Radical Entry into Particles During Emulsion Polymerization of Vinyl Acetate

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SYNOPSIS

The entry of free radicals (formed in the aqueous phase) into polymer particles is the subject of the present work. A model has recently been developed based on the postulate that the aqueous-phase growth of the free radicals to a critical size is the rate-determining step for entry. An experimental strategy was devised to study this phenomena. Polystyrene latex with a water-insoluble inhibitor partitioned into the polymer particles was used as seed for secondary polymerization of vinyl acetate. This was done to form and isolate stable oligomers of the critical size. The presence of vinyl acetate oligomers was detected with Fourier transform infrared spectroscopy and thin-layer chromatography. Fast atom bombardment-mass spectroscopy (MS) was used to determine the molecular weights of the oligomers. Though it was not possible to determine the precise size of the vinyl acetate oligomers formed, the MS results show that the number of monomer units in the oligomers has an upper bound of 12–14. The number of units in the oligomer of critical size was estimated to be about 5–6. These experimental results are quite close to model predictions; thus this work helps in corroborating the model. Additional work is necessary to conclusively validate this model. The experimental strategy used in this work has made it possible to determine the approximate size of oligomers formed in the aqueous phase during emulsion polymerization. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Emulsion polymerization is a process for the production of polymer colloids. It consists of free radical reactions with vinyl monomers in a heterogeneous medium. Monomers are dispersed in a continuous phase, commonly water, with oil-in-water emulsifiers. The reaction is normally carried out by employing a water-soluble initiator. The end product is a polymer latex (colloid) which consists of polymer particles dispersed in the continuous aqueous phase. The particles are stabilized by the emulsifier. The latex can be dried to isolate the polymer, but in many cases it is used in the colloid form as a coating, adhesive, or other product.

A water-soluble initiator produces primary free radicals either by chemical reaction, as in the case of redox initiators, or by thermal decomposition. After the particle formation stage (Interval 1) the main locus of polymerization shifts to the interior of the monomer-swollen polymer particles. Since the free radicals are generated in the aqueous phase, they must be transported to and enter the polymer particles. Though a very large number of free radicals are generated in the aqueous phase, not all of them can enter polymer particles and lead to propagation. It has been shown that radical capture efficiencies can be very low.[1,6,15] Since the rate of entry cannot be equated with the rate of free radical generation, the process of entry of free radicals acquires fundamental importance.

The primary free radical is ionic (e.g., the persulfate ion) and hence is unlikely to enter the polymer particle directly. Instead it must add monomer units in the aqueous phase to become sufficiently hydrophobic to be absorbed in a polymer particle.[13] Different theories have been suggested to explain the entry mechanism for these oligomeric free radicals into the polymer particles. The models include

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diffusion control, surfactant displacement, colloidal entry, and collisional entry. None of these models, however, has been found to be totally satisfactory. Maxwell et al. (1991)[12] have proposed a new model for the entry process, in which the aqueous-phase free radicals enter latex particles only when they attain a particular size. Hence it is the rate of growth of aqueous-phase free radicals to this size that is rate-determining for entry of radical species into latex particles. This model offers a better explanation for experimental observations when compared to previously suggested theories, however it must be validated.

This paper describes an attempt to validate this model by experimentally determining the critical size of the oligomeric radicals that enter particles. Information about the size of the entering oligomer will also help in evaluating the other theories of radical entry. An experimental strategy has been developed to isolate the oligomers and determine their molecular weight.

Aqueous-phase Growth Control Model

According to the model proposed by Maxwell et al.,[12] the rate-determining step for free radical capture by latex particles in aqueous-phase propagation to a critical degree of polymerization denoted by z. Mutual aqueous-phase termination of smaller species also occurs. However, when an oligomeric free radical attains the critical size, its capture by a latex particle is essentially instantaneous. This model has been shown to corroborate experimental observations of the entry-rate coefficient as a function of the concentrations of the initiator, surfactant, aqueous-phase monomer, and latex particles, as well as the effect of particle size and ionic strength. The aqueous-growth model considers the following kinetic events involving free radicals in the aqueous phase: initiator decomposition, propagation, bimolecular termination, and entry of free radicals into particles. The model assumes that all entering free radicals are of the same size. The following relationship for the pseudo-first-order entry-rate coefficient is obtained on the basis of this model.

$$\rho = (N_A/N_C)k_p[M_{aq}][M_{z-1}\cdot]$$

where N_A is the Avogadro number, N_C is the number of particles, k_p is the propagation rate constant, $[M_{aq}]$ is the concentration of the monomer in the aqueous phase and $[M_{z-1}\cdot]$ is the concentration of oligomeric free radicals having $(z-1)$ monomer units.

Maxwell et al. have also sought to explain the values obtained for z on the basis of thermodynamics of free radical adsorption. The minimum requirement for a primary free radical generated in the aqueous phase to enter a polymer particle would be for the radical to add sufficient monomer molecules in the aqueous phase to render the resultant oligomeric species surface-active and hence less likely to desorb from the surface of a polymer particle. Surface activity refers to the ability of the oligomeric species to adsorb strongly onto the surface of a polymer latex particle. However at a large enough degree of polymerization the oligomeric species becomes essentially insoluble in water. Maxwell et al.[12] have proposed the following equation for the minimum value of z necessary for surface activity of the oligomeric species starting with a sulfate anion primary free radical.

$$z_{min,surf} = 1 + \text{int}(-23 \text{ kJ mol}^{-1}/\{RT \ln[M_{aq,sat}]\})$$

Here int refers to the integer function which rounds off the quantity in brackets to the lower integer value. The concentration $[M_{aq,sat}]$ is in mol/l. The value of z required for incipient insolubility is given by

$$z_{min,insol} = 1 + \text{int}(-55 \text{ kJ mol}^{-1}/\{RT \ln[M_{aq,sat}]\})$$

Values of $z_{min,surf}$ and $z_{min,insol}$ of oligomers of various monomers with persulfate initiator were estimated by Maxwell et al.[12]

Oligomeric Size

Qualitative and quantitative characterization of oligomers formed in emulsion polymerization have been carried out by a number of researchers. Goodall et al. (1977)[5] report that oligomers of styrene consisted of about four to five units of the monomer. Fitch and Tsai (1971)[4] have studied oligomer formation in the case of methyl methacrylate, using the technique of gel permeation chromatography to determine molecular weights. In the case where low monomer concentration was used in order to prevent particle formation, they found the maximum degree of polymerization to be 65 or 66. This, however, was the size of oligomer required for homogeneous nucleation (self-nucleation). In the case where particles were formed, the maximum degree of polymerization was about 166. Litt et al. (1970)[10] found that the number of monomer units in the case of vinyl acetate was between 50 and 300. This, again, was in the case of self-nucleation. The degree of polymer-

ization is unlikely to be the same in the case of seeded emulsion polymerization without secondary particle formation. Ammerdorffer et al. (1990)[2] used the technique of isotachophoresis for molecular weight determination. They found that the oligomers in the case of surfactant free emulsion polymerization of butadiene consisted of 1–3 monomeric units. The monomer content and conversion were kept low to prevent particle formation.

Water-soluble oligomers produced in the emulsion copolymerization of styrene and acrylic acid have been studied by Wang and Poehlein (1993).[14] They measured oligomer composition, molecular weight, and copolymer sequence distribution for seeded and unseeded systems at varying conversions. They found that the content of acrylic acid in the oligomer increased significantly as the amount of acrylic acid in the monomer feed was increased. The water-soluble oligomeric molecules formed during the preparation of 10/90 acrylic acid/styrene copolymer were found to consist of 6–9 monomer units. Those formed from 40/60 acrylic acid/styrene ratios were comprised of 13–16 monomer units. High concentration of acrylic acid in the monomer mixture leads to a higher number of acrylic acid units in the water-soluble oligomer.

EXPERIMENTAL

Experimental Strategy

A seeded emulsion polymerization without secondary particle formation was employed in this project. Thus the oligomer size obtained was not affected by the kinetics of particle nucleation. Thereby, it becomes possible to study the event of free radical capture by polymer particles in seclusion. It was necessary to devise an experimental strategy that would enable the isolation of oligomers formed during seeded emulsion polymerization. A necessary prerequisite was that the growth of the oligomers had to be curtailed to their critical size. In other words, the propagation of the oligomeric free radical was to be prevented as soon as it attained the critical size which enabled entry into polymer particles.

An experimental strategy, based on a water-insoluble inhibitor which would permit aqueous phase propagation but prevent polymer particle-phase propagation, was visualized. It was thought that if an inhibitor could be selectively located inside the polymer particles, growth of the oligomers within the particles would be prevented or limited. The oligomeric free radical would instantaneously react with the inhibitor and form a low molecular weight species incapable of further propagation. This low molecular weight species could then be isolated and analyzed.

In order for the above strategy to succeed, a water-insoluble inhibitor had to be found. Such a compound would partition almost exclusively in the particle phase with negligible solubility in the aqueous phase. Blackley (1975)[3] indicated that 2,5-di-*tert*-butylhydroquinone has very low water solubility and this species was employed as the water-insoluble inhibitor.

The second important step in this strategy was the isolation of the oligomers, i.e., separation of the oligomeric species from the seed polymer. Obviously, different monomers had to be used for the seed polymer and the secondary polymerization leading to the formation of oligomers. Since chemical separation of two polymeric species was desired, it was decided to use polystyrene for the seed polymer and vinyl acetate for the secondary polymerization. It is possible to separate polystyrene and poly(vinyl acetate) by selectively extracting poly(vinyl acetate) in methanol. Hence the vinyl acetate oligomers could be isolated and analyzed. Maxwell et al.[12] predicted the critical oligomer size for vinyl acetate, which could then be compared with the experimentally determined values.

The most important step in the analysis of the oligomer is the determination of its molecular weight. A technique capable of measuring molecular weights as low as a few hundred daltons was desired, since the predicted values indicate a critical oligomer size consisting of 7–8 monomer units. The common techniques used in the measurement of polymer molecular weights, such as viscometry, GPC, and light scattering, are unable to measure such low molecular weights. Mass spectroscopy measures the absolute molecular weights of compounds. Though originally developed to study low molecular weight compounds, it has been extensively used to measure molecular weights as high as 10000 daltons.[11] Mass spectroscopy has been used to measure the molecular weights of polymeric oligomers.[8,9] Hence this method was chosen to measure the molecular weights of the vinyl acetate oligomers.

Materials

Acetone: CH_3COCH_3 (MW = 58.08); Certified ACS.; supplied by Fisher Scientific Company, Fair Lawn, NJ. Amberlite MB-3 monobed resin: mixture of Amberlite IR-120 cation exchange resin (hydro-

gen form) and Amberlite IRA-410 anion exchange resin (hydroxide form); supplied by Sigma Chemical Company, St. Louis, MO. 2,5-Di-*tert*-butyl hydroquinone: $C_{14}H_{22}O_2$ (MW = 222.33); purum grade; supplied by Fluka Chemika, Switzerland. Hydroquinone: $C_6H_4(OH)_2$ (MW = 110.11); purified; supplied by Fisher Scientific Company, Fair Lawn, NJ. Chloroform: $CHCl_3$ (MW = 119.38); HPLC grade; supplied by Aldrich Chemical Company, Milwaukee, WI. Methanol: CH_3OH (MW = 32.04); acetone free, absolute; supplied by Fisher Scientific Company, Fair Lawn, NJ. Precoated TLC sheets: silica gel on polyester; supplied by Aldrich Chemical Company, Milwaukee, WI. Potassium persulfate: $K_2S_2O_8$ (MW = 270.33); certified grade; supplied by Fisher Scientific Company, Fair Lawn, NJ. Sodium dodecyl sulfate: $CH_3(CH_2)_{10}CH_2OSO_3Na$ (MW = 288.38); specially pure; supplied by BDH Limited, Poole, England. Styrene: $C_6H_5CH{=}CH_2$ (MW = 104.15); inhibited with 10–15 ppm 4 *tert*-butylcatechol; Aldrich Chemical Company, Milwaukee, WI; vacuum distilled before use. Vinyl acetate: $CH_3COOCH{=}CH_2$ (MW = 86.09); inhibited with 3–5 ppm hydroquinone; supplied by Aldrich Chemical Company, Milwaukee, WI; vacuum distilled before use. Nitrogen: N_2; high purity; supplied by Holox Company, Atlanta, GA. Deionized water: Used as received from the deionization unit in the lab.

Operating Procedure

Emulsion polymerizations were carried out in a 1.0 L 3-neck glass reactor. A paddle agitator with a Teflon blade was used as a stirrer. The reaction temperature was maintained with a constant temperature water bath. The reaction mixture (before addition of monomer) was purged with nitrogen. The nitrogen purge line was pulled above the level of the emulsion after the monomer addition to prevent polymer from coagulating at the interface of the nitrogen bubbles. Tap water was constantly passed through the condenser to prevent the loss of monomer during the reaction.

Table I Recipe for Styrene Seed Polymerization

Recipe for Polystyrene Seed Latex	
Water	500 g
Sytrene	194 g
Potassium persulfate	0.676 g
Sodium dodecyl sulfate	2.884 g
Temperature	Varied from 50°C to 60°C

Table II Recipe for Secondary (Vinyl Acetate) Polymerization

Recipe for Secondary Polymerization	
Seed latex	557 g
Solid content in seed latex	31 g
Vinyl acetate	7.76 g
2,5-di-*tert* butyl hydroquinone (inhibitor)	0.005 g
Potassium persulfate	0.7 g
Temperature	50°C

Preparation of Seed

Polystyrene seed latex was made using the recipe shown in Table I. Potassium persulfate was used as the initiator and sodium dodecyl sulfate as the emulsifier. The reaction was carried out to nearly 100% conversion. The reaction time was around 24 h. The unreacted styrene was stripped off by bubbling nitrogen through the latex.

Secondary Polymerization

The secondary polymerization involved swelling of the polystyrene seed with vinyl acetate, followed by reaction in the presence of the water-insoluble inhibitor (2,5-di-*tert* butylhydroquinone). The inhibitor is oil soluble and could dissolve in the monomer droplets. Hence it was necessary to prevent the formation of monomer droplets during secondary polymerization. This was achieved by limiting the amount of monomer used and by removing the soap from the seed latex. A monobed ion exchange resin (Amberlite MB-3) was used for this purpose. To aid the transfer of the inhibitor across the aqueous phase and into the polymer particles, it was dissolved in about 50 ml acetone. This solution was added to the seed latex with constant agitation. The reaction mixture was equilibrated for about 8 h. The acetone was then removed by a nitrogen purge. The second-stage monomer (i.e., vinyl acetate) was then added at a very slow rate with constant stirring to prevent the formation of droplets. The reaction mixture was again equilibrated for about 2 h. The initiator (potassium persulfate) was added as an aqueous solution at a slow rate with low stirring speeds to prevent "shocking" of the latex. The reaction was allowed to proceed for about 4 h. Finally the reaction was stopped by the addition of a small amount of hydroquinone.

The amount of vinyl acetate had to be such that it caused sufficient swelling of the seed particles but at the same time prevented the formation of mono-

mer droplets. The amount of vinyl acetate added was one-fourth the solid content of the polystyrene seed latex. Proper amounts of the initiator and inhibitor were determined by trial and error. If the inhibitor were added in excess, it could kill the reaction because of the minute amount partitioned into the aqueous phase. The correct quantities of these compounds were determined by carrying out the reaction and subsequently detecting the presence of oligomers. A successful recipe for the secondary polymerization is shown in Table II.

Analysis of Oligomers

After the completion of the reaction the polymer latex was dried. The oligomeric poly(vinyl acetate) was extracted from the dry polymer using methanol. A Soxhlet extractor was employed for this purpose.

Fourier transform infrared (FTIR) spectroscopy was used to detect the presence of vinyl acetate oligomers in the methanol solution. A Nicolet 520 FTIR single-beam spectrometer and a Perkin–Elmer 1600 series FTIR double-beam spectrometer were used for this purpose. The results obtained by FTIR spectroscopy were confirmed by the use of thin-layer chromatography (TLC). TLC is a very sensitive method and can be used to detect the presence of individual polymers in a mixture. Precoated TLC sheets, which consisted of silica gel supported on polyester, were used. These sheets were pretreated with a mixture of equal parts of chloroform and methanol. The sample solution (the methanol extract) was applied at one end of the plate. The plate was then developed using an appropriate solvent, either methanol or chloroform. Inagaki and Tanaka[7] indicate that poly(vinyl acetate) can be developed with methanol and polystyrene with chloroform. Development was continued until the solvent front traversed two-thirds of the plate. The mobile phase was removed from the plate by drying in an oven for about 5 minutes. The plates were then placed in a box containing iodine crystals in order to stain the component zones. The various zones were marked after staining, since iodine staining lasts for only a short time.

The final step in the analysis of oligomers consisted of mass spectroscopy (MS). Fast atom bombardment (FAB) was used as the ionization method in the MS analysis. The bombarding beam in FAB consists of atoms of high translational energy. The compound of interest is ionized by this high-energy beam. In FAB the molecular ion $[M^+]$ is not usually seen, but adduct ions (such as $[M + H]^+$) are prominent, as are fragment ions. A VG Analytical 70-SE mass spectrometer was used for analysis. The instrument specifications were: high resolution, 2-sector, forward geometry, 11-250J data system. The FAB analysis was done at resolutions of 1000 and 1500.

RESULTS AND DISCUSSIONS

A standard polystyrene IR spectrum shows very strong absorption peaks at 699 cm^{-1} and 758 cm^{-1}. These arise from the out-of-plane deformation modes of the hydrogen atoms attached to the aromatic ring. Another strong absorption peak at 1600 cm^{-1} corresponds to the aromatic "breathing" vibration. Five smaller bands at 1670, 1740, 1800, 1870, and 1940 cm^{-1} indicate monosubstituted aromatic rings. The strong peaks between 2800 and 3000 cm^{-1} indicate saturated C—H groups and those between 3000 and 3100 cm^{-1} denote =C—H groups. The polystyrene IR spectrum also shows strong peaks at 540, 1028, 1454, and 1495 cm^{-1}.

A standard poly(vinyl acetate) spectrum shows very strong bands at 1237 and 1737 cm^{-1}. The latter peak is the C=O stretching mode of a carbonyl compound. The peak at 1237 cm^{-1} is indicative of an acetate group. The spectrum also shows strong absorption at 1373 and 1022 cm^{-1}.

Figure 1 shows the IR spectrum of a dry polymer sample before extraction with methanol. Thus this sample is likely to contain a large quantity of polystyrene. This spectrum shows strong peaks at 699, 1452, 1493, 2922, and 3025 cm^{-1}. It also shows smaller peaks between 1600 and 1900 cm^{-1}. There is no peak at 1237 and 1737 cm^{-1}. This indicates either that this sample consists solely of polystyrene or that the poly(vinyl acetate) content is very small. This sample was obtained during the trial-and-error runs carried out to determine proper amounts of initiator and inhibitor to be used for favorable results. The dry polymer in this case was extracted with methanol and the methanol solution was dried. The residue was dissolved in benzene and a film was formed on a KBr disc using the benzene solution. The spectrum for this film is shown in Figure 2. This spectrum shows the characteristic peaks for polystyrene only and indicates that some polystyrene was also extracted into the methanol.

Figures 3 and 4 show the IR spectra of films made from methanol extract solution. Figure 3 shows the peaks distinctive of polystyrene. In addition to these peaks it shows moderately strong peaks at 1217, 1365, and 1736 cm^{-1}. These peaks indicate the presence of poly(vinyl acetate). However the amount

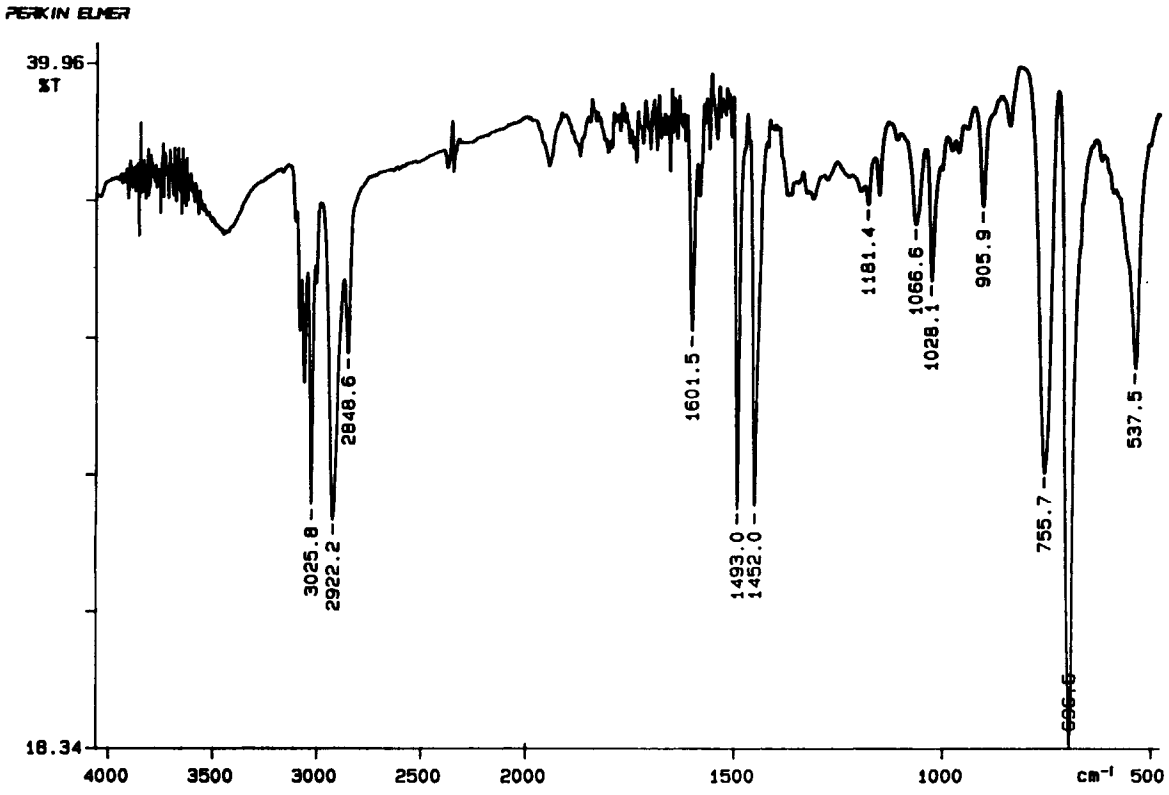

Figure 1 Infrared spectrum of dry polymer sample before extraction.

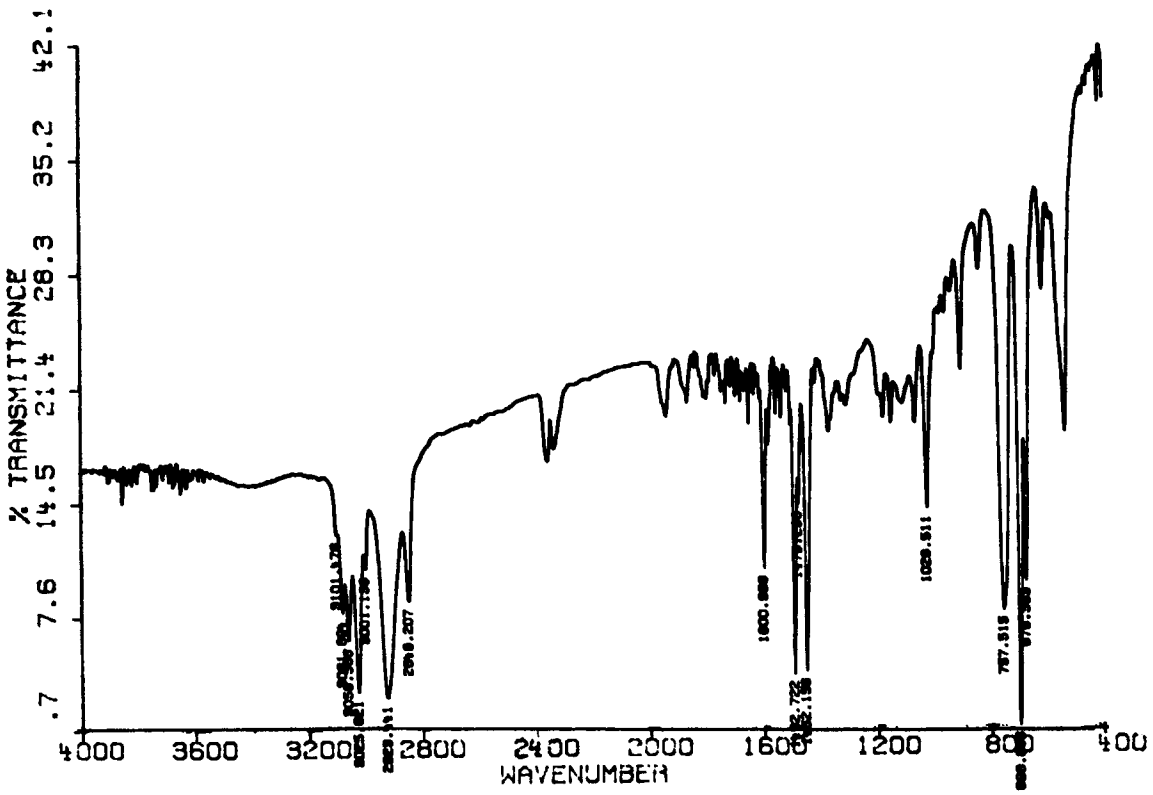

Figure 2 Infrared spectrum of film of methanol extract on KBr disc.

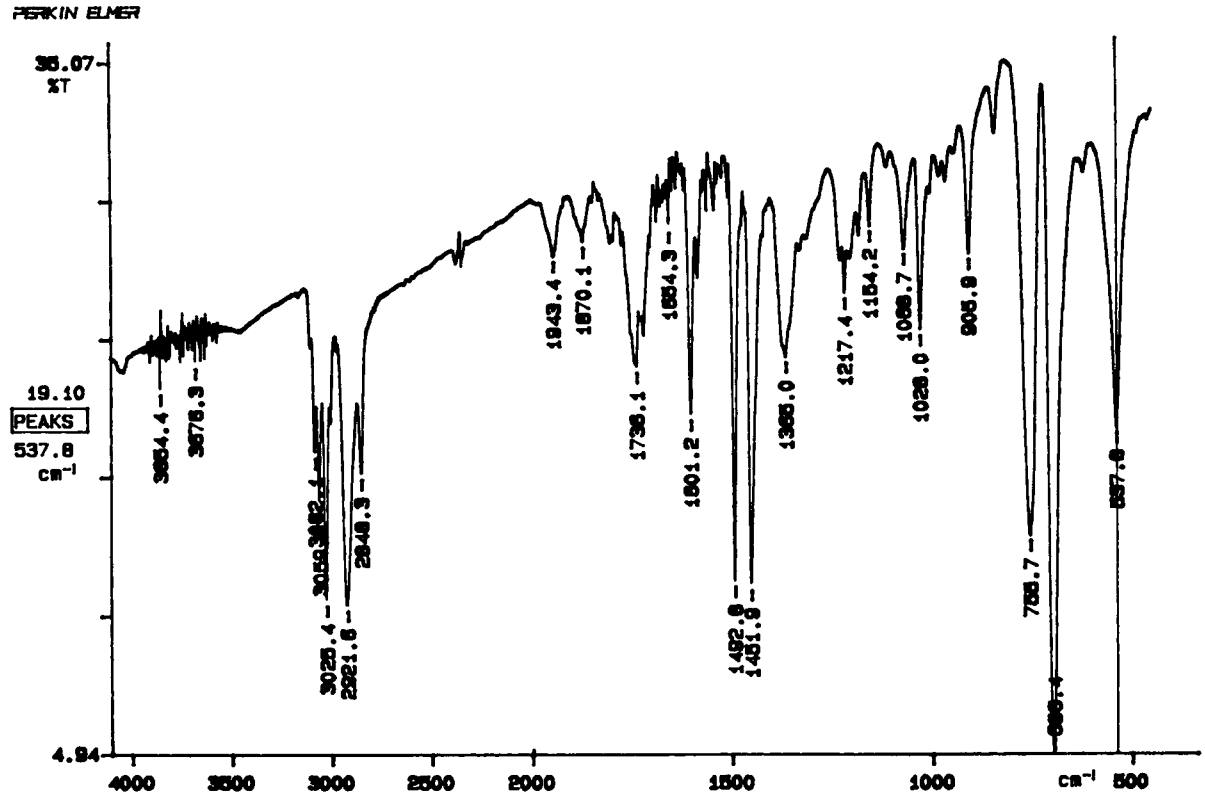

Figure 3 Infrared spectrum of film of methanol extract showing presence of poly(vinyl acetate).

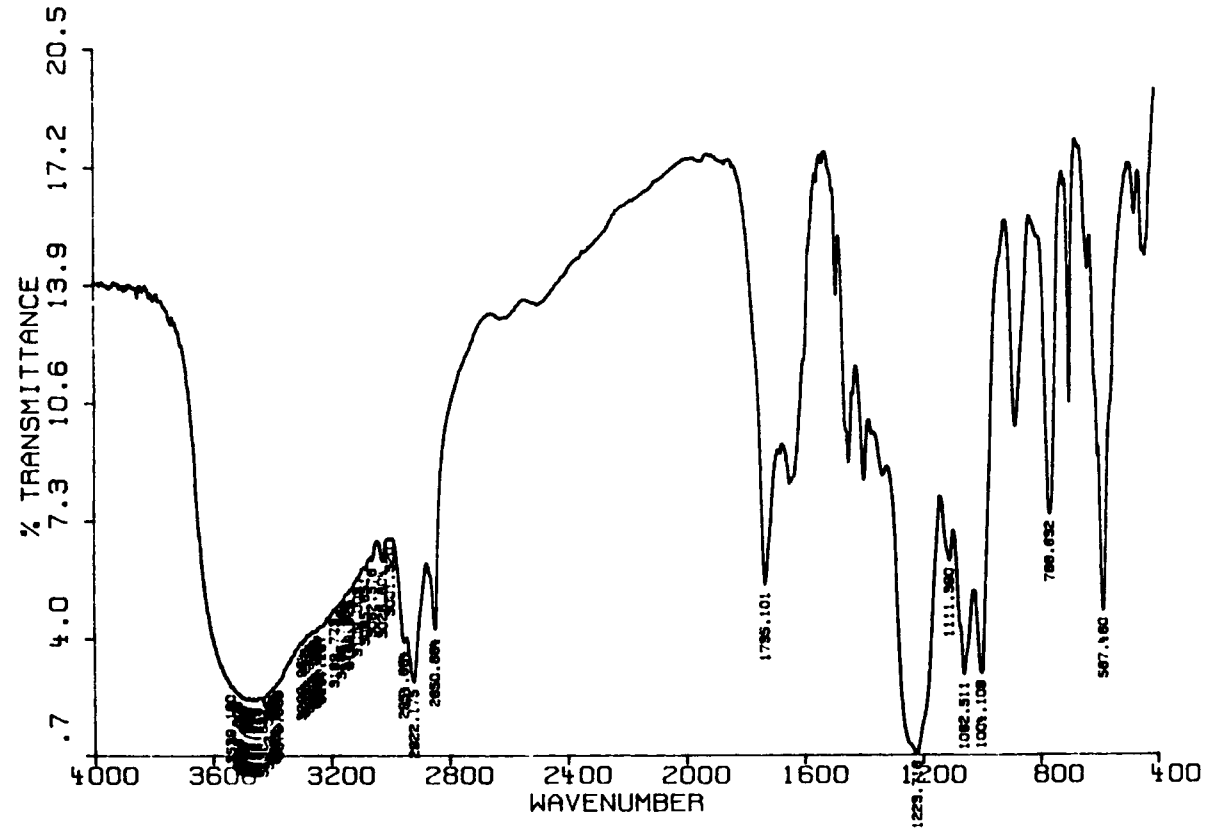

Figure 4 Infrared spectrum of film of methanol extract showing strong presence of poly(vinyl acetate).

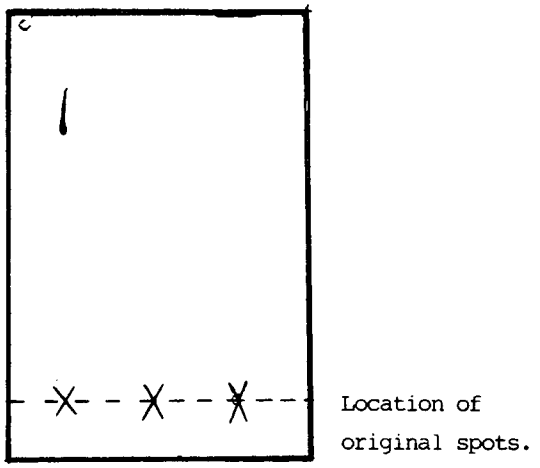

Figure 5 TLC plate spotted with pure poly(vinyl acetate) solution in methanol, methanol extract, and pure polystyrene solution in chloroform (from left to right), and developed with methanol.

of poly(vinyl acetate) is small compared to the amount of polystyrene. Figure 4 shows the peaks indicative of styrene (587, 768, 1450, 1490, 2850, 2922, and 2954 cm^{-1}). However the spectrum also shows very strong peaks at 1229 and 1735 cm^{-1}. These peaks also indicate the presence of poly(vinyl acetate). Since the peaks relating to poly(vinyl acetate) are very strong compared to the other peaks, poly(vinyl acetate) is present in relatively larger proportion. The large hump noticed at around 3400 cm^{-1} could indicate either poly(vinyl alcohol) or 2,5 di-*tert*-butylhydroquinone. It is possible that some poly(vinyl acetate) reacts with methanol and forms poly(vinyl alcohol). It is also likely that the water-insoluble inhibitor forms the vinyl acetate oligomer chain-end segments. The samples represented by the above two spectra were obtained by using the successful recipe shown in Table II.

TLC results corresponding to the sample results shown in the previous section are described below. Figure 5 shows a TLC plate which had been spotted with pure poly(vinyl acetate) solution in methanol, the methanol extract, and pure polystyrene solution in chloroform (from left to right). The plate showed that the pure poly(vinyl acetate) moved to the top of the solvent front. The other spots did not move. This indicates that the methanol extract does not contain any poly(vinyl acetate). This result thus confirms the FTIR result. Figure 6 shows a plate which had been spotted in a similar manner. However in this case the pure poly(vinyl acetate) as well as the methanol extract have shifted to the top of the solvent front. (In this case the order of spotting was: pure poly(vinyl acetate), pure polystyrene, and methanol extract, from left to right). Thus this shows the presence of poly(vinyl acetate) in the methanol extract.

The results obtained from the TLC experiments corroborate those obtained from the FTIR spectra. The above analysis indicates the success of the experimental strategy. A small amount of poly(vinyl acetate) oligomer has been produced in the secondary polymerization stage. The FTIR and TLC experiments also demonstrate the importance of the recipe in the experimental strategy. The formation of poly(vinyl acetate) oligomers, in the presence of water-insoluble inhibitor located within the polymer particles, was achieved by manipulating the amounts of the inhibitor and the initiator used in the secondary polymerization. The experimental results also showed that some polystyrene was extracted into methanol along with the poly(vinyl acetate). It is quite likely that some low molecular weight polystyrene molecules partitioned into methanol at the high temperature (slightly below the boiling temperature of methanol) during extraction. Thus a "clean" separation of the two components was not achieved. This is likely to have an effect on the mass spectra of the oligomeric sample.

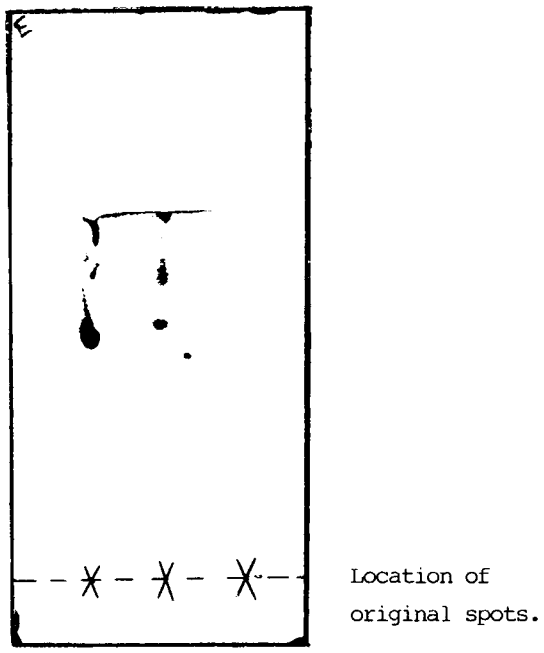

Figure 6 TLC plate spotted with pure poly(vinyl acetate) solution in methanol, methanol extract, and pure polystyrene solution in chloroform (from left to right), and developed with methanol. The TLC plate shows the presence of poly(vinyl acetate) in the methanol extract.

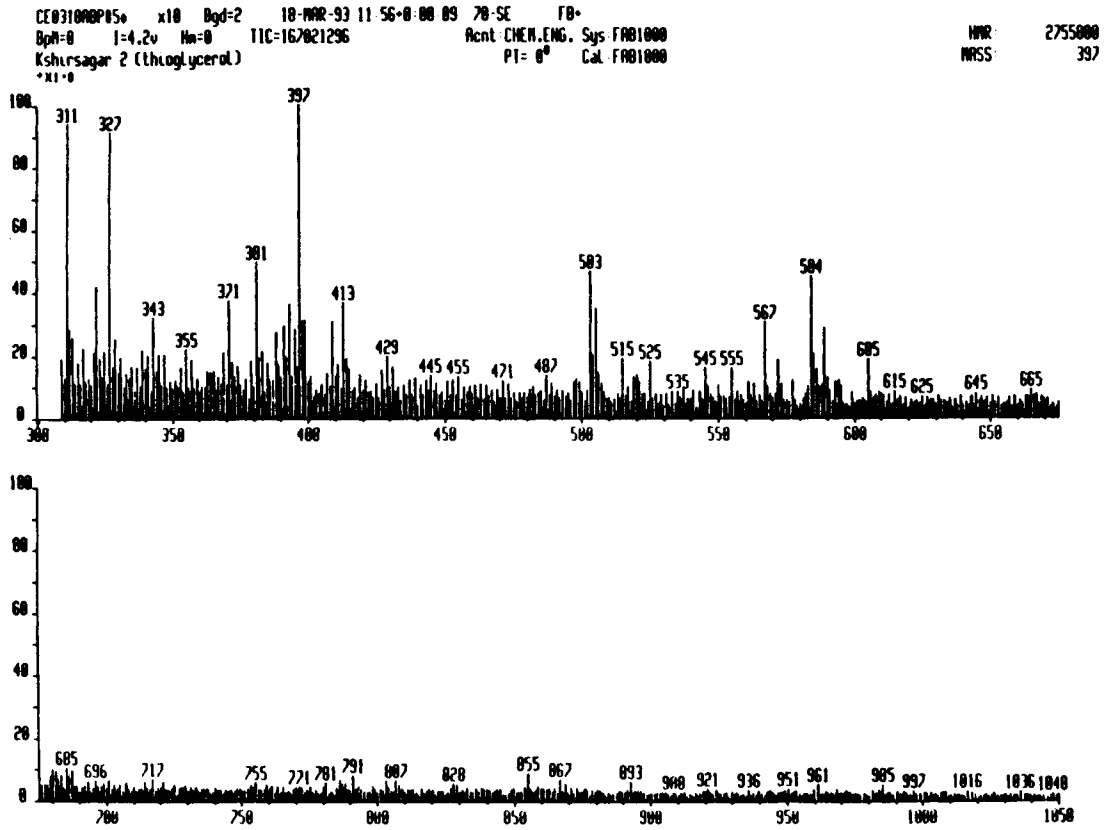

Figure 7 Mass spectrum of oligomer solution at a resolution of 1000.

The successful recipe [which lead to the formation of poly(vinyl acetate) during the secondary polymerization] was used to prepare samples whose mass spectra were then determined. Figure 7 shows one such spectrum. The sample in this case consisted of a solution of oligomers in methanol. The presence of oligomers had been established through FTIR and TLC. The FAB resolution in this case was 1000. The spectrum is cluttered with a large number of peaks. The molecular weights of the components in the sample range between ca. 300 to 1100. Figure 8 shows a mass spectrum of the same sample as in Figure 7 at a resolution of 1500. In this case it is seen that the spectrum is quite cluttered below an m/e value of about 950. The molecular weights in this case range from 400 to 1400.

Figure 9 shows the mass spectrum of another sample at a resolution of 1000. The spectrum, again, is very cluttered, with m/e values ranging from 300 to 1300. Figure 10 shows the mass spectrum for the same sample at a resolution of 1500. The spectrum in this case is not as cluttered with peaks as the previous three spectra, especially at an m/e value greater than 500. The range of m/e values is from 400 to 1300.

Interpretation of MS Results

Interpretation of MS results mainly involves identification of a compound through its molecular weight. The mass spectra of even a single compound may not appear simple, due to the presence of extensive fragmentation during ionization and the presence of various isotopes of elements. In the case of a sample consisting of a mixture of compounds, it is quite natural for the mass spectrum to appear cluttered with peaks. The oligomeric samples analyzed are mixtures of several compounds. In addition to the poly(vinyl acetate) oligomers, the sample contains 2,5-di-*tert*-butylhydroquinone, potassium persulfate, and sodium dodecyl sulfate. Further, each x-mer is, chemically, a different compound. Also, termination of oligomeric free radicals in the aqueous phase leads to the formation of many more chemical species. Moreover, FTIR and TLC experiments indicate that the separation of the two polymers [polystyrene and poly(vinyl acetate)] during extraction has not been total. Thus some polystyrene molecules find their way into the methanol solution. These polystyrene molecules constitute another set of chemical species, further increasing the number

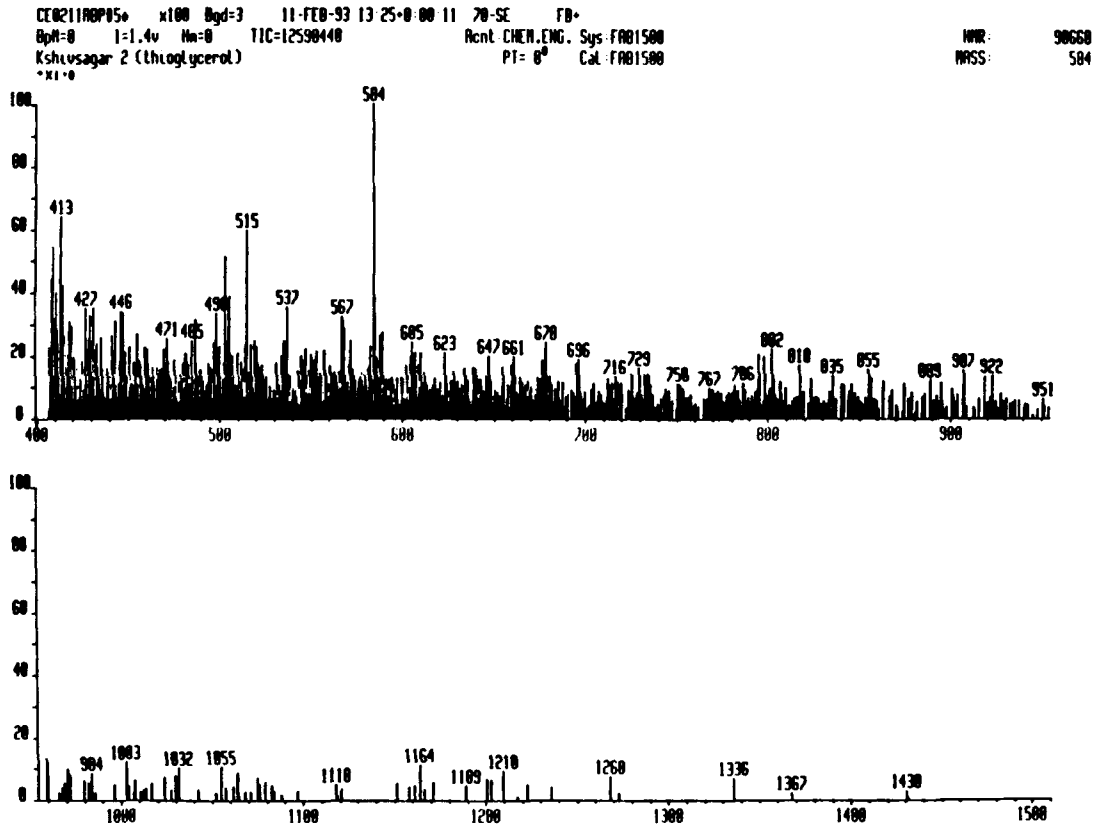

Figure 8 Mass spectrum of same sample as in Fig. 7, at a resolution of 1500.

of peaks. The net effect of all these factors is the formation of a spectrum cluttered with peaks. Interpretation of such a spectrum is difficult.

A necessary prerequisite for compound identification through mass spectra is the knowledge of the chemical formula of the species. In the case of poly(vinyl acetate) the structure of the body of the chain is known to consist of vinyl acetate molecules. However the identity of the terminal groups is not known beyond doubt. The mechanism of initiation by the persulfate radical and the mechanism of inhibition in the case of 2,5-di-*tert*-butylhydroquinone are not completely understood. In effect, the exact chemical structure of the poly(vinyl acetate) oligomers is not known.

The above discussion shows that it is extremely difficult to identify the individual components in the mass spectra of the poly(vinyl acetate) oligomers. This inhibits the identification of the exact oligomeric size capable of entering free radicals. However, it is still possible to draw significant conclusions regarding the poly(vinyl acetate) oligomers.

In all the mass spectra (Figs. 7 through 10) the range of molecular weights does not extend beyond 1400. Assuming that the primary initiating radical is the $SO_4^{\cdot-}$ radical and that 2,5-di-*tert*-butylhydroquinone forms a quinonoid structure before attaching to the oligomer, it is possible to arrive at a rough estimate for the molecular weight of the poly(vinyl acetate) oligomer as follows.

$$\begin{pmatrix}\text{Molecular weight of}\\ \text{the largest oligomer}\end{pmatrix} = \begin{pmatrix}\text{Upper limit of}\\ \text{the MS range}\end{pmatrix} - \begin{pmatrix}\text{Molecular weight}\\ \text{of } SO_4^{\cdot-}\end{pmatrix} - \begin{pmatrix}\text{Molecular weight of}\\ \text{the inhibitor segement}\end{pmatrix}$$

$$\begin{pmatrix}\text{Molecular weight of}\\ \text{the largest oligomer}\end{pmatrix} = 1400—96—222 = 1082$$

Units of vinyl acetate monomer in the oligomer $= 1082/86 \approx 12$–13.

This estimate would represent the upper bound for the size of oligomer. If the primary initiating free radical is assumed to be the hydroxyl radical, the number of vinyl acetate units in the upper bound for the oligomer size would be about 13–14. The largest oligomer in the system is definitely to be found in the aqueous phase and could be formed by the mutual termination of two aqueous-phase free

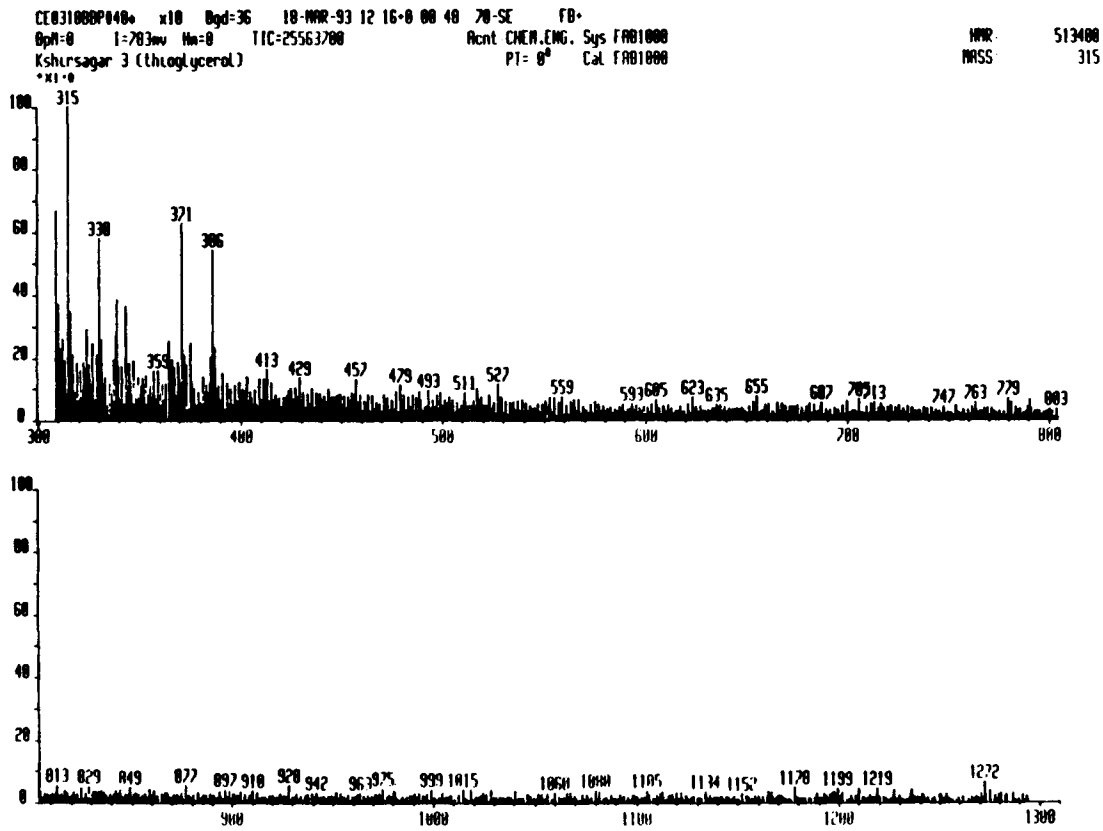

Figure 9 Mass spectrum of another oligomeric sample at a resolution of 1000.

radicals. Maxwell et al.[12] predicted from the thermodynamic point of view the value of z required for incipient insolubility to be 15–18 in the case of vinyl acetate. The approximate upper estimate obtained from the MS results is 12–14.

The mass spectra are not closely packed with peaks around 1400. It is reasonable to expect that more oligomers undergo entry as compared to aqueous-phase termination. Maxwell et al.[12] indicate that termination in water is not significant at low conversions. Thus many more oligomeric free radicals would enter polymer particles and react with the water-insoluble inhibitor than mutually terminate in the aqueous phase. Thus, higher concentration of oligomers of critical size (for entry) would lead to a larger number of fragmented ions. This would manifest itself in a more cluttered region of the spectrum. An enhanced peak density in the spectrum is seen to begin at around 800 daltons. With the same assumptions as used in the earlier case, the number of units of vinyl acetate in the oligomer of critical size is estimated to be $(800–96–222)/86 \approx 5–6$. Maxwell et al.[12] predict this value to be around 7–8.

The approximate estimates obtained from the mass spectra results are quite close to the predictions made by Maxwell et al.[12] on the basis of thermodynamics. Though the results from the mass spectra are certainly not definitive, they are helpful in gaining a better understanding of the sizes of oligomers formed in the seeded polymerization of vinyl acetate.

The approximate estimates of the critical oligomer size are important in more ways than one. As shown above, they do corroborate the thermodynamics of the entry mechanism. Moreover, they give an estimate of the size of oligomeric radicals in the case of polymerization of vinyl acetate. Previously, the oligomeric size in the case of homogeneous nucleation of vinyl acetate had been proposed to be in the range of 50–300 monomer units. The present estimates are much less than that. Thus an attempt in achieving the separation of entry and self-nucleation has been successfully made. The kinetic events involved in the two cases are vastly different and this has been brought out through the present work.

The estimates of the oligomeric size also help in better understanding the colloidal entry model. For the colloidal entry model to hold in the case of seeded

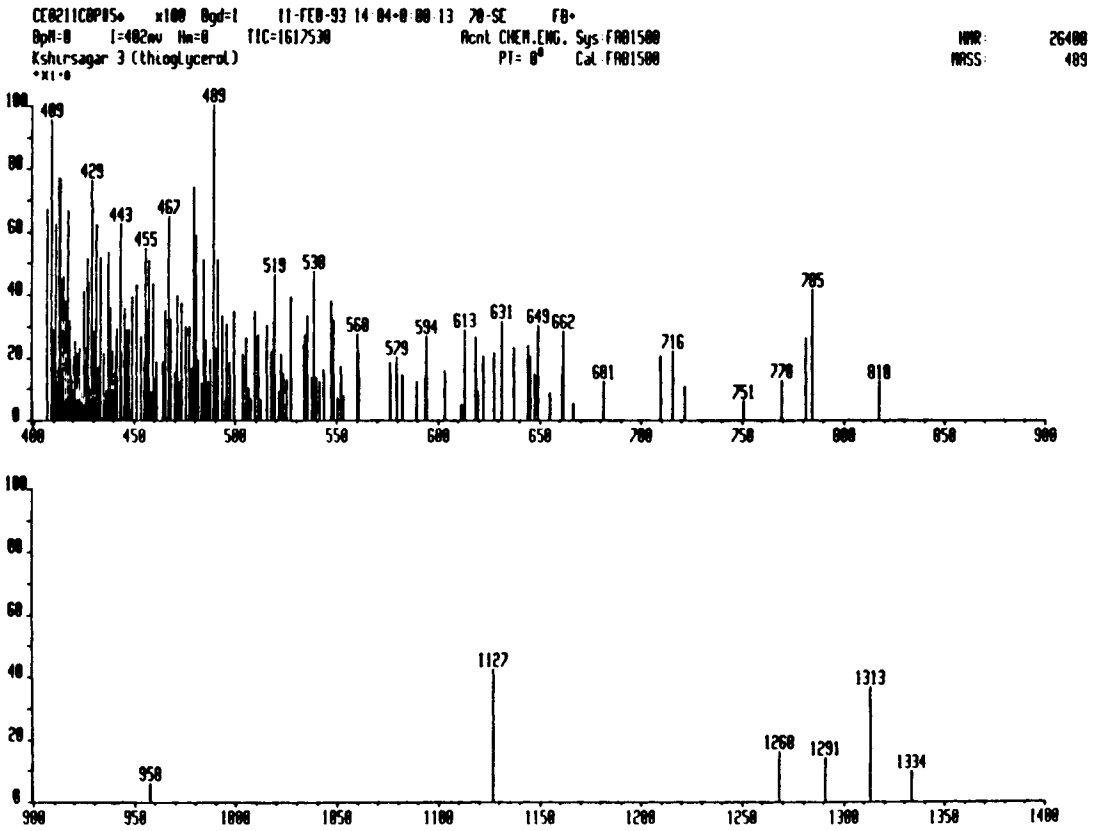

Figure 10 Mass spectrum of same sample as in Fig. 9, at a resolution of 1500.

emulsion polymerization, it is essential that the oligomeric sizes be quite large (large enough for the entering free radicals to attain a colloidal status). However the mass spectra of the oligomers show in clear terms that the oligomers are much smaller. Thus it is highly unlikely that the controlling mechanism for free radical entry could be colloidal coagulation. Since the oligomer sizes are much larger in the case of self-nucleation, the colloidal entry model could, perhaps, be valid in that case.

CONCLUSIONS

Though the experimental technique fails to give definitive values of the size of the vinyl acetate oligomers, approximate estimates have been obtained which closely match the predicted values—however, the results obtained from mass spectra are in no way conclusive. Also, merely showing that the critical oligomer sizes obtained experimentally are close to those predicted does not constitute proof for the model proposed. The predicted values were suggested by Maxwell et al.[12] as thermodynamic rationalization of their kinetic model. Thus the predicted values indirectly constitute support for their model. It is possible that the oligomers, after attaining a critical size, enter the polymer particles through a process of diffusional control. The thermodynamics remain the same in this case, too. Thus it is essential to test the model in terms of kinetics of free radical entry in the case of several monomers in order to determine its applicability. Without a proper experimental value of the critical oligomer size, however, the kinetic model alone cannot be considered to be adequate proof of the model's validity. The present work needs to be coupled with a kinetic model and tested with different monomers. Only then can the general applicability of the aqueous-phase growth model be fully validated.

The estimated oligomer sizes also help in bringing out the differences between seeded emulsion polymerization without secondary particle formation and unseeded emulsion polymerization accompanied by homogeneous nucleation. An attempt to achieve the separation of entry and self-nucleation has been successfully made. That the kinetic events involved in the two cases are vastly different has been brought

out through the present work. The size range estimate also helps in refuting the theory of colloidal entry as a possible mechanism for free radical capture by polymer particles.

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