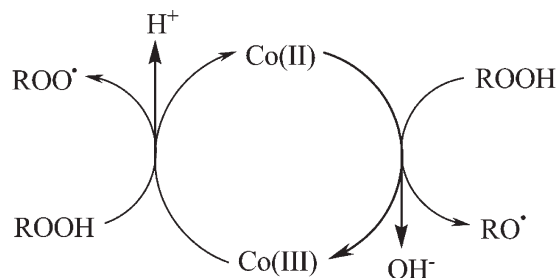
The 4-methylstyrene was selected as the monomer for investigation as it has a slightly lower vapor pressure than styrene and hence allows studies to be performed at higher temperatures. The polymerization kinetics was characterized using a combination of differential scanning calorimetry—DSC and rheological measurements. The nature of the cobalt catalyst was investigated using UV-visible spectroscopy.

## EXPERIMENTAL

Materials

All the reagents were used as received: 4-methylstyrene, lauroyl peroxide and cobalt acetylacetonate, a 10% solution of cobalt bis(2-ethylhexanoate) in white spirit and diethylaniline were purchased from ç-Aldrich Company, The Old Brickyard, New Road, Gillingham, Dorset SP8 4XT. The vinyl monomer and peroxide were both stored in a fridge at 4°C.

Sample preparation

The catalysts mixture was prepared by combining the three components in the proportions; cobalt complex [1]: tertiary amine [10]: peroxide [100]. To the catalyst mixture was added 2 g of 4-methylstyrene. The mixing procedure was carried out in a fume cupboard until a homogeneous solution was achieved.

UV-visible spectroscopy

The UV-visible spectroscopic measurements were made using a Varian Cary300 UV-VIS spectrophotometer, Varian Limited, 10 Mead Road, Yarnton, Oxford, OX5 1QU. The concentrations of the cobalt complex and the peroxide were chosen to give conform to a stoichiometric ratio of 1 : 1 as given by the redox reaction:

$$Co(III) + ROOR \longrightarrow Co(III) + RO^\bullet + RO^-$$
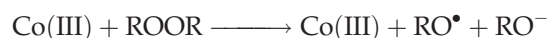
Dichloromethane was used as solvent to give optical clarity. Disposable polymethyl methacrylate

plastic cuvettes with a 5 mL capacity were used to record the spectra. The baseline was determined using a solvent filled cuvette. Spectra were obtained using ambient conditions.

Differential scanning calorimetry–DSC measurements

Experiments were carried out on a Q1000 DSC Instrument, TA Instruments, Block D, The Fleming Centre, Fleming Way, Manor Royal, Crawley, West Sussex, RH10 9NB, working over a temperature range from −100 to 450°C, fitted with a liquid nitrogen cooling accessory and a 50-positions autosampler. Observation of the reaction exotherm allowed determination of the extent of reaction with time. High pressure DSC pans were used to overcome the problem of volatility of the monomer. The pans were sealed with a copper disc and the pan had the capability of standing a pressure of 10 MPa and a sample size of 35 μL. Measurements were made using both dynamic and isothermal observations. The dynamic scans were used to locate the region of activity of the catalysts and isothermal studies were used to obtain time-temperature conversion plots from which kinetics data were derived.

Viscosity measurements

The change in viscosity as a function of time was observed using the "Strathclyde curometer."[20] This instrument consists of vibration probe whose motion allows the change in the viscosity to be measured as a function of time. To conduct this investigation the normally opened vial containing the reactants mixture had to be sealed. The probe was feed through a flexible membrane. The dynamic range of the instrument was slightly reduced by the damping produced by the flexible membrane but using this configuration enabled measuring the viscosity over the range $10–10^5$ Pa s. A check was performed at targeted temperatures between 70 and 90°C to determine the efficiency of the seals. The mass from the vial containing 4-methylstyrene was recorded every 5 min over a period of 2 h and no loss of weight was observed. Curometer measurements traced the reaction in terms of change in viscosity during the polymerization process and used the calculations outlined elsewhere.[20] Data points were taken every second for the duration of the study. The data was collected via the computer program Picolog.

RESULTS AND DISCUSSION

Previous workers have identified the potential role of cobalt complexes in the redox polymerization of vinyl monomers and have favored the Haber–Weiss
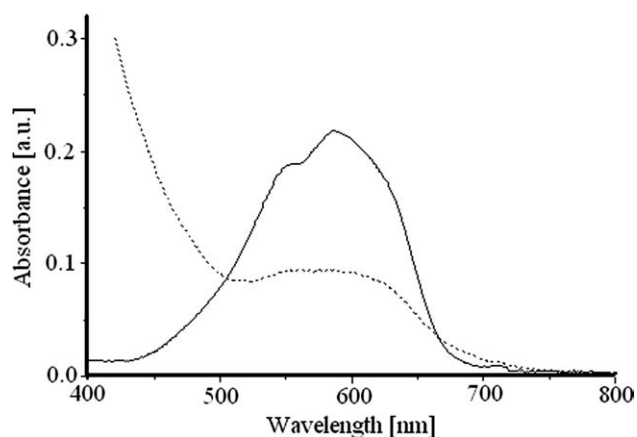

Figure 1 UV-visible spectra of Co(II) (solid line) and Co(II) + Lauryl peroxide (dashed line) in dichloromethane.

cycle as the route to polymerization.[18,19] However, an alternative scheme has been proposed in which the cobalt(II)-catalyzed decomposition of t-butyl hydroperoxide at 25°C is influenced by the nature of the ligands attached to the cobalt atom. The high catalytic activity observed with 2-ethylhexanoate is attributed to the formation of a bridged dicobalt complexes and does not directly generate an alkoxy radical.[21] Change in the coordination about the cobalt atom can be observed by changes in the UV spectra.[22,23] Two catalysts were selected for investigation; cobalt (III) acetylacetonate and cobalt (II) bis(2-ethylhexanoate).

UV-visible spectroscopic measurements

The UV spectra of Co(II) obtained from cobalt bis(2-ethylhexanoate) is shown in Figure 1. The Co(II) exhibits a strong absorption due to the d-d transition in the 450 nm to 700 nm and the solution at this stage has a brown color. Addition of the lauroyl peroxide immediately causes the solution to turns purple, reflected in the hypsochromic shift of the absorption with the formation of the Co(III) oxidation state. The shoulder still observed at approximately 580 nm indicates that some Co(II) still remains. The addition of the tertiary amine, diethyl aniline (DEA) to both the nonoxidized and oxidized forms of the cobalt complexes (Fig. 2), was marked by a slight red shift which in part reflects the addition of the π (π* transitions of phenyl rings.[24] The addition of the tertiary amine appears to have little effect on the electronic properties of the Co(III) formed be the action of the laurylperoxiode on the Co(II) complex. If the amine is acting axially in an octaohedral coordinated structure then changes in the functional groups attached to the nitrogen might be expected to have some effect on the nature of the electronic transition. Solutions were prepared using
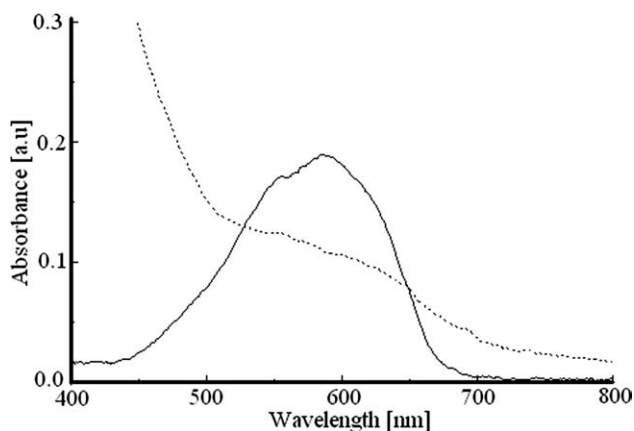
Figure 2 UV-visible spectra of Co(II) (solid line) and Co(II) + LPO (dashed line) in dichloromethane with DEA.

DEA, dimethylaniline (DMA) and N-methylaniline (NMA). The spectra for the addition of the amines to Co(II) are shown in Figure 3. The addition of DEA to the Co(II) complex produces a small hypochromic shift, however the location of the main UV transition is unchanged. Addition of the less sterically hindered DMA produces spectra which are very similar to those of DEA implying that steric interactions do not play a significant role in determining the interaction of the amine with the cobalt. In contrast NMA, while it also does not shift position of the main d-d transition, there is evidence of a stronger interaction manifested by the increase in absorption in the region of 400 nm. The UV spectra indicate that the amine does not strongly interact with the Co(II) species, however, absorption in the 400 nm region is consistent with the formation of cobalt (III) oxide complexes. In the Haber–Weiss cycle it is assumed that in solution there is a dynamic equilibrium between Co(II) and Co(III) spe-
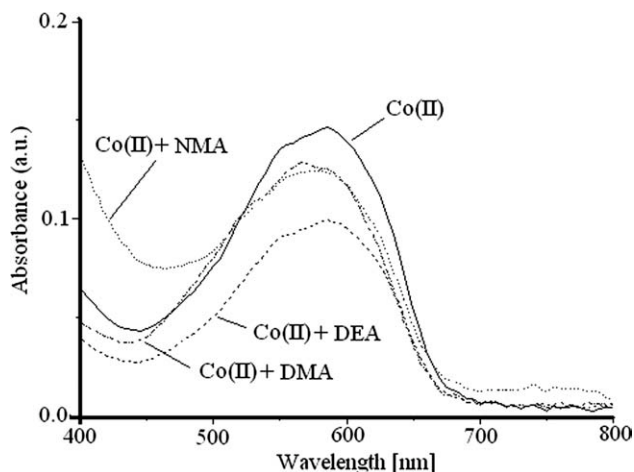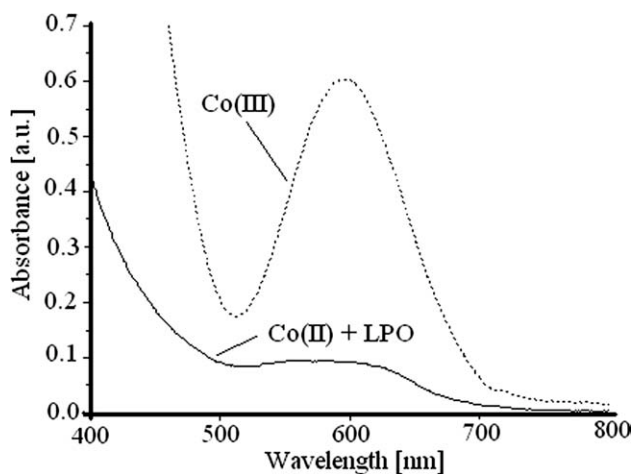

Figure 4 UV-visible spectra of Co (III) acetylacetonate (dashed line) and Co (II) + LPO (solid line).

cies. It was therefore appropriate to explore the UV spectra of a Co(III) complex and cobalt (III) acetylacetonate was selected for this study. The UV spectra of the Co(III) and Co(II) + LPO are compared in Figure 4. The spectra of the Co(II) which has been oxidized by the LPO and the Co(III) complex are very similar. The differences in intensities reflect the differences in the coordination around the cobalt atom. In both cases there is an absorption at approximately 570 nm characteristic of the Co(II) state indicating that there is probably a small concentration of the Co(II) present in both systems. This observation would be consistent with the Haber–Weiss cycle. As an addition to the study of the amine interactions, spectra for mixtures of the cobalt (III) acetylacetonate with the amines were investigated (Fig. 5). The substituents on the nitrogen atom do not have any effect on the electronic properties of the Co(III) complex. The four spectra are essentially the same indicating
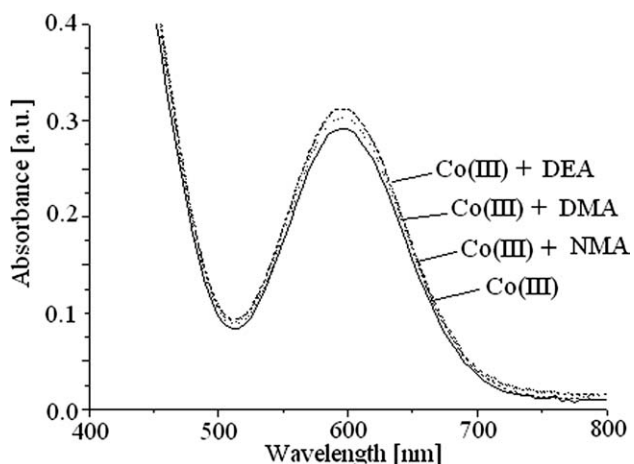

Figure 3 UV-visible spectra of Co(II) mixed with diethylaniline–DEA; dimethylaniline–DMA and N-methylaniline–NMA. (molar ratio 1 : 2).

Figure 5 UV-visible spectra of Co(III) mixed with DEA, DMA and NMA (molar ratio 1 : 2).
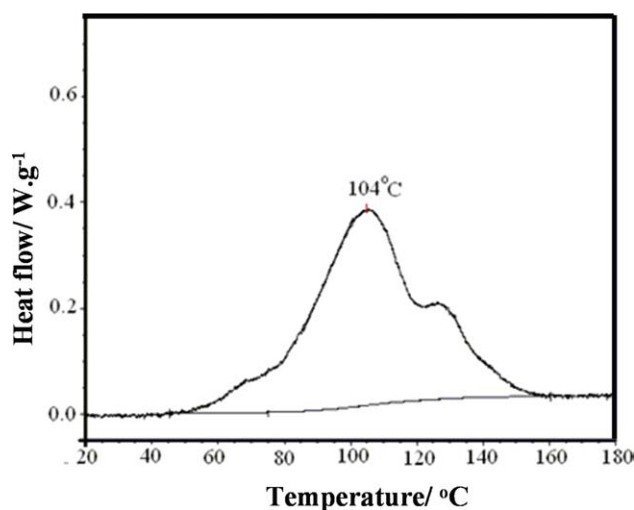
Figure 6 Dynamic DSC thermogram, 2°C/min, catalysed Co(III) system. Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.

that the amine has little or no effect on the *d*-d transition.

The UV visible spectra demonstrate that interaction with the lauryl peroxide changes the oxidation state of the Co(II) to the Co(III) oxidation state. There is no evidence of strong interaction between the Co and the amine although it is known that the amine plays a key role in achieving a high activity of the Co catalysts. In both the Co(II) complex and the Co(III) complex there is evidence exists of there being an equilibrium between the Co(II) and Co(III) oxidation states.

Differential scanning calorimetry measurements

In an attempt to understand the influence of the ligand coordination the relative activities of the two Co complexes were explored using DSC. According to the Haber–Weiss scheme, radical creation accompanies the redox process. To determine the total heat of polymerization a dynamic scan was performed. The heating rate was selected to be 2°C/min to give the system enough time to fully polymerize. Data for the LPO:DEA:Co(III) molar ratio [100 : 10 : 1] is shown in Figure 6. Previous studies have shown that the exotherm obtained using a slow dynamic run can be related to the total energy of polymerization.[25] A post cure scan on the material showed no discernable exotherm. The dynamic scan shows that there is an initial exotherm at about 60°C which then develops into the main feature which at this scan rate peaks at 104°C and a second feature occurs at 130°C. To study the kinetics of the reaction, isothermal measurements were performed at 75, 85, 90, 100, 105, and 110°C, for a period of ∼ 100 min at each temperature. Heat flow curves were measured

at each temperature. The partial integration of the area under the curve allows calculation of the percentage of conversion as a function of time using:

$$(\% \, \text{Conversion})_t = \frac{\Delta H_t}{\Delta H_{\text{total}}} \times 100 \qquad (1)$$

where ΔH_t and ΔH_{total} are respectively, the heat of reaction at time t and the total heat of reaction. The percentage of conversion against time was plotted, Figure 7(a). As anticipated for a thermally activated process, the initial slopes increase with increase in temperature, however the final degree of conversion ($t = 7000$ s) shows an unexpected temperature dependence. The maximum degree of conversion is observed to occur at 90°C and polymerization at higher temperatures leads to lower degrees of conversion. The variation of the degree of conversion with temperature is shown in Figure 7(b). A possible explanation for the observed behavior is that as the temperature is increased, high molecular weight polymers are formed which will cause the mixture to form a gel. At this point, the reaction is no longer thermally activated but becomes diffusion
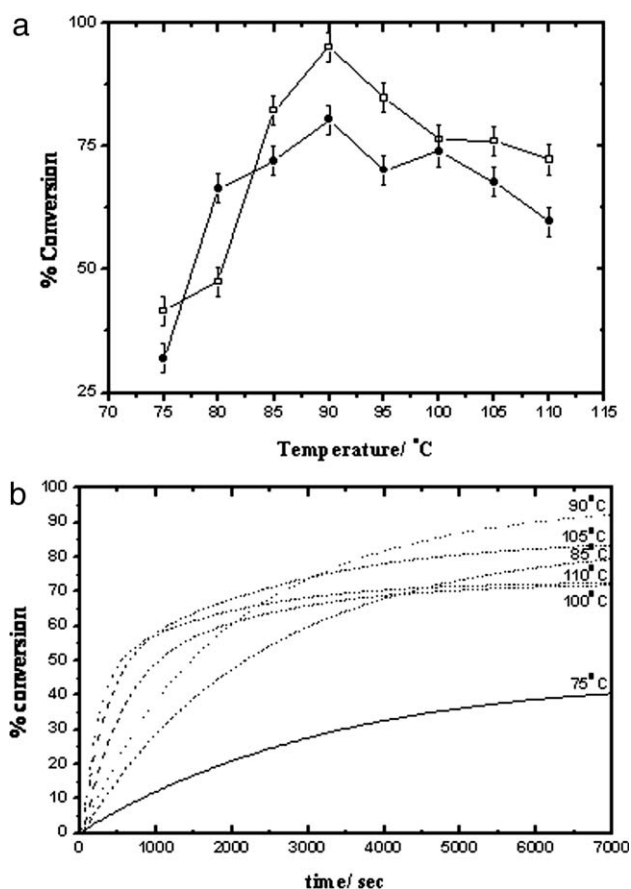

Figure 7 Conversion time and temperature plots; (a) rate of conversion against time for Co(III) system; (b) % conversion against polymerization temperature; ●–Co(II) system □–Co(III) system.

controlled. The formation of the gel phase would lead to a slowing down of the reaction and the possibility of trapped and polymerized monomer being retained in the final material. This explanation is consistent with the conversion curves presented in Figure 7(a). The glass transition temperature of poly(4-methylstyrene) is between 93 and 101°C.[26–29] The observation of the second polymerization feature at ∼ 130°C in Figure 6, would be indicative of a second stage process occurring once the vitrification temperature of the mixture has been exceeded. The effect of diffusion/mobility control on polymerization reactions has been observed previously.[29] It was observed that at the transition from the rubbery to the glassy state, the rate of reaction drops sharply due to the onset of mobility control.
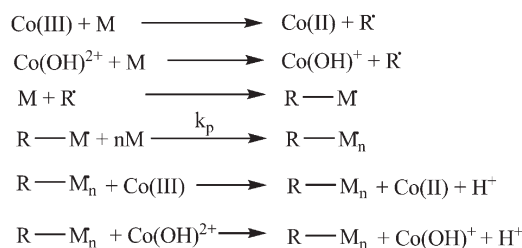
A parallel study was carried out on the Co(II) complex and similar effects were observed. The degree of conversion, Figure 7(b), showed the same temperature sensitivity; however, the degrees of conversion achieved with the catalysts were lower than those obtained using the Co(III) catalyst.

It is clear that the Co(III) catalyst is more effective than the Co(II) system. In both cases the UV spectra indicate that when combined with the laurylperoxide the Co(III) oxidation state is achieved. It is possible that the effects observed can in part be attributed to differences in activity arising form the nature of the ligands attached to the cobalt atom. Differences in catalytic activity with change in the nature of the coordinating species have been reported previously for 1,3-dicarbonyl compounds.[23] The high activity of the 2-ethylhexanoate, is consistent with the radical chain decomposition of the hydroperoxide being initiated by a catalytic cycle which involves bridged dicobalt complexes. The proposed mechanism for the polymerization involving Co(II) and 2-ethylhexanoate is as follows:
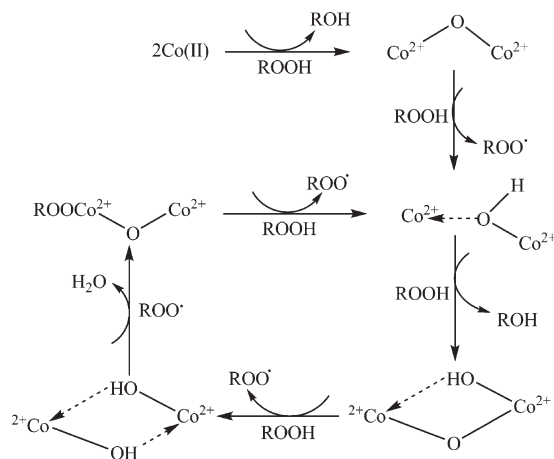

Considering the nature of the ligands and the oxidation state of the metal centers, the Co(II) complex displays a tetrahedral symmetry whereas the complex Co(III) will have octahedral symmetry. Cobalt complex in a tetrahedral geometry can easily react with oxygen.[9,10] It is thus possible that in the presence of the Co(II) catalyst, dissolved oxygen causes side reactions and decreases the rate of reaction. Loss of catalytic activity in the case of cobalt 2-ethylhexanoate has been attributed to complex formation with carboxyl functions.[30] The alternative mechanism involving the Co(II) pathway is characterized by the formation of the Co(II)—O—Co(II) complex which has a green color. Although we cannot completely exclude this as being a possible mechanism in the case of the Co(II)-peroxide system, where there is evidence for increased absorption in the region around 400 nm, it is clearly not a pathway in the case of the Co(III) catalysts. Both systems demonstrate the presence of the Co(II)—Co(III) species which is consistent with the predictions of the Haber–Weiss scheme. The mechanism presented by Jijie et al.[5,6] offers a better explanation of the observed behavior:

$$Co(III) + M \longrightarrow Co(II) + R^{\cdot}$$
$$Co(OH)^{2+} + M \longrightarrow Co(OH)^{+} + R^{\cdot}$$
$$M + R^{\cdot} \longrightarrow R\!-\!M$$
$$R\!-\!M + nM \xrightarrow{k_p} R\!-\!M_n$$
$$R\!-\!M_n + Co(III) \longrightarrow R\!-\!M_n + Co(II) + H^+$$
$$R\!-\!M_n + Co(OH)^{2+} \longrightarrow R\!-\!M_n + Co(OH)^{+} + H^+$$

The above mechanism assumes the formation of the Co(OH) species. The decomposition of the alkylperoxide forms RO˙ species and act in a similar manner to peroxide forming a complex with the cobalt. Hence in the above scheme it is the ROCo^{2+} which introduces the alternative pathway. The Co(III) species once formed reacts with monomer entities on the one hand and can be regenerated into Co(II) on the other hand. These competitive and overlapping mechanisms could explain the higher percentage of conversion given by the Co(III) system. Another factor which will explain the difference in activity is the nature of the ligands themselves; acetylacetonate unlike 2-ethylhexanoate can be a source of acidic protons through tautomerism:

Acetylacetonate   2-Ethylhexanoate
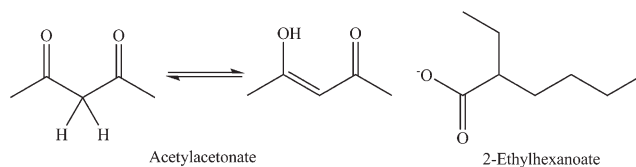
It is clear that there are a number of possible routes involved in the polymerization and the possibility arises from the fact that the mechanism may change with temperature.
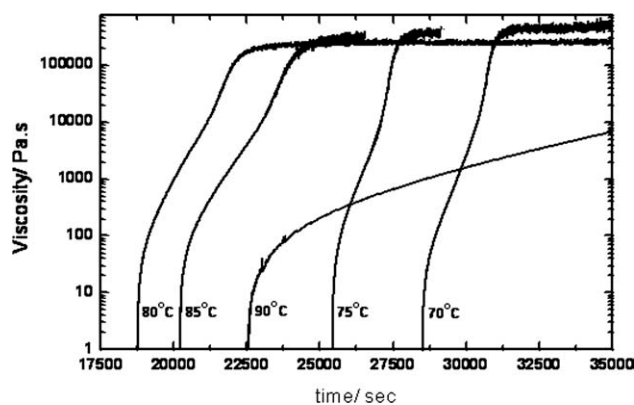
Figure 8 Plots of the viscosity against time for Co(II) cure.

Viscosity measurements

To study the effects of temperature on the rate of the polymerization process, a modification was made to the conventional configuration of the Strathclyde curometer. The introduction of a flexible membrane seal suppresses the loss of monomer and allows observation of the cure behavior, however introducing an initial additional damping mechanism. The contribution to the damping is only observed while the liquid viscosity is very low and has not significant effect on the later stages of the cure process or no effect on the gel time measurements. Plots of the viscosity against time are shown in Figure 8. As the temperature is increased, the point at which the viscosity achieves a value of 1 Pa s decreases. Unlike the normal cure curves for a thermosetting resin, the viscosity in the case of the redox polymerization rises and then goes up slower before reaching a value of $\sim 10^4$ Pa s which is associated with gelation of the material. The profile exhibited by these systems reflects that rise in the viscosity is associated with the creation of high molecular weight polymer. The high molecular weight polymer will thicken the reaction media and slow down the polymerization process. The slight upward curve just after gelation can be associated with the inefficiency of heat transfer allowing the media to exotherm and the reaction to speed up with the increasing mobility. The material ultimately vitrifies and this is shown in the plateau region which follows the rapid rise in the viscosity. The curves were repeated and shown to be reproducible.

The expected decrease in the time to gelation is observed for 70, 75, and 80°C, however 85 and 90°C show an apparent slower rate of polymerization the data collected at 90°C showing a much more gradual rise than that observed at lower temperatures. This type of behavior is not expected in terms of simple Arrhenius type of kinetics but can be directly correlated with the DSC investigation were gel and vitrifi-

TABLE I
Times to Gelation Defined in Various Ways

Temperature [°C]	Time to gelation [min]		
	Viscosity = 10^4 Pa s	Loss peak maxima	Half real curve height
70	217	465	487
75	163	410	430
80	60	306	327
85	93	326	353
90	305	368	436

cation effects were observed to influence the degree of conversion (Fig. 7). The times to gelation are summarized in Table I. The gelation of the system can be defined as the point at which the viscosity reaches a value of 10^4 Pa s when the phase shift is a maximum or the amplitude of the vibration has been reduced to half its initial value. Differences are observed for these times however they all exhibit the same trends with temperature. When the technique is used for a thermoset, there is usually close correspondence between the values and it is probable that a contributing factor to the observed differences is the effect of the membrane on the probe motion.

Figure 9 shows a decrease in time to gelation as the temperature is increased up to about 80°C where upon the time increases. It appears that there is some form of inhibition occurring to the polymerization. A possible explanation could be that as the temperature is increased, the rate of consumption of peroxide also increases and that the slowing down of the polymerization is a consequence of depletion of the peroxide.

However, if this were the case then the observed increase in the rate reflected in the second peak in Figure 6 is difficult to explain. An alternative explanation may be that the effect of the cobalt catalysts is
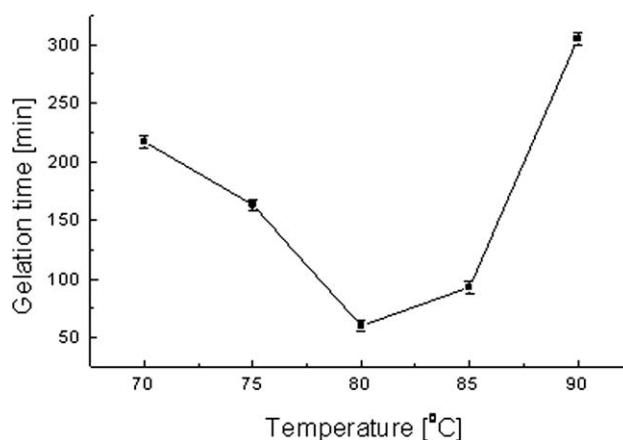

Figure 9 Gel time, defined as the time for the viscosity to attain a value of 10^4 Pa s plotted against temperature.

being lost due to poisoning through interaction with carbonyl functions generated in side reactions leaving peroxide decomposition as the main initiation step.

Inhibition of the reaction by oxygen

Cobalt amine complexes are used with peroxides to facilitate polymerization at low temperatures. An experiment was carried out in which three ~ 20 g samples of the cobalt (II) amine mixture with peroxide initiator were placed in Petrie dishes. The first dish [A], had a polyethylene film placed over the polymer, the second dish [B] was covered with a second slightly larger Petrie dish restricting the available air supply and the third dish [C] was left open to the atmosphere. The dishes were examined after a period of 24 h. The polymer in dishes [A] and [C] had polymerized, whereas that in dish [B] was still uncured. Heating dish [C] failed to convert the mixture to a solid polymer and an infrared spectrum was taken of the sticky liquid residue which exhibited a strong characteristic absorption of a carbonyl. The dish exhibited a characteristic odour of an aldehyde. Similar experiments have been conducted with other peroxides and the inhibition effect appears to be essentially independent of the peroxide, although the efficiency of creation of the aldehyde depends on the ease with which the peroxide can interact with the cobalt salt.

The aerobic oxidation of styrene using Co(III) catalysts has been reported previously,[31–38] A redox active Co(II) has been reported to be able to a 96% conversion of styrene to benzaldehyde.[33,34] The efficiency of the reaction is increased by lowering the temperature and is optimum with low oxygen pressures.[34–38] At high concentrations the benzaldehyde can bind to the cobalt complex and block further reaction. The catalysts used in the benzaldehyde synthesis are different form those used in the polymerization process but the detection of aldehyde is consistent with an aerobic oxidation process occurring. Subsequent poisoning of the catalyst and consumption of the peroxide without effective initiation of the polymerization are all a result of the presence of this completing reaction.

Double peaks observed in the DSC measurements have been reported for the polymerization of vinyl ester and attributed to a redox process at lower temperatures and decomposition of the peroxide at higher temperatures. The average value of the activation energy of the second peak is 89.4 kJ/mol and that of the second peak, depends on the heating rate, but has a value of 43.1 kJ/mol.[35,36] It is probably that the apparent high temperature inhibition indicates the loss of efficiency of the redox catalysts due to poisoning combined with the effects of a dramatic increase in the viscosity slowing the process

and consumption of peroxide by the lower temperature competing reactions. The second peak is consistent with the thermal decomposition of the peroxide initiating a radical reaction.

CONCLUSIONS

This study demonstrates that the Co catalyzed redox polymerization of 4-methylstyrene is a complex process. At low temperature the possibility of oxidation of the vinyl monomer to acetophenone is possible. The aldehyde produced can poison the catalysts and consume the peroxide without involving initiation of polymerization. The DSC traces exhibit double peaks indicating the potential of more than one process being involved in the polymerization reaction. The polymerization at intermediate temperature $\sim 90°$C appears to be influenced by rapid increases in molecular weight leading to the creation of conditions where viscosity starts to influence the rate of reaction. The lower temperature reaction is dominated by the Co catalyzed process whereas the higher temperature processes reflect the increasing contribution arising from peroxide decomposition.

References

1. Sarac, A. S. Redox polymerization. Prog Polym Sci 1999, 24, 1149.
2. Pintauer, T.; Matyjaszewski, K. Chem Society Rev 2008, 37 1087.
3. Kwak, Y.; Nicolay, R.; Matyjaszewski, K. Australian J Chem. 2009, 62, 1384.
4. Whited, M. T.; Grubbs, R. H. Acc Chem Res 2009, 42, 1607.
5. Jijie, K.; Santappa, M.; Mahadevan, V. J Polym Sci A 1966, 4, 377.
6. Jijie, K.; Santappa, M.; Mahadevan, V. J Polym Sci A 1966, 4, 393.
7. Santappa, M.; Mahadevan, V.; Jijie, K. Proc Ind Acad Sci 1966, 64A, 128.
8. Horner, L. J Polym Sci 1955, 18, 438.
9. Horner, L.; Kirmse, W. Annalen 1955, 48, 567.
10. Parshall, G. W.; Ittel, S. D. Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes, 2nd ed; John Wiley and Sons Inc.: New York, 1992, pp 238–240.
11. Wu, X. A. E. V.; Gorden, A. E. V. Eur J Org Chem 2009, 4 503.
12. Eaton, D. R.; O'Reilly A. Inorg Chem 1987, 26, 4185.
13. Wilkins, R. G. Uptake of Oxygen by Cobalt(II) Complexes in Solution. In Advances in Chemistry; Dessy, R., Dillard, J., Taylor L., Eds.; American Chemical Society: Washington DC, 1971; Vol.100, pp 111–134.
14. Emanuel, N. M.; Maizus, Z. K.; Skibida, I. P. Angew Chem Int Ed 1969, 8, 97.
15. Chuev, I. I.; Shushunov, V. A.; Shchennikova, M. K.; Abakunoov, G. A. Kinet Katal 1969, 10, 75.
16. Chuev, I. I.; Shushunov, V. A.; Shchennikova, M. K.; Abakunoov, G. A. Kinet Katal 1970, 11, 426.

17. Haber, F.; Weiss, J. Naturwissenschaften 1932, 20, 948.
18. Kamiya, Y.; Ingold, K. Can J Chem 1964, 42, 2424.
19. Black, J. F. J Am Chem Soc 1978, 100, 527.
20. Affrossman, S.; Collins, A.; Hayward, D.; Trottier, E.; Pethrick, R. A. J Oil Col Chem 1989, 72, 452.
21. Harris PG, Houghton RP, Taylor PL, Polyhedron 1997, 16, 2651.
22. Barreto, W. J.; Ando, R. A.; Santos, P. S.; Silva, W. P.; Spectrochimica Acta Part A 2007, 68, 612.
23. Lu, Y-H, Lu, Y-W.; Wu, C.-L.; Shao, Q.; Chen, X-L. Bimbong, R. N. B. Spectrochimica Acta Part A 2006, 65, 695.
24. Bottcher, A.; Takeuchi, T.; Hardcastle, K. I.; Meade, T. J.; Gray, H. B. Inorg Chem 1997, 36, 2498.
25. Gatta, G. D.; Richardson, M. J.; Sarge, S. M.; Stølen, S. Pure Appl Chem 2006, 78, 1455.
26. Lucas, J. C.; Borrajo, J.; Williams, R.J. J. Polymer 1993, 34, 3216.
27. Kennedy, G. T.; Morton, F. J Chem Soc 1949, 2383.
28. Corrado, L. C. J Phys Chem 1969, 50, 2260.
29. Assche, G. V.; Hemelrijck, A. V.; Rahier, H.; Mele, B. V. Thermochimica Acta 1995, 268, 121.
30. Mallégol J, Lemaire J, Gardette J-L. Prog Org Coat 2000, 39, 107.
31. Raja, R.; Sankar, G.; Thomas J. M., Chem Commun 1999, 829.
32. Suprun, W. Chemische Technik 1997, 49, 67.
33. Tang, J.; Yang, X-L.; Zhang, X-W.; Wang, M.; Wu, C-D, Dalton Trans 2010, 39, 3396.
34. Wang, C. C.; Chen, H. C.; Bin, H. H.; Chen, C. Y. Polymers Adv Technol 2003, 14, 349.
35. Gao, D.; Gao, Q. Catal Commun 2007, 8, 681.
36. Martin, J. L. Polym Eng Sci 2007, 47, 62.
37. Choudhary, V. R.; Jha, R.; Jana, P. Catal Commun 2008, 10, 205.
38. Lin, Y. H.; Williams, I. D.; Li P. Appl Catal A 1997, 150, 221.