Grafting of polystyrene on to poly(vinyl alcohol) (PVA) by a PVA–CuCl$_2$ complex initiating system in an aqueous medium

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(Received 12 August 1992; revised 27 January 1993)

Dispersion polymerization of styrene in an aqueous medium using poly(vinyl alcohol)–copper(II) chloride (PVA–CuCl$_2$) produces grafted chains on PVA in addition to the dispersion of polystyrene. The polymerization kinetics are found to be greatly affected by the amount of poly(vinyl alcohol), the amount of carbon tetrachloride, the pH of the initial solution and the reaction temperature. A typical plot of percentage weight increase of polymer *versus* time of polymerization shows a rapid increase after an induction time. This induction time is postulated to occur because of the formation of PVA-*g*-polystyrene, which, owing to thermodynamic factors, diffuses to the monomer droplet or polymer particle interphase. We determined the molecular weights of the homopolymers and the grafted polystyrene and it was found that the molecular weight of the latter is always higher. The particle size distribution undergoes a drastic narrowing owing to the formation of the grafted copolymer. Existing theories for dispersion and emulsion polymerization fail to explain the experimental data, and the complexity of the mathematical modelling of this process is indicated.

(Keywords: grafting; poly(vinyl alcohol); polystyrene)

INTRODUCTION

Graft copolymers are branched polymers having a backbone of one polymeric species and one or more side chains of another polymeric species. These copolymers show specific properties which have led to their use in a number of important applications such as emulsifiers, surface-modifying agents and compatibilizers in polymer blends[1]. When present in small amounts in materials, graft copolymers improve the physical properties of the host material by reducing the tendency towards phase separation[2].

The chemistry of graft copolymer formation has been discussed elsewhere[1,2]. In the 'grafting from' process, active sites are generated on the polymer chain which initiate the polymerization of the second monomer. In the 'grafting onto' process, a polymer backbone having reactive functional groups combines with another polymer molecule having reactive sites at its ends to give the graft copolymer. Lastly, in the 'grafting through' process, a growing polymer chain of one kind reacts with the pendant unsaturation of another. Besides these, grafting can also be effected by gamma irradiation of a polymer chain, chain transfer by a suitable transfer agent, photochemical synthesis, mechanical degradation, ionic synthesis and so on. Of these methods, the chain transfer reaction is the most common process for producing graft copolymers[3], where chain transfer to a preformed polymer present in the reaction mixture occurs through monomer, solvent, or chain transfer agent, giving rise to radical formation on the backbone where grafting can take place.

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Because of the interesting properties of the graft copolymers, the literature is full of studies of these materials and their kinetics of formation[4–33]. Grafting on to poly(vinyl alcohol) gives a variety of materials and their methods of preparation have been reported[34–39]. A solution of cerium(IV) ammonium nitrate in nitric acid has been used in conjunction with a solution of acrylamide and poly(vinyl alcohol) in water[37]. Experiments were carried out at 20°C for 1 h in a nitrogen atmosphere and the polymer formed was precipitated in acetone. The cerium(IV) salt forms a redox system with organic reducing agents such as poly(vinyl alcohol) and oxidation proceeds by single-electron transfer, forming free radicals on the PVA chain. This method gives the graft copolymer in addition to the homopolymer. A graft copolymer of PVA has also been made by adding vinyl acetate monomer and aqueous potassium persulfate (KPS) initiator to a stirred solution of PVA and sodium carbonate[38]. The reaction was carried out at 80°C and the graft copolymer was detected by turbidimetric titration, paper chromatography and continuous gradient elution chromatography. It was proposed that the initiating radical from the ammonium persulfate catalyst attacks the poly(vinyl alcohol) molecules first and produces polymer radicals which give graft copolymers. Ikada et al.[39] have studied the graft copolymerization of poly(vinyl alcohol) and methyl methacrylate (MMA). Potassium persulfate initiator was dissolved in an aqueous solution of PVA at 0°C to avoid decomposition. Polymerization was carried out in two different ways: with water-swollen PVA film containing potassium persulfate, and with PVA solutions containing KPS in water and dimethyl sulfoxide (DMSO). The reaction in

aqueous medium was carried out at 60°C but in DMSO the temperature was varied from 30°C to 80°C.

The poly(vinyl alcohol)–copper(II) chloride complex can initiate polymerization of vinyl monomers and the factors affecting the formation of the PVA–Cu(II) complex have been studied. This complex is a semiconducting polymer and its electrical properties have been reported[40–44]. The polymerization of vinyl monomers using the PVA–Cu(II) complex as catalyst has also been reported[45–47]. The polymerizations were carried out in sealed tubes which contained vinyl monomer (styrene/methyl methacrylate/acrylonitrile), carbon tetrachloride and an aqueous solution of the complex. The effects of the [Cu(II)]/[OH⁻] ratio, pH, temperature of the system and the degree of polymerization of PVA on the conversion have been reported. Formation of the PVA–Cu(II) complex has been shown to occur when a copper(II) salt solution (nitrate or chloride) is added to an aqueous solution of PVA and sodium hydroxide at a pH higher than 5.7. This complex initiating system has recently gained considerable importance in polymer coatings[40]. The PVA molecules can be easily adsorbed on to a surface (say calcium carbonate) and the resulting thin layer is capable of initiating polymerization of monomers directly from the surface. Goddart *et al.*[40] have reported improved mechanical properties for the coating and they attribute these improvements to the formation of polymer grafts on PVA. They report that PVA does not get grafted if the initiating system is in solution or an aqueous medium.

In this paper, we report the dispersion polymerization of styrene by the PVA–Cu(II) initiating system. We have worked out an experimental technique for separating grafted PVA from the mixture of homopolymeric poly(vinyl alcohol) and polystyrene. We first established that there is no polymerization without carbon tetrachloride. This observation is not consistent with the initiating mechanism proposed in earlier works. Using the experimental technique developed in this work, we determined the masses of homopolymeric poly(vinyl alcohol), homopolymeric polystyrene and graft copolymer. Results show that the amount of polystyrene formed first rises but then falls with increasing polymerization time. The amount of grafted PVA continues to increase and for long times in the reaction mass grafted PVA is present predominantly. This is an interesting experimental observation in that it indicates a convenient method of producing the graft copolymer relatively free from its homopolymers. The study of the rate of polymerization shows that there is an induction time during which the rate is slow, but for times beyond this polymer formation is fairly rapid. With increase in pH and temperature of the reaction mass the induction time falls.

The polymer formed in this polymerization is in the form of a dispersion in water and the reaction mass is highly heterogeneous. Using a Coulter counter we studied the particle size distribution (*PSD*) and found that for short polymerization times the *PSD* is extremely broad. However, after about two hours of polymerization, the *PSD* becomes considerably narrower. Several theoretical and experimental studies have been reported on dispersion and emulsion polymerizations[48–64] and it is well known that the *PSD*s in the former are considerably broader than those in the latter. In our studies, the grafting of PVA occurs continuously and is known to stabilize the dispersion of polystyrene particles. The narrowing of the *PSD* in our experiments further confirms the formation of grafted poly(vinyl alcohol). We prepared computer programs based on theories of emulsion and dispersion polymerization and attempted to explain the experimental data collected in this work. The existing theories were found to be inadequate and we have attempted to elucidate the difficulties of mathematically modelling this complex polymerization system.

EXPERIMENTAL

Reagents

The reagents and chemicals used in our experiments were analytical reagent grade poly(vinyl alcohol), styrene, carbon tetrachloride, fused calcium chloride, copper(II) chloride, sodium hydroxide and acetone. Styrene contained a hydroquinone inhibitor which was removed by washing three times with 0.1 N NaOH and three times with distilled water in a separating funnel. The absence of NaOH from styrene was confirmed by red litmus paper. After this, pellets of fused calcium chloride were added to the washed styrene to remove trace amounts of water. The dry styrene was subsequently stored in a freezer before use.

Preparation of the PVA–Cu(II) complex[40]

PVA was dissolved in distilled water with stirring. A known amount of aqueous copper(II) chloride solution was then added and the mixture was stirred for at least four hours. The PVA–Cu(II) complex was formed on addition of sodium hydroxide solution and the mixture was stirred for several more hours. The pH of the complex was then adjusted by adding more sodium hydroxide solution and the mixture was allowed to stand overnight at room temperature before polymerization was attempted.

Separation of PVA graft copolymer[5]

The samples collected from the reactor were further analysed to ascertain the amounts of graft copolymers and homopolymers. The total polymer from each sample was obtained by adding an excess of acetone. The mixture of polymers was then filtered and dried. To a known mass of polymer, a stock solution (consisting of equal quantities of methyl ethyl ketone (MEK) and distilled water) was added. The contents were gently heated until a macroscopically homogeneous (although turbid) solution was formed. This solution was subsequently centrifuged for one hour at 10 000 rev min⁻¹ at 25°C. The seemingly homogeneous solution split into three phases under centrifugation. The upper, MEK-rich phase contained polystyrene (PS) homopolymer, the middle layer contained swollen graft copolymer and the lower, water-rich phase carried the ungrafted poly(vinyl alcohol). The phases were separated and the graft copolymer fraction was again treated with the stock solution. The procedure described above was repeated at 40°C to ensure complete removal of homopolymers. The collected phases were dried in an oven and weighed.

Oxidative degradation of PVA[40]

Hydrolysis of PVA using potassium dichromate(VI) solution has been described in the literature. We found that within one hour PVA was completely degraded. To
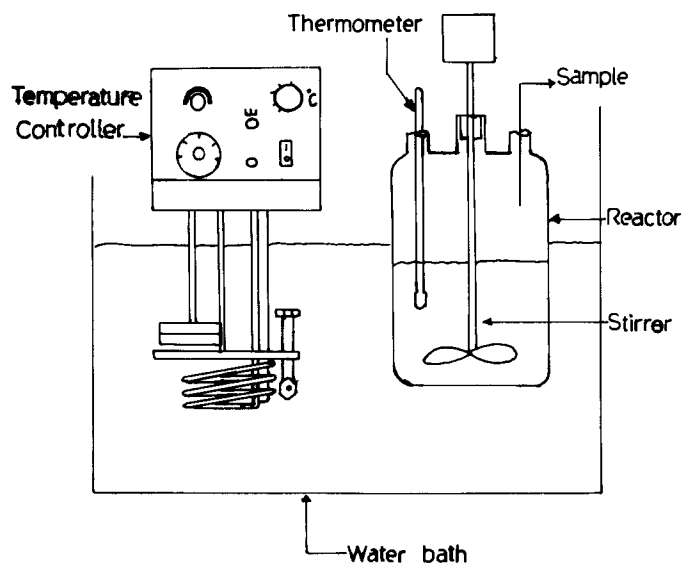
Figure 1 The experimental set-up used in our study

see if this dichromate(VI) solution degraded polystyrene, we left the polymer overnight in it and found that it produced no effect on the polystyrene molecular weight (determined by viscometry). In order to determine the molecular weight of the branches on PVA, the graft copolymer was treated with sodium dichromate(VI) solution overnight. The polymer was separated using methanol and dried. The viscometric method was then used to determine the molecular weight of the grafts.

Experimental set-up for dispersion polymerization

A 500 ml, four-necked glass reactor fitted with a stirrer was kept in a water bath with a temperature controller as shown in *Figure 1*. The reactor was purged with nitrogen before 100 ml of purified styrene were added, along with a given amount of carbon tetrachloride. Finally, 250 ml of the PVA–Cu(II) complex solution were added to the reactor. A 20 ml sample was withdrawn every half hour. The pH of the sample was measured by a suitable pH meter and each sample was added to an excess of acetone for removal of the polymer. The precipitated samples in acetone were kept at 0°C overnight to ensure total precipitation. The precipitated polymers were filtered and then dried on preweighed Petri dishes. These samples were kept inside an oven at 40°C for 24 hours and then weighed. In our study, we investigated the effects of parameters like temperature, quantity of carbon tetrachloride in the reaction mixture, pH of the reaction mixture and the initial weight of homopolymer on the polymerization process.

RESULTS AND DISCUSSION

The PVA–CuCl₂ complex has been studied previously as an initiator in free radical polymerization and these studies report negligible formation of the branched copolymer of PVA. In our studies, we carried out the dispersion polymerization of styrene with the PVA–CuCl₂ complex dissolved in water. We successfully investigated a means of enhancing branching and studied the effects of variables like temperature, pH, poly(vinyl alcohol) concentration and carbon tetrachloride concentration on the process of polymerization. We increased the temperature of polymerization and the reaction time was

raised to as much as 24 hours for different runs. The copolymer yield was found to increase considerably. For example, the branched polymer formation increased to as high as 450% in four hours at 85°C.

The polymerization of styrene by the PVA–Cu(II) complex yields the product as a polymer dispersion and is found to be greatly affected by the reaction temperature (*Figure 2*). We obtained results for temperatures between 60°C and 85°C, keeping other reaction variables (like initial pH, CCl₄ and PVA concentrations) of the system constant. Unlike a typical emulsion polymerization, initiation by the PVA–Cu(II) complex has an induction time during which there is negligible polymerization. This induction time decreases as the temperature is increased, and is nearly zero for the experimental runs taken at 85°C. After the induction period, polymerization picks up rapidly and shows a very high weight increase in polymer formation. The reaction mass is a polymer dispersion and is highly heterogeneous with monomer droplets dispersed in it. The role of diffusion of the reacting species in dispersion polymerization is well established and in the following we explain the phenomenon of the induction time along this line[64]. The PVA and the PVA–Cu(II) complex[40] (shown in *Figure 3*) are in the water phase and the carbon tetrachloride molecules present in the monomer droplet phase must diffuse out to the water phase and initiate the polymerization. The PVA–Cu(II) complex radicals thus generated begin to add on to the monomer in the water phase. Owing to the incompatibility of the polystyrene branches on it, the grafted PVA migrates to the droplet surfaces for thermodynamic stability and would prefer to have the branches hanging into the monomer droplet phase. The PVA–Cu(II) complex is expected to propagate in the water phase at a much slower rate because of the very low concentration of styrene in water. The migration of growing, branched PVA–Cu(II) complex radicals and their accumulation in the monomer droplets to a sufficiently high concentration through diffusion are expected to take some time and are proposed to be responsible for the induction time. As the
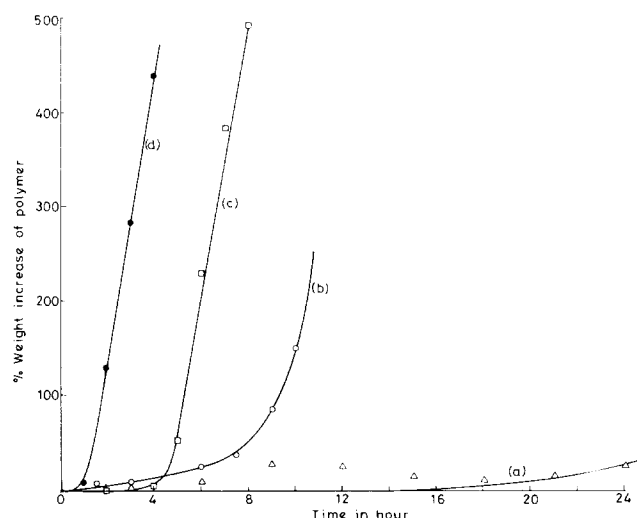

Figure 2 Effect of temperature on the percentage weight increase of polymer. The initial pH of the reaction mass was 8.1. The reaction mixture comprised: PVA–Cu(II) complex solution (250 ml), styrene (100 ml), CCl₄ (50 ml). Composition of PVA–CuCl₂: PVA (100 g) in water (300 ml); CuCl₂ (0.1657 g) in water (100 ml); NaOH added depending on the required pH of the complex. Temperature: (a) 60°C; (b) 70°C; (c) 80°C; (d) 85°C
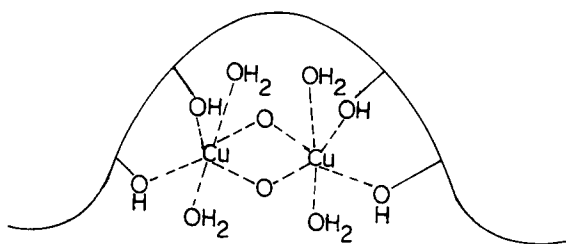
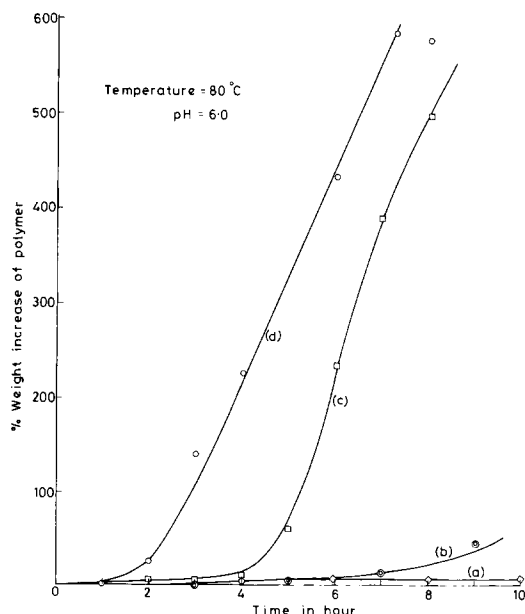**Figure 3** Structure of the PVA–Cu(II) complex

Figure 4 Effect of CCl₄ concentration on the percentage weight increase of polymer (the rest of the reaction mixture was the same as that given for *Figure 2*). CCl₄ concentration: (a) 0; (b) 25 ml; (c) 50 ml; (d) 65 ml

temperature of polymerization is increased, the solubility and diffusivity of styrene both increase and lead to a reduced induction time, as observed in *Figure 2*.

We subsequently examined the effect of CCl₄ concentration on the course of polymerization and in *Figure 4* the results are reported. The results show that there is negligible polymerization when there is no CCl₄ and the weight of polymer formed increases with increasing CCl₄ concentration in the system. This indicates that without the interaction between CCl₄ and the PVA–Cu(II) complex there is no initiation of polymerization. Bamford and his group[4,5] have shown that the Cu(II) in the complex is reduced to Cu(I) through electron transfer by CCl₄ and initiation of the polymerization occurs through Cu(I). During the polymerization the pH of the reaction mass changes with time. The changes in pH of the reaction mass with time at different temperatures are shown in *Figure 5*. The pH decreases with increasing polymerization time and approaches an asymptotic value. As the temperature is increased, this asymptotic value is reached at a faster rate. The fall in the pH is attributed to the fact that as CCl₄ reacts with the complex, hydrogen ions are liberated.

We next examined (*Figure 6*) the effect of initial pH on the course of polymerization at 80°C keeping all other variables constant. The pH was adjusted by varying the quantity of NaOH added during the PVA–Cu(II)

complex formation process. It was found that pH has a considerable effect upon the polymerization. In *Figure 6* the curves showing percentage weight increase *versus* time first increase as the pH of the system is increased but then decrease. Earlier studies on PVA complexation have shown that complex formation starts at pH 5.7 and beyond pH 8 complexation is 100%. Hence the increase in the rate of polymerization with increasing pH is expected because of the increase in the PVA–Cu(II) complex concentration in the reaction system. The decrease in the rate of polymerization at a pH lower than 8 is because of the precipitation of the PVA–Cu(II) complex, as reported in earlier studies. In this way a lower effective concentration of growing polymer radicals is achieved. To confirm this, one run was made at 80°C using a PVA–Cu(II) solution containing no NaOH. This gives a pH for the reaction mass of 5.34 and curve (a) in *Figure 7* shows that there was negligible polymerization during the run time studied.

The concentration of PVA in the reaction mass also has an effect on polymerization. *Figure 7* shows the experimental results when the quantity of PVA present in the system is changed. Different curves in the figure
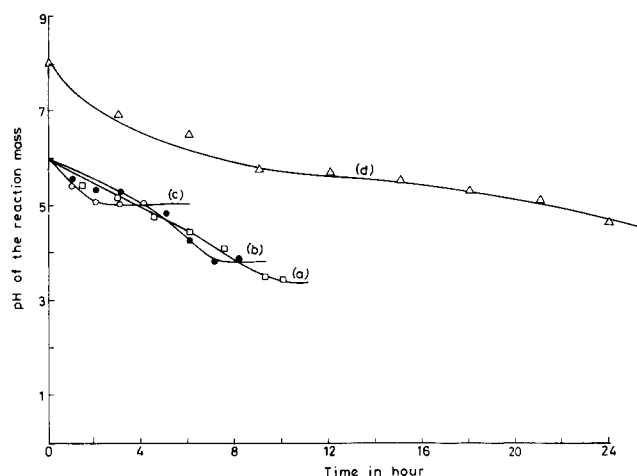

Figure 5 Effect of temperature on the pH of the reaction mass (reaction mixture given in *Figure 2*). Temperature: (a) 77°C; (b) 80°C; (c) 85°C; (d) 60°C
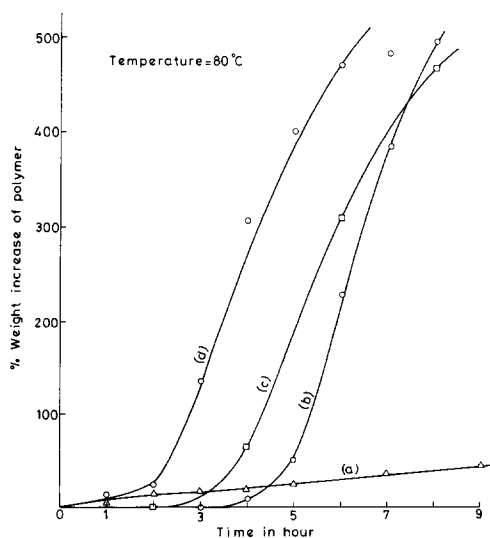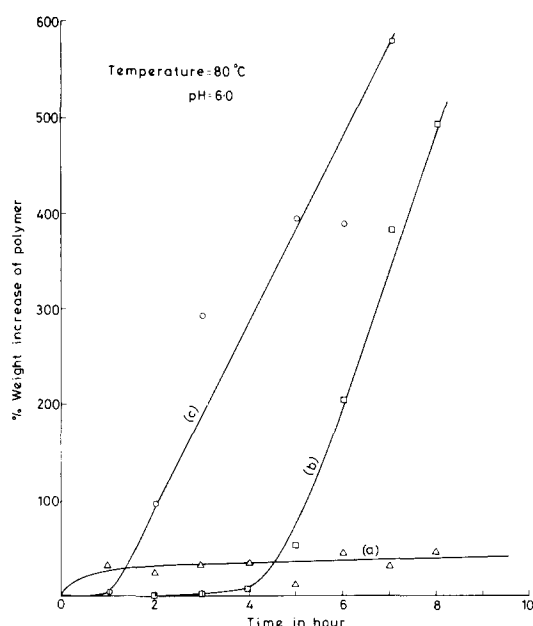

Figure 6 Effect of initial pH of the reaction mass on the percentage weight increase of polymer *versus* time (reaction mixture given in *Figure 2*). pH: (a) 5.35 (no NaOH added); (b) 5.99; (c) 10.69; (d) 6.9

Figure 7 Effect of PVA concentration on percentage weight increase of polymer *versus* time (the rest of the reaction mixture was the same as that given for *Figure 2*). PVA added: (a) 3.125 g; (b) 6.250 g; (c) 9.375 g
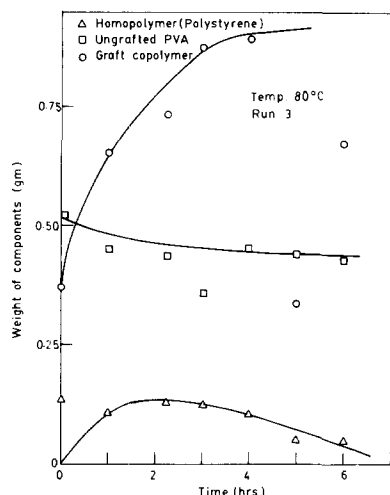

Figure 8 The weights of unreacted PVA, homopolymer polystyrene and graft copolymer formed *versus* time (reaction mixture given in *Figure 2*)

show that the percentage weight increase of the formed polymer increases as the PVA concentration in the system is increased. This is because higher concentrations of PVA give more PVA–Cu(II) complex molecules in the solution, thus giving increased concentrations of polymer radicals in the reaction system. As a result, polymer radicals propagate for longer times to give higher yields.

We carried out the dispersion polymerization of styrene with the PVA–Cu(II) complex initiating system and withdrew samples every hour to analyse for the amount of graft copolymer formed. Each sample was poured into excess methanol to precipitate the entire polymer which was then dissolved in a solvent mixture of water and methyl ethyl ketone as described earlier. After centrifuging the solution, the graft copolymer was removed from the interphase and dried. The results are reported in *Figure 8* as a function of polymerization time and a dramatic rise in the formation of the graft copolymer is seen to occur after one hour of

polymerization. The figure suggests that after six hours of polymerization there is a negligible amount of homopolymer and most of the product is grafted. If one observes the amount of ungrafted poly(vinyl alcohol), it appears that there are several branches of polystyrene per PVA chain. It may be recalled that once the grafted copolymer of PVA is initiated it has a natural tendency to migrate towards the interphase of the monomer droplets or the polystyrene particles. Once it has reached the interphase, the growth of the polystyrene branches would occur with the monomer molecules existing therein. It is likely that the polymer particles as a whole may remain stuck to the copolymer branches through chain entanglements. The fall in the amount of homopolymer formed for long polymerization times might also suggest that our scheme for separating graft copolymer from the entangled polymer particles is not sufficient. It is possible to determine the viscosity average molecular weight of the grafted polystyrene chains and the results are in *Figure 9*. For comparison we have also given the molecular weight of the homopolymer. It is seen that the grafted chains always have a higher molecular weight compared to the homopolymers. Over short polymerization times, the molecular weights for both the grafted chains and the homopolymers are essentially constant; however, for long polymerization times the molecular weights drift to higher asymptotic values, as seen in the figure.

We have already mentioned that the reaction mass is a dispersion of polymer and initially it consists of a water phase and a monomer droplet phase. Owing to its low solubility in water, styrene remains as droplets dispersed in the system (*Figure 10*). The PVA–Cu(II) complex is soluble in water and is therefore present in the water phase. Similarly, owing to its higher solubility in styrene, CCl_4 remains mostly in the droplet phase. For initiation to occur, interaction between the PVA–Cu(II) complex and CCl_4 must occur, which means that CCl_4 must diffuse through the monomer droplet phase to the water phase and then interact with the complex. As soon as this occurs a free radical is produced on the backbone of PVA and the propagation reaction starts in the aqueous phase through styrene reacting with the radical. There exists a thermodynamic equilibrium between the
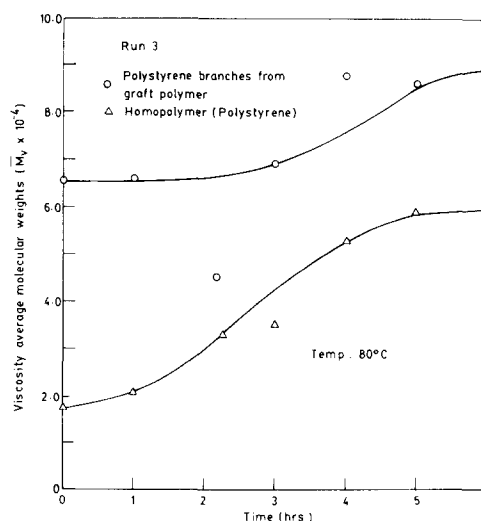
Figure 9 Molecular weights of homopolymer and grafted polystyrene chain *versus* time (reaction mixture given in *Figure 2*)

aqueous and the droplet phases and as soon as the polymerization starts this equilibrium is disturbed[64]. Diffusional gradients for CCl_4 and styrene are immediately set up to supply these to the reacting sites on PVA. Propagation of the PVA free radicals starts by the reaction of monomer with the growth centres and the graft copolymer radicals are formed in this way. The graft copolymer radicals can also diffuse through the aqueous phase to the interphase of the droplets.

The Cu(II) complexes could form on droplet surfaces with the graft copolymer in the following way. The graft copolymer chains on the droplet surface have several unreacted OH groups which can react with copper chloride present in the water phase to give PVA–Cu(II) complexes. From these, free radicals can be generated by CCl_4 present in either the water or the droplet phase. These radicals then propagate in the usual fashion. The polymer radical concentration in the water phase is expected to be higher than in the droplet phase since the concentration of the PVA–Cu(II) complex is higher therein. In addition, owing to the low concentrations of CCl_4 and monomer in the water phase and the slow diffusion process, termination and chain transfer will be pronounced in the water phase. As opposed to this, in the droplet phase propagation will be prominent, giving larger molecules with more branching.

During the dispersion polymerization of styrene, PVA grafted with polystyrene is being formed. Since this serves as an emulsifier, we might expect that the particle size distribution (PSD) should change in nature as the polymerization progresses. To test this, we carried out the polymerization at 60°C using the PVA–Cu(II) initiating system and the results are reported in *Figures 11* and *12*. It can be seen that for short polymerization times the PSD is bimodal, the small initial peak corresponding to the nucleated (or primary) particles and the broader peak corresponding to particles formed through coalescence of these. The PSD for up to 1.5 hours of polymerization shows almost no initial peak and is unimodal. The particle size distributions for samples beyond two hours of polymerization are considerably narrower. This can be easily understood if one refers to *Figure 8*, where it is seen that by this time
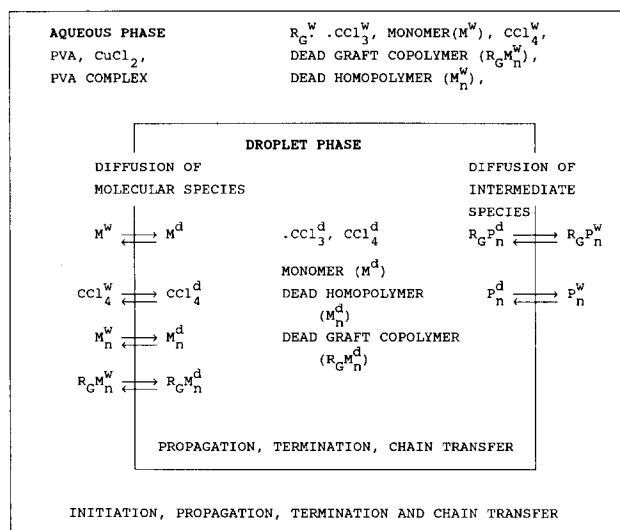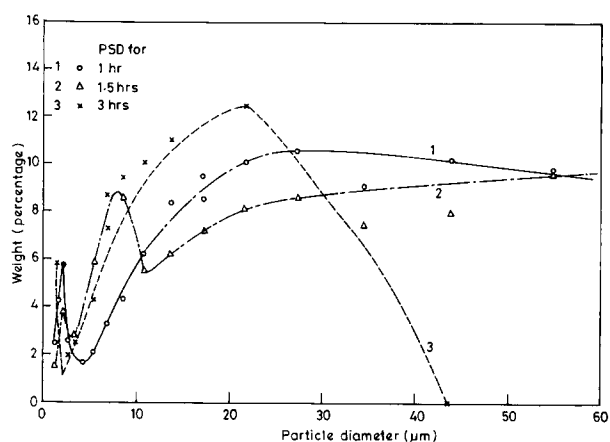

Figure 11 Particle size distribution for short polymerization times
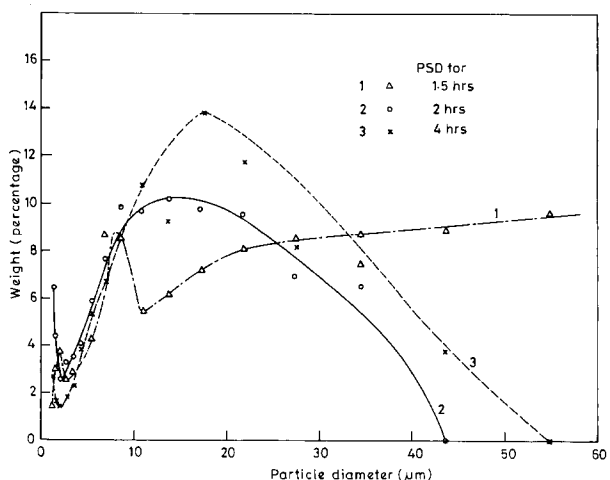

Figure 12 Particle size distribution for long polymerization times

a considerable amount of graft copolymer has been formed. As a result, the nature of the reaction medium changes from a dispersion polymerization to an emulsion polymerization. In the presence of the continuously produced graft copolymer of PVA the very nature of the coalescence and breakage of particles is altered which, to a large extent, controls the PSD. To test whether our system could be described by the existing theories of dispersion and emulsion polymerization, we modified the theories of the kinetic mechanism for the grafting of PVA and implemented them on computer. We found that the results predicted by theory are completely different from the experimentally observed results. All mathematical models of the particle size distribution in emulsion or dispersion polymerization define rate constants k_c and k_b for coalescence and breakage which are assumed not to change with time. This can be so only when the surface characteristics do not change. In the presence of graft copolymer being continuously produced, the rate constants k_c and k_b would be expected to change with time. Since we do not know as yet how k_c and k_b depend on the concentration of the graft copolymer of PVA, a rational mathematical modelling of the system poses great difficulty.

Figure 10 Physical representation of the reaction mass. P_n^d and P_n^w represent growing polymer chains in the droplet and aqueous phases, respectively

CONCLUSIONS

The dispersion polymerization of styrene was carried out using a PVA–CuCl₂ complex initiating system. The

polymerization occurs in the presence of CCl_4 which participates in generating radicals in the reaction mass. There is an induction time which reduces with increasing temperature for the following reasons. Carbon tetrachloride in the droplet phase must diffuse out to the aqueous phase and interact with the PVA–Cu(II) complex to form polymer radicals. As soon as the branches begin to propagate, the graft copolymer of PVA migrates towards the monomer droplet or polymer particle surface where the polystyrene grafts penetrate the particles to give chain propagation. The time taken to build up the concentration of the graft copolymer at the droplet interphase to a sufficient level corresponds to the induction time. The polymerization is affected by the initial pH as well as the amounts of CCl_4 and PVA in the reaction mass, and these effects were described.

The experimental technique reported in the literature was used to separate the graft copolymer of PVA from the reaction mass. Also, the formation of the graft copolymer was determined as a function of time. The experiments showed that for long polymerization times there is a considerable amount of grafting on PVA. Using a Coulter counter, we determined the *PSD* and showed that initially it is extremely broad but as more graft copolymer is formed the *PSD* becomes narrower. The existing mathematical theories predicted results contrary to those observed experimentally in this work. In the presence of the continuously produced graft copolymer, the types of coalescence and breakage are continuously changing with the progress of the polymerization. As a result of this the kinetics cannot be modelled within the available mathematical framework.

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