

# Crosslinking of Poly(vinyl acetate) Nanolatices by Gamma and UV Radiation

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Received 6 August 2011; accepted 10 February 2012

DOI 10.1002/app.37002

Published online in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Poly(vinyl acetate) PVAc, in nanolatices with 10% polymer content, prepared by microemulsion polymerization was crosslinked by gamma and UV radiation. PVAc colloidal nanoparticles (average diameter,  $D_p = 58$  nm) had  $M_w = 562,000$  g/mol and about 95% conversions. PVAc nanolatices irradiated by gamma rays (1–13 kGy) at room temperature without crosslinking agent and by UV light (30–300 s exposure times) in the presence of divinylbenzene and allyl methacrylate showed crosslinking of up to 96% (high gel content),  $D_p < 100$  nm and did not degrade as shown by

FTIR spectroscopy. DSC and TGA characterization of irradiated PVAc samples indicated that  $T_g$  temperatures increased from 28°C for PVAc to 42°C and 39°C for UV and gamma rays crosslinked PVAc, respectively, whereas 10% weight losses occurred at 261°C for uncrosslinked PVAc and at 320 and 313°C for UV and gamma rays crosslinked PVAc. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** microemulsion; crosslinking; gamma radiation; poly(vinyl acetate); nanolatex

## INTRODUCTION

Polymer latices and emulsion polymerization are commercially important products and processes with applications in the manufacture of adhesives, protective coatings, engineering thermoplastics, etc. The applications of polymer latices are dominated mainly by the polymer and particle properties, such as, particle size distribution, molecular weight distribution, long chain branching, and crosslinking density. These latices are prepared mainly by emulsion polymerization. An alternative process to prepare polymer latices is microemulsion polymerization.

Microemulsions are thermodynamically stable and transparent oil–water systems stabilized by interfacial layers of surface-active agents.<sup>1–3</sup> There are three types of microemulsions, namely oil-in-water (o/w), water-in-oil (w/o), and bicontinuous microemulsions. The microstructures in each type of microe-

mulsion can be used as micro-reactors for polymerization to obtain ultrafine latex particles. These particles are almost always in the submicron range with narrow size distribution.<sup>4,5</sup> This type of polymerization yields polymers of high molecular weights at rapid reaction rates because of the fact that the free radicals grow in relative isolation. Thus, microemulsions appear to be excellent media for facilitating chemical reactions and could become an attractive alternative for emulsion polymerization.<sup>6,7</sup>

Among polymers synthesized by microemulsion polymerization, we find poly(vinyl acetate) (PVAc).<sup>8–11</sup> Some copolymers of PVAc have become very useful in the transportation industry as thermal insulators, in the electric industry as cable insulator, in the shoe industry used as soles, and in many other industries as a hot melt adhesive, a coating, etc.

Besides, a major practical use of gamma radiation to modify materials has been in the crosslinking of polymers.<sup>12–15</sup> This can result in a dramatic change in such properties as mechanical behavior, solubility, and swelling. In polymers that crosslink under radiation, chemical bridges are formed in the same molecule (intra crosslinking) and between adjacent molecules, which become permanently linked (inter crosslinking). The process ultimately causes formation of insoluble gel if crosslinking predominates

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Contract grant sponsor: CONACYT; contract grant number: CB 61345 (2006).

Contract grant sponsor: ICN-UNAM.

over scission. The gel/sol analyses of irradiated polymers allow the estimation of important radiation parameters such as, yield of crosslinking and scission, gelation dose, etc.<sup>16</sup> Therefore, gamma radiation could be a useful technique for preparing cross-linked PVAc nanolatices in microemulsion with unusual properties because of its unique advantages, such as the relatively simple composition of the system (without additional initiators), temperature independence, and strong penetrability. On the other hand, UV radiation has proven its efficacy for crosslinking reactions for some polymeric systems.<sup>17–20</sup> The most important applications of such technique are found in printing inks, and in the coating industry, namely varnishes and paints.

However, few studies related to radiation-initiated PVAc crosslinking have been published.<sup>21,22</sup> Among the first studies reported in the literature for PVAc crosslinking, are those published by Geuskens et al.<sup>23,24</sup> They reported PVAc crosslinking in solid state by using gamma and UV radiation. Recently, some authors have reported the formation of cross-linked-PVAc seminterpenetrating networks<sup>25–27</sup> and nanocomposites<sup>28</sup> by chemical methods. Finally, Poly et al.<sup>29</sup> synthesized PVAc nanogels by xanthate-mediated radical crosslinking copolymerization in solution. They found that high concentrations of crosslinker produced PVAc nanogels of high molar masses.

As far as we know, no studies involving radiation initiated crosslinking processes have been reported for nanolatices obtained by microemulsion polymerization. Thus, the aim of this work was to obtain crosslinked PVAc colloidal particles from nanolatices prepared by microemulsion polymerization by means of both gamma (without use of crosslinking agents) and UV irradiation with high crosslinking degree under mild reaction conditions to avoid degradation of the PVAc. The use of gamma rays for crosslinking of polymers is a simple and clean technique that facilitates the preparation of improved polymers. It is expected also, that smaller diameter particles (<100 nm) containing crosslinked-PVAc would have better penetration in covered surfaces improving the coating applied. Polymer latices of vinyl acetate are widely used in industrial and architectural applications (adhesives, coatings, and paints) because of the physical characteristics of the films, low cost, and availability.

## EXPERIMENTAL

### Materials

Vinyl acetate (VAc), potassium persulfate (KPS), divinylbenzene (DVB), allyl methacrylate (AMA), and tetrahydrofuran (THF) were purchased from

Aldrich ( $\geq 99\%$ ); VAc was distilled under reduced pressure. Sodium dodecylsulfate (SDS) from Fluka ( $\geq 99\%$ ) was used to stabilize the microemulsion. Deionized and tridistilled grade water (obtained from a system of two ionic interchange columns, Cole-Parmer Instruments) and argon of ultrahigh purity from Infra were used.

### Preparation of PVAc nanolatices

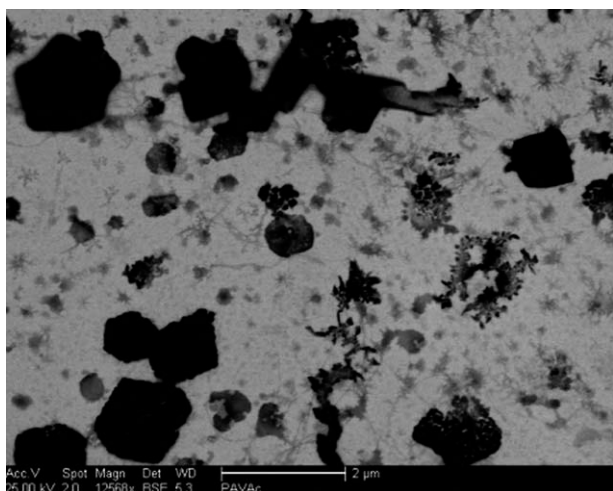
The heterophase polymerization of VAc was carried out in a 500 mL glass-jacketed reactor equipped with magnetic stirring. The SDS (1.1 g), water (360 g), and KPS (0.4 g) were charged to the reactor, cooled to 0°C and vacuum degassed during 1 h, and then the system was saturated with argon. At the same time, the monomer (48 g) was vacuum degassed during 90 min and then saturated with argon. The reactor was heated at 60°C, and the oxygen-free monomer was added continuously to the reactor at a feeding rate of 0.375 mL/min using a gas-tight syringe (Hamilton GASTIGHT<sup>®</sup>) adapted to a calibrated addition pump (Kd-Scientific<sup>®</sup>). After the semicontinuous addition period, the reactions were allowed to continue for 60 min. Polymer content was determined gravimetrically.

### Crosslinking of PVAc nanolatices by gamma and UV radiation

PVAc nanolatices were crosslinked by gamma radiation by placing 5 g of nanolatex sample in a glass ampoule which was then irradiated with a <sup>60</sup>Co  $\gamma$  source (Gamma Beam 651 PT, Nordion International) at irradiation doses between 1 and 13 kGy, and dose rates of 9.0 and 3.6 kGy h<sup>-1</sup>. To crosslink PVAc nanolatices by UV radiation, 5 g of nanolatex were placed into wide-mouth vials. Then, a crosslinking agent (DVB or AMA) was added (5 wt % with respect to polymer content). The mixture was homogenized by stirring during a few minutes and then irradiated with a UV lamp (Fusion UV Systems, Dreb6-110) with a power of 300 Watts, from 30 to 300 s.

### Gel/sol analyses

To investigate the influence of both gamma and UV radiation on the gelation of PVAc nanolatices, gel-sol analyses were performed by soxhlet extraction. Previously, PVAc nanolatices were freeze dried (Labconco Freeze Dry System/R45). The weight of polymer was determined by subtracting the known weight of SDS from the total weight of the freeze-dried samples. Then, dried samples were washed with hot water in order to eliminate surfactant. THF was used as solvent in the soxhlet extractor and it



**Figure 1** STEM micrograph of PVAc nanoparticles obtained by microemulsion polymerization.

was refluxed through each sample for 9 h. Gel percentages were calculated gravimetrically according to the eq. (1):

$$\% \text{ Gel} = m/m_0 \times 100 \quad (1)$$

where  $m_0$  and  $m$  are the masses of a sample before and after extraction, respectively.

### Characterization

Sample preparation for STEM analysis was carried out by placing a drop of diluted latex (1 : 1000) with distilled water and allowed to dry. Afterwards, a drop of phosphotungstic acid [0.5% (w/w)] was placed on the sample, the excess was carefully wiped out with a clean absorbent paper, and the prepared sample was dried. Electron micrographs were obtained with a Philips XL30 Feg ESEM in STEM operation with an acceleration of 25 kV in clear field.

FTIR spectra were determined in an FTIR Nicole Magna 550 spectrophotometer. The spectra were recorded in the transmittance mode. Particle size was measured at room temperature in a Malvern Zetasizer nano-s90 apparatus by diluting a sample of the nanolatex with deionized and filtered water in a 1 : 3 proportion. Average molar masses and molar mass distributions (MMD) of PVAc nanolatex were determined in a Waters 2695 separation module gel permeation chromatograph equipped with a refractive index detector and using high-performance liquid chromatography-grade THF (Aldrich) as mobile phase. A solution of PVAc/THF (1 mg/mL) was prepared and then it was passed through a filter (size 0.45  $\mu\text{m}$ ). Differential scanning calorimetry results were obtained under nitrogen flow using a DSC 2920 calorimeter from 0 to 200°C at a heating

rate of 10°C min<sup>-1</sup>. Decomposition temperatures were determined under nitrogen flow using a TGA Q500 apparatus (TA Instruments, New Castle, DE).

## RESULTS AND DISCUSSION

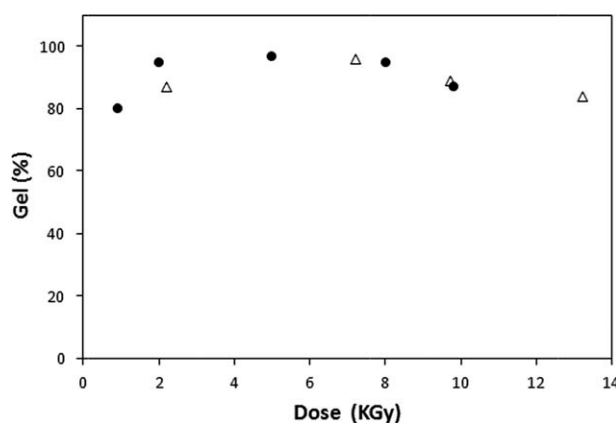
### PVAc nanolatices

PVAc nanolatices were obtained by microemulsion polymerization with polymer content of 10%, weight average molecular weight ( $M_w$ ) of 562,000 Da, and average particle size of 58 nm. The initially transparent reaction media turned bluish and turbid as the reaction progressed because of the growth of the nanoparticles. The synthesis of PVAc in microemulsion systems has been reported in several communications by our group.<sup>30-34</sup> In all cases, the same changes have been observed. The presence of the particles was confirmed by electron microscopy. Figure 1 shows a STEM micrograph of a typical nanolatex and particles are shown as the gray and/black spots. Individual particles can be observed as well as agglomerates.

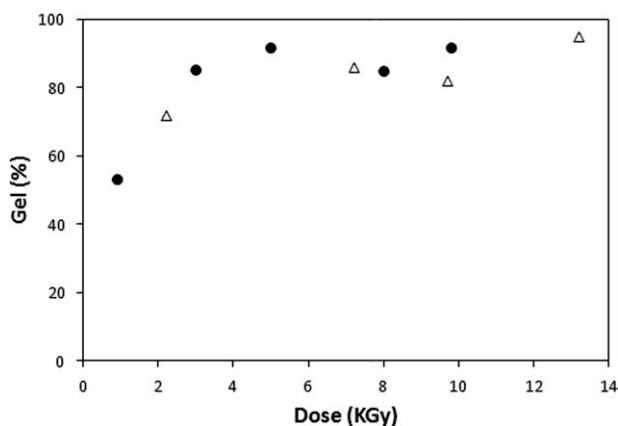
### Crosslinking of PVAc nanolatices by gamma radiation

Gelation in polymers is generally referred as crosslinking of macromolecules by means of covalent bonds. Figure 2 shows the behavior of gel percentage (with an estimated error of  $\pm 1.9\%$ ) with respect to radiation dose at different dose rates. It can be seen that high gel percentages are quickly obtained at 2 kGy. Also, it shows that there is not dependence of dose rate (3.6 and 9.0 kGy h<sup>-1</sup>) on gel percentage.

To investigate the dependence of gel percentage on the PVAc nanolatices concentration, samples were diluted with water (1 : 3 v/v) and then irradiated. Figure 3 shows influence of radiation dose on gel percentage at dose rates of 3.6 and 9 kGy h<sup>-1</sup> for



**Figure 2** Dependence of gel percentage with respect to radiation dose for PVAc nanolatices at different dose rates: 3.6 kGy h<sup>-1</sup> (●) and 9 kGy h<sup>-1</sup> (△).



**Figure 3** Influence of radiation dose on gel percentage at different dose rates: 3.6 kGy h<sup>-1</sup> (●) and 9 kGy h<sup>-1</sup> (△) for diluted PVAc nanolatices.

diluted PVAc nanolatices. This figure shows that there is a slight decrease of the gel percentage values for these PVAc nanolatices when compared with nondiluted PVAc nanolatices (Fig. 2). This is because crosslinking predominates over chain scission for nondiluted polymers. This result agrees with values for crosslinking and chain scission yields (see Table I).

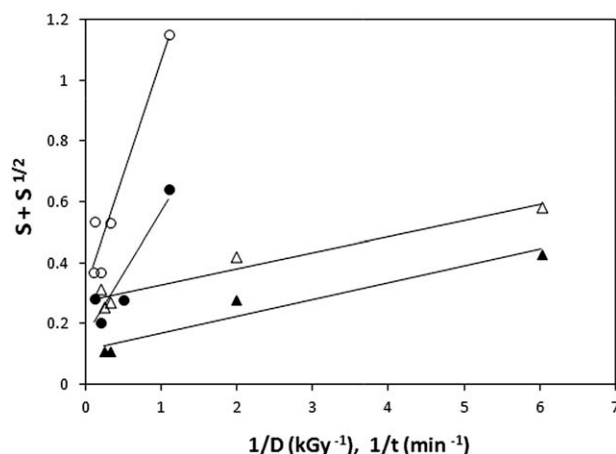
To determine the extent of the crosslinking and the chain scission reactions occurring when PVAc nanolatices are irradiated with gamma rays, the Charlesby–Pinner equation was used,<sup>35</sup> eq. (2).

$$s + \sqrt{s} = p_0/q_0 + 2/(q_0 u_{2,0} D) \quad (2)$$

In eq. (2),  $s$  is the sol fraction,  $p_0$  is the chain scission yield,  $q_0$  is the crosslinking yield,  $u_{2,0}$  is the weight average degree of polymerization (6534 for this work), and  $D$  is the radiation dose. Equation (2) was initially proposed to investigate the extent of crosslinking and scission reactions in gels of infinitely large polymer networks.<sup>16</sup> The use of this equation under conditions differing from the original assumptions remains as an unsolved problem. In spite of this inconvenience the equation has been used for researches to calculate the extent of both crosslinking and scission reactions in polymeric gels.<sup>36,37</sup> In our case, the use of this equation for PVAc with initial  $M_w = 562,000$  g/mol Da and up to 90% gel content

**TABLE I**  
Crosslinking and Chain Scission Yields for Gamma Rays Irradiated PVAc Nanolatices at a Dose Rate of 3.6 kGy h<sup>-1</sup>

Ratio latex : water (v/v)	$q_0$ (10 <sup>-4</sup> )	$P_0$ (10 <sup>-4</sup> )	$p_0/q_0$	Determination coefficient
1 : 0	7.35	1.10	0.15	0.8726
1 : 3	4.07	1.26	0.31	0.9355



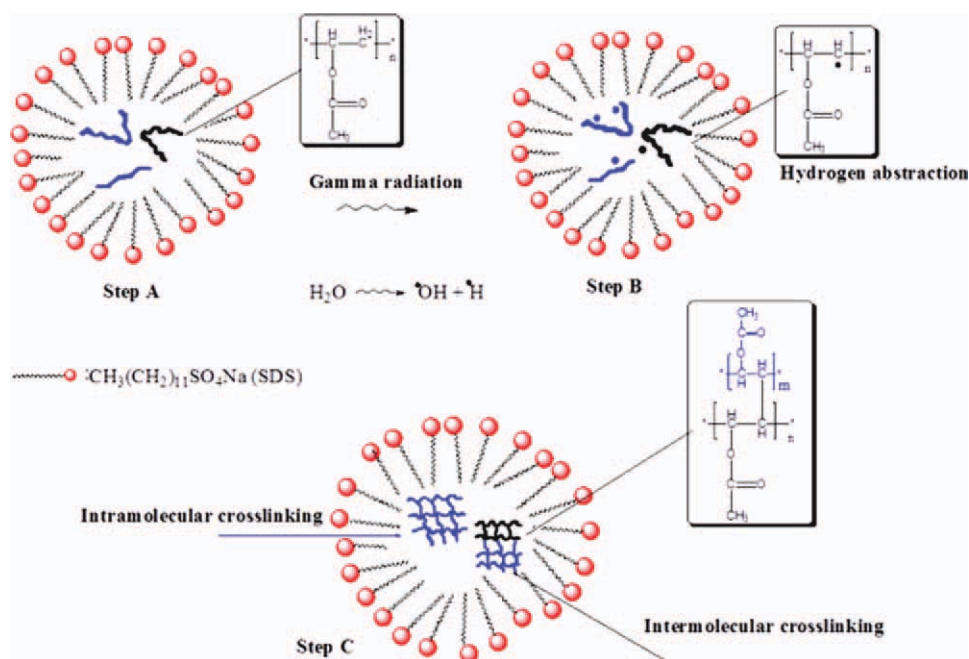
**Figure 4** Gel-sol analysis of irradiated PVAc nanolatices with gamma rays: (●) nondiluted PVAc nanolatices and (○) diluted PVAc nanolatices and for irradiated nanolatices with UV light using different crosslinking agent: DVB (△) and AMA (▲).

after irradiation (gamma rays, UV) was applied to get an indication of the extent of crosslinking and scission reactions occurring in the process. A plot of the reciprocal radiation dose ( $1/D$ ) versus  $s + \sqrt{s}$  yields a straight line, Figure 4. The value of the ratio  $p_0/q_0$  was calculated from the intercept of the straight line with the “Y” axis while the  $q_0$  value was determined from the slope. The results are shown in Table I. It can be seen from this table that nondiluted PVAc nanolatices present a higher crosslinking yield than those that were diluted before irradiation at a dose rate of 3.6 kGy h<sup>-1</sup>. The  $p_0$  and  $q_0$  values indicate that both crosslinking and chain scission are present during the irradiation process. However, the  $p_0/q_0$  ratio values indicate that crosslinking predominates in both cases: nondiluted and diluted irradiated PVAc nanolatices.

Table II shows the average particle sizes ( $D_p$ ) for nonirradiated and gamma rays irradiated PVAc nanolatices. It can be seen that diluted irradiated PVAc nanolatices exhibit average particle sizes ( $D_p$ ) between 90 and 99 nm. The increase in particle

**TABLE II**  
Average Particle Sizes ( $D_p$ ) for PVAc and Gamma Rays Irradiated PVAc Nanolatices

Dose rate (kGy h <sup>-1</sup> )	Dose (kGy)	Ratio latex : water (v/v)	Gel (%)	$D_p$ (nm)
–	–	–	0	58
3.6	9.8	1 : 3	92	99
3.6	9.8	1 : 0	87	47
9	7.2	1 : 3	84	93
9	9.7	1 : 3	82	90
9	13.2	1 : 3	95	93
9	7.2	1 : 0	96	41
9	9.7	1 : 0	89	44
9	13.2	1 : 0	85	42



**Figure 5** Schematic representation of the PVAc nanolatices crosslinking process by gamma-radiation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).].

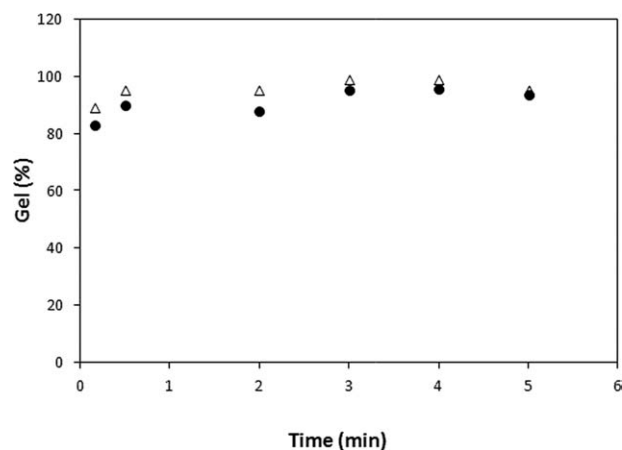
diameter could be due to three contributing factors: (1) conversion of unreacted monomer to polymer from the polymerization step by action of the gamma rays; (2) degradation of SDS because of the gamma rays<sup>38,39</sup>; (3) swelling of the nanoparticles due to the large excess of water present in the medium. Recent research carried out by our group<sup>40</sup> indicates that particle diameter increases as conversion increases because of the formation of polymer inside the particles. On the other hand, surfactant concentration has a dramatic effect on particle diameter: it was found that as the surfactant (SDS) concentration is increased from 0 to 11 mmol/L, the average particle diameters decreased between 277 and 18.7 nm.<sup>40</sup> It can also be seen in Table II, that  $D_p$  for nondiluted nanolatices decreases. This may be so because nondiluted nanolatices have a larger crosslinking yield (see Table I), which causes that the particles become more hydrophobic (smaller  $D_p$ ) and therefore swelling decreases.<sup>41</sup> In fact, it has been reported that high crosslinking density causes swelling decrease for nanohydrogels<sup>42,43</sup> and macrogels.<sup>44,45</sup> This is due to the decreasing mesh size of the network with increasing crosslinking density, which limits the diffusion of water molecules into the nanogel network. This means that increasing crosslinking density enhanced hydrophobic bonding.

Also, these  $D_p$  values suggest that crosslinking is carried out inside each particle, which works like a nanosize reactor and prevents interparticle crosslinking during the irradiation process and therefore forming colloidal PVAc particles. Some authors have

prepared well-defined nanogels by microemulsion polymerization techniques and no coagulation processes have been reported.<sup>46–48</sup> In addition, large dose rates (large free radical flux) were used in this work for preventing any possibility of coagulation processes<sup>49</sup> by inducing the formation of a large number of particles. The proposed mechanism for crosslinking of the PVAc inside the particles is shown in Figure 5. Firstly, the action of ionizing radiation on PVAc occurs mainly through an indirect effect. Most part of the energy is absorbed by water. Ionization of water molecules and the subsequent cascade of events lead to the formation of some reactive species: among them, hydroxyl radicals and hydrogen atoms (Step A). Subsequently, hydroxyl radicals and hydrogen atoms react rapidly with PVAc chains by hydrogen abstraction (Step B). Recombination of polymeric radicals may occur either between two radicals localized on separate macromolecules (intermolecular crosslinking) or between two radicals within the same chain (intramolecular crosslinking, Step C). The first of these processes leads to increase in molecular weight whereas intramolecular recombination does not influence molecular weight. The formation of new C—C bonds between the formerly independent chain segments, yields nanogels.<sup>50</sup>

#### Crosslinking of PVAc nanolatices by UV-radiation

To analyze the effect of UV radiation on PVAc nanolatices, the gel percentages were determined under different irradiation conditions. Firstly, influence of



**Figure 6** Gel percentage as a function of UV-irradiation time for PVAc nanolatexes using different crosslinking agents: DVB (●) and AMA (△) with a concentration 5% wt with respect to polymer content in the latex.

the photo-initiator (Irgacure 2959) on gel percentage was studied at constant irradiation time of 5 min. The results showed that even without use of photo-initiator, crosslinking takes place obtaining gel percentages around 30%. Also, it was observed that when the photo-initiator concentration increases gel percentages raise.

On the basis of these results, further experiments were carried out without photo-initiator. Figure 6 shows the gel percentage (with an estimated error of  $\pm 2.6\%$ ) as a function of irradiation time using DVB and AMA as crosslinking agents. This figure shows that high gel percentages ( $>80\%$ ) are obtained at short irradiation times (less than 1 min) for both crosslinking agents DVB and AMA.

Although, the Charlesby–Pinner equation is used for determination of crosslinking and chain scission yields for irradiated polymers with ionizing radiation, such as, gamma rays or electron beam, it is assumed that this general equation can also be used for the UV crosslinked and degraded polymers by simple replacement of dose with irradiation time, eq. (3). Replacing the UV irradiation time instead of irradiation dose of ionizing radiation in the Charlesby–Pinner equation, it becomes:

$$s + \sqrt{s} = p_0/q_0 + 2/(q_0 u_{2,0} t) \quad (3)$$

Equation (3) yields a straight line of  $s + \sqrt{s}$  vs.  $1/t$ ,

**TABLE III**  
Crosslinking and the Chain Scission Yields for PVAc Nanolatexes Irradiated by UV

Crosslinking agent	$q_0$ ( $10^{-3}$ )	$P_0$ ( $10^{-3}$ )	$p_0/q_0$	Determination coefficient
DVB	5.90	1.59	0.27	0.9402
AMA	5.56	0.61	0.11	0.9443

**TABLE IV**  
Average Particle Sizes (Dp) for PVAc and UV Irradiated PVAc Nanolatexes for Different Irradiation Times with 5% wt of Crosslinking Agent with Respect to Polymer Content in the Nanolatex

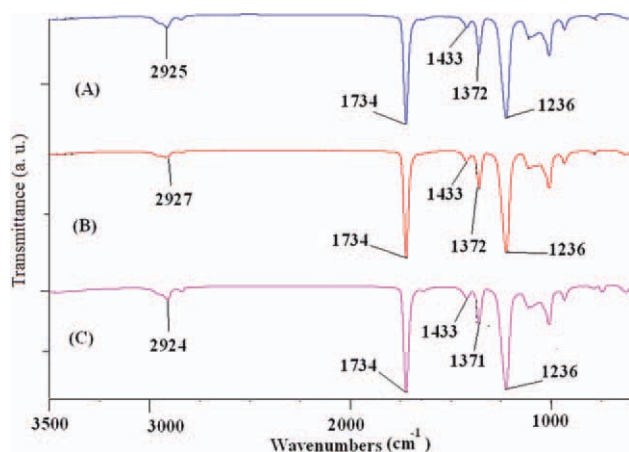
Crosslinking agent	Irradiation time (min)	Gel (%)	Dp (nm)
–	–	0	58
DVB	1	79	68
DVB	2	87	59
DVB	3	95	75
DVB	4	95	59
DVB	5	93	56
AMA	2	87	62
AMA	3	95	59
AMA	4	95	59
AMA	5	93	59

Figure 4. Table III exhibits the crosslinking and the chain scission yields for irradiated PVAc nanolatexes by using UV with DVB and AMA as crosslinking agents. This table shows that PVAc nanolatexes irradiated in the presence of AMA present a very similar crosslinking yield value by comparing with those that were irradiated in the presence of DVB. Both crosslinking and chain scission are present during the irradiation. However, the values of the ratio  $p_0/q_0$  indicate that crosslinking predominates in both cases.

Table IV shows the Dp for irradiated PVAc nanolatexes by UV with DVB and AMA at different reaction times. The gel content in the UV irradiated samples was between 79 and 95% and the irradiated PVAc nanolatexes exhibited average diameters (Dp) of up to 75 nm. Most of the average particle diameters were very close to the initial value (58 nm) except the ones corresponding to the use of DVB as crosslinking agent and 1 and 3 min of irradiation time with UV light. Repeated measurements of particle diameters for these two latices gave the same results. Contrary to gamma rays, UV light does not degrade SDS by itself but only in the presence of ozone as used for water pollution remediation.<sup>51</sup> Thus, the loss of surfactant cannot be the reason for explaining this irregular behavior. An explanation to this deviation is not clear at this point. The results for AMA as crosslinking agent show that Dp do not depend on irradiation time and that no significant coagulation process occurs during irradiation, indicating that crosslinking is taking place mainly inside each particle and that little coagulation occurs because of interparticle crosslinking.

### Characterization

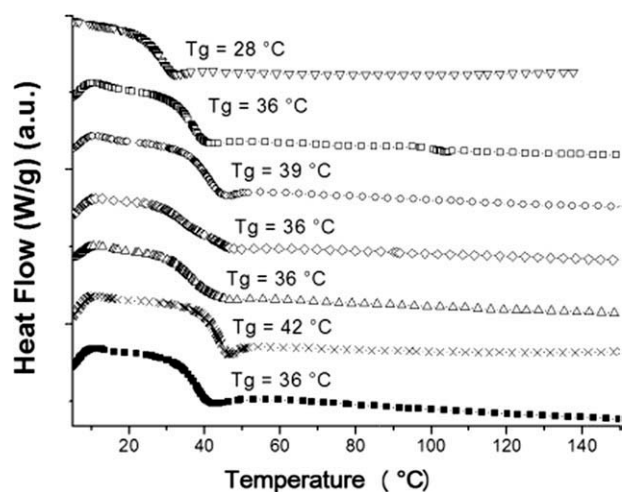
Figure 7 shows the infrared spectra of PVAc (a), gamma rays irradiated PVAc (b), and (c) UV irradiated PVAc. PVAc exhibited signals at 1372 and 1433



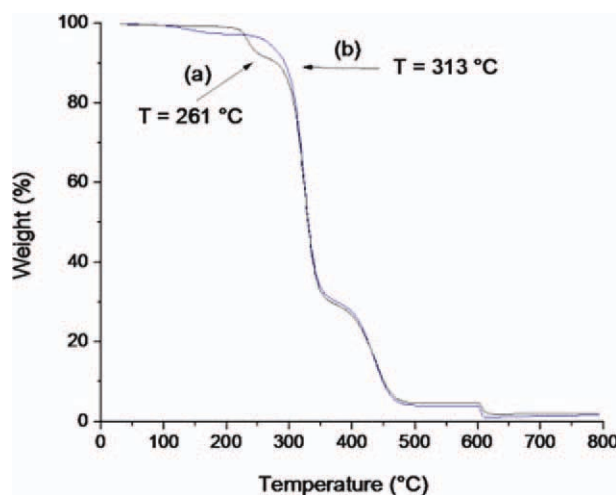
**Figure 7** IR Spectra for: (a) PVAc, (b) gamma rays irradiated PVAc at 10 kGy, and (c) irradiated PVAc by UV during 5 min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$\text{cm}^{-1}$  because of symmetrical and asymmetrical bending vibrations of the  $\text{CH}_3$  group, respectively. Also it shows stretching vibrations at  $1236 \text{ cm}^{-1}$  for the C—O bond and a signal at  $1734 \text{ cm}^{-1}$  attributed to the C=O group. Spectra for irradiated PVAc did not show differences when they are compared with the spectrum of PVAc. This could indicate that during both processes, UV and gamma radiation, PVAc does not suffer degradation. Additionally, we carried out FTIR analyses for PVAc samples irradiated from 3 to 20 kGy (gamma radiation) and different radiation times (UV radiation). The spectra did not show signals that could indicate degradation processes.

The thermal properties of PVAc and irradiated PVAc were studied by DSC and TGA. Glass transition temperatures ( $T_g$ ) were determined by DSC.



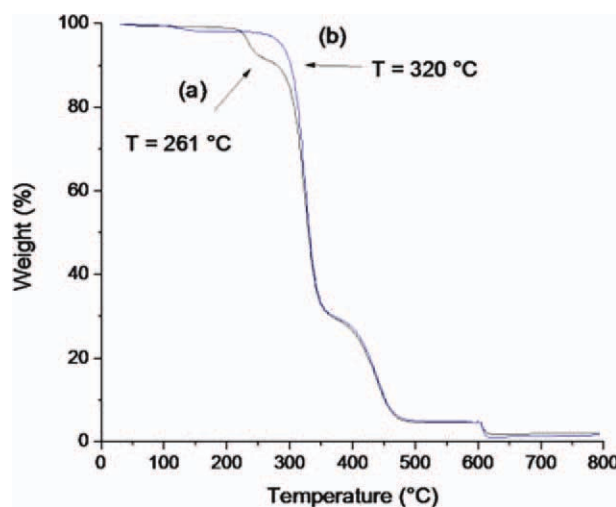
**Figure 8** DSC thermograms for PVAc ( $\nabla$ ) and irradiated PVAc samples at different gel content. For gamma radiation: 53% ( $\square$ ), 72% ( $\circ$ ), 87% ( $\diamond$ ), and 97% ( $\triangle$ ); and for UV-radiation: 34% ( $\blacksquare$ ), and 97% ( $\times$ ).



**Figure 9** (a) TGA curves of PVAc and (b) irradiated PVAc by gamma radiation with gel content of 97%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

From Figure 8, it can be seen that PVAc showed a  $T_g$  at  $28^\circ\text{C}$  while irradiated PVAc showed higher  $T_g$  values (from  $36$  to  $42^\circ\text{C}$ ). These higher values for irradiated PVAc samples can be understood as a result of crosslinking, which significantly lowers the mobility of the PVAc chains. That is, a higher temperature is needed to promote some mobility, characterizing the glass transition temperature.

Thermogravimetric analyses of irradiated PVAc samples provided information on their thermal stability when compared to that of the nonirradiated PVAc. Figures 9 and 10 show the TGA results for irradiated PVAc samples with gamma and UV radiation, respectively. The results obtained for the degradation temperatures (10% wt loss) indicate that the



**Figure 10** (a) TGA curves of PVAc and (b) irradiated PVAc by UV-radiation with gel content of 97%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

thermal stability of the irradiated PVAc samples increased when compared with the nonirradiated PVAc. This is because of the crosslinked network in irradiated PVAc promotes higher polymer-polymer junctions, as discussed earlier, resulting in lower chain mobility. So, a higher temperature is needed for degradation. Similar results were shown by all irradiated PVAc samples for both gamma and UV radiation. El-Din et al.<sup>52</sup> report that PVAc increases its thermal stability upon irradiation with gamma rays and found that 10% degradation occurs at about 315°C, which is similar to our own values (313°C). These findings plus FTIR results show that crosslinking predominates over scission when PVAc is irradiated with gamma rays. Our UV light results show the same trend (320°C).

### CONCLUSIONS

A novel, simple and facile technique was developed for obtaining nanogels of PVAc by radiating PVAc nanolatices prepared by microemulsion polymerization with both gamma and UV radiation. Average particle diameters for PVAc nanolatices irradiated by both gamma rays and UV light were less than 100 nm with up to 96% gel content. UV radiation showed to be a good tool for crosslinking PVAc nanolatices using either DVB or AMA as crosslinker agent under mild conditions and very short exposure times. FTIR studies indicated that PVAc nanolatices do not suffer degradation under the conditions used in this work. DSC and TGA studies showed that irradiated PVAc nanolatices increased their  $T_g$  and thermal stability, respectively. Gamma and UV irradiation techniques are useful procedures for the crosslinking of PVAc nanolatices obtained by microemulsion polymerization. The choice of production process will depend on the desired product as well as the available instrumentation: gamma rays irradiation (e.g., <sup>60</sup>Co source) will produce a PVAc nanogel without crosslinking agent residues whereas UV irradiated (lamp or photoreactor) PVAc does (plus photoinitiator residues, if used).

The authors gratefully acknowledge CIQA for technical assistance to J. Sanchez and to P. Siller, D. Alvarado, J. L. de la Peña, and R. Berlanga for valuable support to collect some of the previous work reported in the literature. They also thank IPICYT, San Luis Potosí, México for facilities to obtain STEM micrographs.

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