Characterization of Grafting in the Emulsion Polymerization of Vinyl Acetate Using Poly(vinyl Alcohol) as Stabilizer

HÉLÈNE EGRET, VICTORIA L. DIMONIE, E. DAVID SUDOL, ANDREW KLEIN, MOHAMED S. EL-AASSER

Emulsion Polymers Institute and Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

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ABSTRACT: Emulsion polymerizations of vinyl acetate (VAc) with polyvinyl alcohol (PVA) as emulsifier were carried out by both batch and semicontinuous processes. The extent of grafting of vinyl acetate onto the PVA chains was investigated by a new method for separating the various polymer fractions in high solids content latexes. The quantification was carried out by a three-step separation and selective solubilization of the PVAc latexes. After the separation, the water-soluble PVA and the solvent-soluble PVAc components were characterized by gel permeation chromatography and ^{13}C–NMR, from which the accuracy of this method was verified. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1739–1747, 2001

Key words: vinyl acetate; emulsion polymerization; polyvinyl alcohol; grafting; latex fractionation

INTRODUCTION

Vinyl acetate (VAc) homopolymer and copolymer latexes, containing polyvinyl alcohol (PVA) as emulsifier, have been widely used for 50 years, mainly for wood adhesives and fast-setting packaging adhesive applications. The choice of emulsion polymerization conditions and the polyvinyl alcohol characteristics may influence both latex characteristics and film properties. Parameters such as the degree of hydrolysis and the degree of blockiness of the PVA, its molecular weight, and mode of addition can all have a significant influence on the polymerization process. These can affect the particle size, the reaction kinetics, as well as the degree of grafting of vinyl acetate onto the polyvinyl alcohol.

The effect of grafting is one of the most important aspects of this reaction. Its influences on the physical properties[1] and on the kinetics and particle nucleation[2,3] were previously established by monitoring the degree of grafting during the course of emulsion polymerization. Grafting of vinyl acetate onto polyvinyl alcohol can occur by hydrogen abstraction from either of two backbone tertiary C—H bonds [sites (1) and (2) in Fig. 1] or from the methyl side groups of the partially hydrolyzed chain [site (3)]. Branching occurs by chain transfer to monomer, which creates a terminal double bond, followed by subsequent polymerization of this terminal bond, thus creating branched PVAc.

Combinations of fractionation and selective solubilization techniques were previously used to measure the degree of grafting.[4–6] The determination of the water-soluble, solvent-soluble, and solvent-insoluble species, and their comparison with the initial composition, gives the amounts of linear PVA (water-soluble), linear PVAc (solvent-soluble), grafted polyvinyl alcohol (PVA-*g*-PVAc), and crosslinked (or highly branched) PVAc (water and solvent-insoluble). Using water and acetonitrile as solvents, Magallanes González et al.[7] performed the extraction of low solids content latexes

Correspondence to: M. S. El-Aasser.

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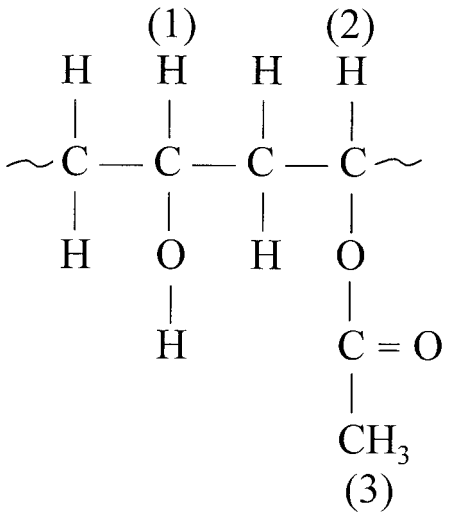

Figure 1 Grafting sites on partially hydrolyzed PVA.

by a new technique, employing two consecutive solubilization steps. In this study, the separation of high solids content and/or highly grafted latexes using a new fractionation method, based on the preceding method, is reported. The latexes are first ultracentrifuged to separate the latex serum from the polymer phase. Then, selective solubilizations with acetonitrile and water are used to separate the water-soluble PVA from the serum and particles, and acetonitrile-soluble PVAc and water-insoluble PVA-*g*-PVAc from the polymer phase. This method allows the quantification and characterization of each fraction using ^{13}C–NMR and gel permeation chromatography analyses.

EXPERIMENTAL

Materials

For the emulsion polymerization, vinyl acetate (VAc, 99%; Sigma–Aldrich, St. Louis, MO) was distilled under nitrogen at atmospheric pressure (bp = 72°C), using a Rashig ring-packed column, and stored at −5°C. Ammonium persulfate (APS, ACS grade 99%, Sigma–Aldrich), polyvinyl alcohol (Airvol 823; Air Products and Chemicals, Allentown, PA), nonyl phenol ethoxylate (Rhone–Poulenc, Cranbury, NJ), and sodium bicarbonate ($NaHCO_3$; Mallinckrodt–Baker, Paris, KY) were used as supplied. Deionized (DI) water was used in all polymerizations. Hydroquinone (99%; Sigma–Aldrich) was used as an inhibitor to stop the polymerization.

For latex fractionation and polymer characterization, the following materials were used as supplied: acetonitrile (AcN, HPLC grade; Sigma–Aldrich), DI water, sodium nitrate ($NaNO_3$, cell culture grade; Sigma), tetrahydrofuran (THF, HPLC grade; Fisher Scientific, Springfield, NJ), dimethyl-d_6-sulfoxide (DMSO-d_6; Cambridge Isotopes Laboratories, Andover, MA).

Polymerization Procedure

Emulsion polymerizations of vinyl acetate using PVA as emulsifier were carried out by both batch and semicontinuous processes in a four-neck kettle, equipped with a mechanical stirrer (stainless steel anchor or Teflon half-moon–shape impeller, depending on the viscosity), an inlet for the feed streams, a nitrogen inlet tube to blanket the reactants, and a reflux condenser. During the semicontinuous stage, two syringe pumps (Harvard 22, Holliston, MA) were used for the feed streams. The reactor was placed in a water bath in which the temperature was controlled at 70°C and 650 g latex was prepared in each experiment. Two aliquots were removed periodically during the reaction, placed in bottles with a preweighed quantity of hydroquinone, and stored at 4°C until use. One sample was used to determine the conversion (gravimetrically) and the particle size. The other (~ 30 g) was used to characterize the degree of grafting.

The solids contents at the end of the seeding and semicontinuous stages were around 20 and 43%, respectively. Each solids content measurement was duplicated to determine exactly the amounts of the different components, which is critically important for the fractionation.

Analysis of the PVAc Latices

Latex Fractionation

To characterize the different PVA and PVAc fractions, separation of the latexes was first carried out by ultracentrifugation of the diluted latexes followed by selective solubilization of the two portions: latex serum and sedimented polymer phase.

Ultracentrifugation. Separation of the latex serum from the particles was carried out by ultracentrifugation (Beckman ultracentrifuge, model L8–70M, rotor SW41; Beckman Instruments, Fullerton, CA). Polyallomer (PP copolymer; Seton) centrifuge tubes (9.5 mL) were used with

swinging buckets. Approximately 10 g of each latex was diluted to 10 wt % solids content, stirred for 1 h, and then centrifuged at 37,000 rpm and 4°C for 12 h. The clear serum (~ 30–40 g) was then removed with a syringe and added to acetonitrile (~ 175 g). The sedimented particles were collected and placed in a pear-shape flask with acetonitrile for extraction.

Serum Fractionation. The formation of high and low molecular weight PVAc was previously observed in the emulsion polymerization of VAc.[2,7,8] The molecular weight of PVAc oligomers in an aqueous solution, investigated by Vanderhoff[9] and Hergeth et al.,[10] was found to be around 1000 g/mol. The purpose of this step is to separate any PVAc oligomers from the water-soluble PVA fraction. The procedure is described as follows:

1. The water was removed from the acetonitrile/serum mixture by distillation of the AcN : water azeotrope (16.3% water in the azeotrope)[11] until the temperature of the vapors reached the AcN boiling point (82°C).
2. The mixture was then poured into two preweighed Teflon tubes (50 mL; Oak Ridge, Teflon FEP, Nalgene) and sealed with polypropylene caps having silicone gaskets (Nalgene). The PVA (AcN-insoluble) was separated from the solvent by centrifugation for 2 h at 20,000 rpm and 4°C (Beckman induction drive centrifuge, model J2–21M, rotor JA-20). The supernatant was carefully collected with a syringe and weighed. The centrifugation step was repeated after redispersing the sediment in fresh AcN. The amount of AcN-soluble species was quantified by drying a known portion of the two solutions and back-calculating the total AcN-soluble material based on the total amount of supernatant.
3. The AcN-insoluble PVA was dried at 75°C overnight, then at 60°C under vacuum for at least 6 h and weighed.

AcN/Water-Selective Solubilization of Sedimented Particles.

1. First, the sedimented latex particles, separated after latex centrifugation, were redispersed for 2 to 7 days under magnetic stirring in the AcN until a fine dispersion was obtained.
2. The residual water was removed by distillation of the AcN : water azeotrope at 76°C and the mixture was decanted into two Teflon tubes.
3. The AcN-soluble PVAc was separated from the sediment by 4-h centrifugation at 20,000 rpm and 4°C. The supernatant was removed with a syringe and collected in a preweighed bottle. The centrifugation was repeated after redispersion of the solids until no more polymer (PVAc) was solubilized (between four and six times). The amount of PVAc solubilized was quantified after each centrifugation by drying a known amount of solution and calculating the total PVAC based on the total amount of supernatant.
4. The AcN-insoluble material was dried, weighed, mixed with DI water, and then heated at 85°C for 48 h with mixing (end-over-end, 40 rpm). During this step, the linear PVA, associated with the sedimented latex particles (adsorbed), was separated from the grafted water-insoluble material (PVA-*g*-PVAc).
5. In a last centrifugation step, the grafted material was separated from the water-soluble material. The mixture was centrifuged 2 h at 20,000 rpm and 4°C and this step was repeated, after redispersion in DI water, until no more polymer was solubilized (three times). The grafted material was dried and weighed and the amount of PVA solubilized was quantified by drying a known amount of supernatant.

From these different steps, the amounts of linear PVA and PVAc and grafted PVA (PVA-*g*-PVAc) together with the crosslinked PVAc were determined by mass balance. The linear PVA was derived from the summation of the water-soluble fractions from the sedimented particles and AcN-insoluble fractions from the latex serum. The linear PVAc represented the summation of the AcN-soluble fractions from the sedimented particles and the latex serum. The amount of grafted PVA in the water-insoluble material was estimated from the difference between the total PVA used in the recipe and the linear PVA in the water-soluble fractions.

Polymer Characterization

Gel Permeation Chromatography (GPC). The linear PVA samples were analyzed by GPC at 35°C

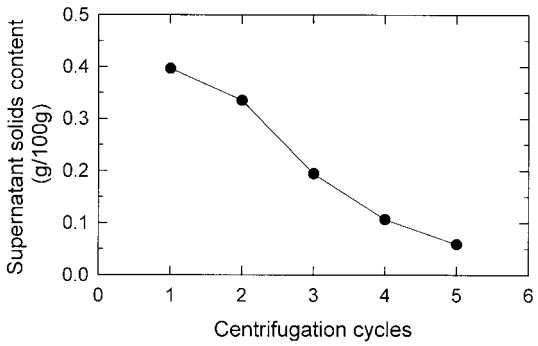

Figure 2 Percentage solids of the supernatant as a function of the number of redispersion/centrifugation cycles.

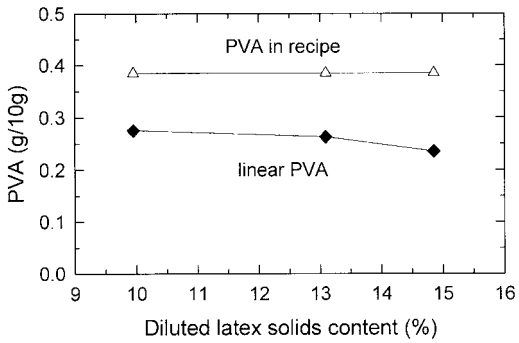

Figure 4 Latex sera solids content as a function of the solids content of the diluted latexes.

using a Waters 515 HPLC pump system (Waters Instruments, Rochester, MN) with two mixed packed columns (TSK-Gel GMPWXL; TosoHaas, Montgomeryville, PA) preceded by a guard column (TSK-Gel PWXL). The mobile phase was a 0.01*M* $NaNO_3$ solution. Poly(ethylene oxide) standards with molecular weights from 10,300 to 730,000 g/mol (Polymer Laboratories, Amherst, MA) were used for the calibration.

The linear PVAc samples were analyzed using the same HPLC system, except that three Ultrastyragel columns in series (Styragel HR3, HR4, and HR6 with pore sizes of 100, 10^4, and 10^6 Å, respectively; Waters Instruments), also preceded by a guard column, were used for the separation. The mobile phase was tetrahydrofuran and polystyrene samples (Polymer Laboratories) with molecular weights from 580 to 2,880,000 g/mol were used as standards.

Nuclear Magnetic Resonance (NMR) Analyses. ^{13}C–NMR analyses were carried out at 80°C using a 500-MHz Bruker AM series spectrometer (Bruker Instruments, Billerica, MA), using 10-mm NMR tubes. PVA and PVAc (5–9 wt %) were dissolved in DMSO-d_6 (internal locking agent). The NMR spectra were recorded with the following analysis parameters: sweep width, 29,412 Hz; pulse delay, 4 s; acquisition time, 1.114 s; temperature, 353 K; number of scans, at least 3000. The peak assignments were taken from Ovenall[12] and Pham et al.[13]

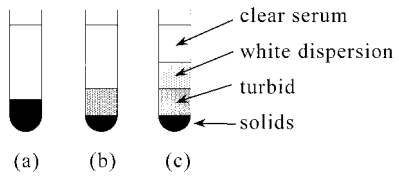

Figure 3 Schematic representation of the separation process achieved after 12-h centrifugation of the original seed latex diluted to (a) 10%, (b) 13%, and (c) 15% solids.

RESULTS AND DISCUSSION

Latex Fractionation

Applying the original AcN/water double-selective solubilization method used to analyze low solids latexes[2,7] to the higher solids (20 and 43%) latexes proved problematic. When the AcN was added to the original latex, it became highly swollen and then impossible to centrifuge properly. As plotted in Figure 2, the percentage solids of the supernatant decreased slowly with the number of centrifugations. After five redispersion/centrifugation cycles (2 h at 20,000 rpm and 4°C) the solids content of the supernatant was still not negligible. Parts of the AcN-soluble fraction seemed entrapped in the highly swollen phase, which could lead to errors in further analyses. Modifying this method by multiplying the number of redispersion/centrifugation cycles and carefully stirring the latex/acetonitrile mixture, the degree of grafting of the PVA in the final sample (43% solids) was found to be around 70 wt %, which was surprisingly high.

Based on these observations in the first separation attempt, the procedure was modified by first ultracentrifuging the latexes to enhance the PVA separation in a first step. However, fractionation of the original latex (20% solids) was not complete, even after centrifugation at high speed (37,000 rpm) and for long times (24 h). When the

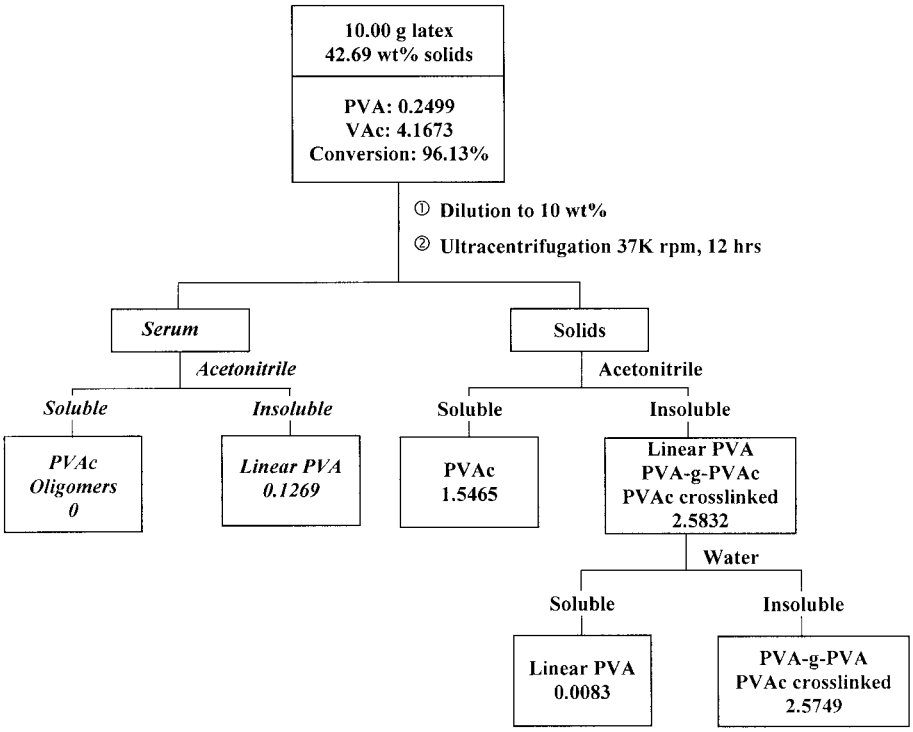

Figure 5 Flow chart and mass balance of the 43% solids latex extraction.

latex was diluted to 15% solids and then centrifuged at 37,000 rpm for 12 h at 4°C, the separation was not complete and more than two layers were formed. As illustrated in Figure 3, the dilution prior to centrifugation is important for the fractionation process to be successful. One can see that the greater the latex dilution, the better the fractionation. At 15% solids, three phases were observed below the clear serum. At the bottom, a portion of the particles were sedimented in a dense white layer; atop these solids was a turbid, gel-like phase, above which layer was a white dispersion. For the 13% solids sample, only two layers appeared in addition to the clear serum: the solids at the bottom and the turbid layer. For the 10% solids, the fractionation seemed to be efficient where only the solids were observed at the bottom below the clear serum.

The measurement of the latex serum solids content (Fig. 4) showed that the percentage solids of the serum was higher for the 10% diluted sample. With the assumption that PVA is the main water-soluble material, this indicates that the turbid layers should be comprised of small particles, stabilized by PVA adsorbed onto their surface. Based on the preceding results, a dilution to 10% solids was deemed necessary to obtain an efficient fractionation of these PVAc latexes.

For each sample, a known amount of approximately 10 g latex was diluted to 10% solids. The solids content of the diluted latex was also verified gravimetrically to improve the accuracy of the method. The fractionation was then performed by the method described earlier in the experimental section. A flowchart of the extraction process is given in Figure 5 for the final

Table I Characterization of the Amount of Grafted Material for the Seed and the Semicontinuous Samples

Sample	PVA Grafted (/10 g latex)	PVAc Grafted (/10 g latex)	PVA Grafted / PVA Recipe	PVAc Grafted / VAc Reacted
Seed latex	0.0684	0.5044	0.18	0.32
Final latex	0.1147	2.4602	0.46	0.60

Table II PVA and PVAc Degree of Grafting Determined by Two Methods of Extraction[a]

	Seed		Final	
	PVA Grafted / PVA Recipe	PVAc Grafted / VAc Reacted	PVA Grafted / PVA Recipe	PVAc Grafted / VAc Reacted
Method (A)	0.23	0.48	0.70	0.60
Method (B)	0.18	0.32	0.46	0.60

[a] (A) Double selective solubilization on the original latexes; (B) serum- and particle-selective solubilization after ultracentrifugation.

sample obtained (43% solids). The numbers shown were back-calculated taking into account the amounts of inerts (buffer, initiator, nonyl phenol surfactant) that could have been solubilized in each solvent and the weight loss occurring between the different steps (less than 5 wt %).

The results in Figure 5 show that the acetonitrile-soluble fraction in the serum was negligible, which means that no PVAc oligomers were detectable in the aqueous phase in this case. One can also see from these results that 3 wt % of the linear PVA material remained in the sedimented particle phase. This PVA could be strongly adsorbed onto the particle surfaces, making it impossible to extract it by centrifugation alone.

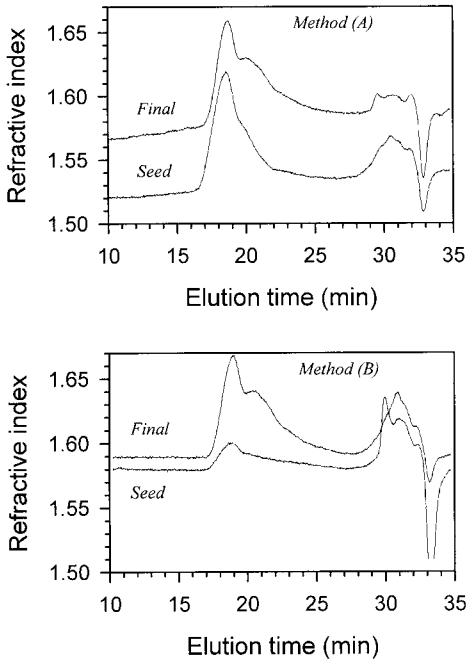

Figure 6 GPC chromatograms of the AcN-soluble PVAc obtained by the two fractionation methods for the seed and the final latexes.

Based on the water-soluble fraction, the amounts of PVA and PVAc grafted were calculated as listed in Table I. A comparison of the grafting percentages obtained with the preceding method and the original acetonitrile/water double-selective solubilization method is given in Table II. These two tables show that the degree of grafting of PVAc is high for these latexes. Another remarkable fact is that all the percentages of grafted materials were lower, as estimated by method (B), the modified method. Using procedure (A), the original method, to fractionate the latexes, some polymer could have remained entrapped in the highly swollen acetonitrile fraction with the soluble polymer chains becoming entangled in the grafted/crosslinked material. Therefore, the mass balance calculations can be influenced by the difficult extractions, leading to lower amounts of linear, soluble material extracted. This translates to higher calculated amounts of grafted material. With method (B), most of the linear PVA material was separated during the first ultracentrifugation step and the entanglement problem was significantly reduced, allowing a good fractionation even for high solids and highly grafted latexes.

Table III Number- and Weight-Average Molecular Weights of the PVAc Acetonitrile-Soluble Fractions

Sample[a]	M_n	M_w	PDI
Seed (A)	135,000	938,000	6.9
Seed (B)	158,000	820,000	5.2
Final (A)	97,000	563,000	5.8
Final (B)	104,000	561,000	5.4

[a] Seed and final samples extracted following methods (A) and (B).

Table IV Weight-average Molecular Weights of the Water-Soluble Fraction (Method A), the Polymer in the Serum (Method B), and the Original PVA

Sample	Original PVA	Seed (A)	Seed (B)	Final (A)	Final (B)
M_w	72,800	64,300	82,200	42,300	66,300

Polymer Characterization

Molecular Weight Analyses

Nonaqueous gel permeation chromatography (THF) was used to investigate the molecular weight of the linear PVAc polymer (AcN-soluble fraction) separated from the latex by both method (A) and method (B). GPC chromatograms are presented in Figure 6. It can be observed that, besides the main polymer peak at low retention times (high molecular weight), there were additional small peaks in the low molecular weight region. These peaks seemed to change with the sample and with the extraction method. To examine the structure of the materials producing these extra peaks, samples were dissolved in DMSO-d_6, to be further analyzed by ^{13}C–NMR.

The main peak in the chromatograms showed a broadening of the molecular weight between the seed and the final sample. The high molecular weight limit remained the same, whereas the shoulder, small for the seed sample, increased for the final latex.

The average molecular weights, determined from the main peak of the four samples, are listed in Table III. It can be observed that the molecular weight decreased during the semicontinuous stage. It was previously shown that because of the high reactivity of the growing PVAc radical, chain transfer reactions take place extensively.[1] For the emulsion polymerization of vinyl acetate using a protective colloid like PVA, it was observed that the monomer/polymer concentration ratio [P]/[M] ([P], the polymer concentration and [M], the monomer concentration) is the dominant factor in determining the branching.[5] The level of branching/crosslinking was found to increase with conversion, which means that the monomer-starved conditions of the semicontinuous stage favor the branching reactions. In this case, the chain transfer reactions to polymer led mostly to shorter chains, resulting in a decrease in the average molecular weight of the sample.

Aqueous gel permeation chromatography was applied to examine the molecular weight of the

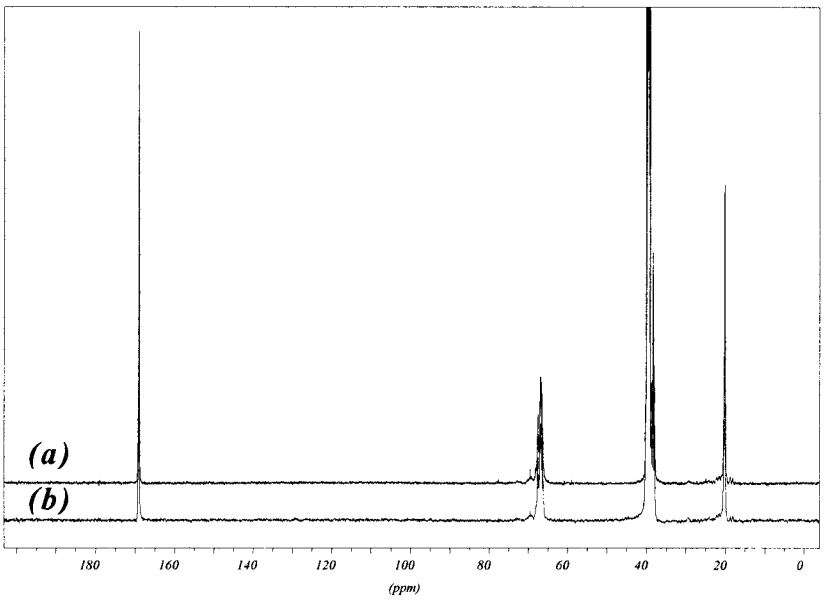

Figure 7 ^{13}C–NMR spectra of the acetonitrile-soluble fractions extracted from the seed with methods A (a) and B (b).

Table V ^{13}C–NMR Peak Assignments for CH_3, CH_2, CH, and CO Groups in PVAc

Peak Assignment	Chemical Shift Region (ppm)
CH_3	20–21
CH_2	38–40
CH	66–68
CO	169–171
DMSO-d_6	39.5

polymer in the serum [method (B)] and the water-soluble fraction [method (A)] for comparison to the original PVA. The weight-average molecular weights of the different fractions are listed in Table IV. It can be observed that the molecular weight of the extracted water-soluble fraction obtained by method (A) is lower than that of the polymer in the serum [method (B)], which is similar to the original PVA. This effect is more significant for the final sample. As a result of the polydispersity of the original PVA, differences were observed in the adsorption of the different molecular weights. Because of the high level of branched or crosslinked PVAc, only the lower molecular weight PVA chains could be extracted, whereas the high molecular weight chains remained entrapped. The greater the amount of grafted material, the greater the entrapment and, therefore, the PVA molecular weight is much smaller for the final sample [method (A)].

^{13}C–NMR Analyses

^{13}C–NMR analyses were carried out on the AcN-soluble PVAc, extracted using the two methods, as well as on the polymer in the serum, the water-soluble fraction, and the original PVA.

A comparison of the two AcN-soluble fractions from the seed in Figure 7 shows that no significant differences exist between the two samples. Both exhibit the same peaks for the PVAc structure (see Table V for the peak assignments). It can be concluded that the low molecular weight peak observed in the GPC chromatograms (THF) is attributed only to the presence of PVAc oligomers. The difference in the peak shape should only be caused by the difference in the extraction process because no traces of others polymers were found.

The ^{13}C–NMR spectrum of the water-soluble polymer is shown in Figure 8 and is compared to the original PVA. It can be observed that the spectrum has no significant differences with respect to the original PVA, which means that only linear (ungrafted) PVA is solubilized in hot water.

The preceding NMR analyses of both the water-soluble PVA and the AcN-soluble PVAc showed that the separations achieved with method (B) were indeed effective with the extraction of pure PVA and PVAc only.

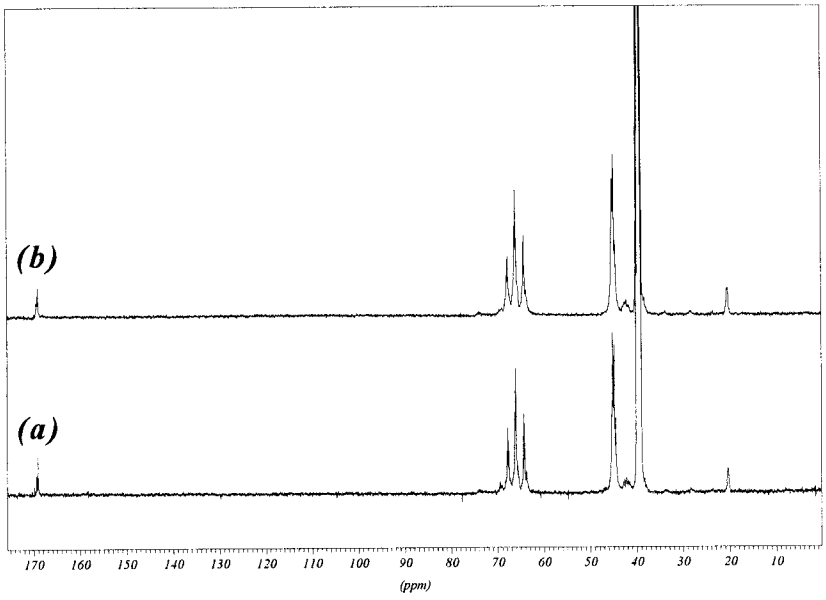

Figure 8 ^{13}C–NMR spectra of water-soluble PVA from the seed (a) and the original PVA (b).

CONCLUSIONS

In the emulsion polymerization of vinyl acetate with PVA as emulsifier, for a recipe giving high solids content latexes and highly branched PVAc polymers, the grafting was successfully quantified by developing a new separation technique. With this fractionation process, the latex serum was first separated from the polymer phase by ultracentrifugation. Then, based on the solubility of PVAc and PVA in acetonitrile and water, respectively, four different fractions were extracted. From the serum, acetonitrile-insoluble PVA can be separated from the PVAc oligomers, which could have been water-soluble. From the polymer phase, PVAc homopolymer is first separated by solubilization in acetonitrile. Then, a subsequent hot water solubilization allowed the separation of the linear PVA adsorbed onto the particles from the water and acetonitrile-insoluble grafted material. PVA and PVAc characterization showed the efficiency of the separation method, where only ungrafted polymers were solubilized in the two solvents used. By using this characterization method, the physical properties of the final latexes can be correlated to the amounts of grafted PVA and branched/crosslinked PVAc.

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