Crosslinking in Acetoacetoxy Functional Waterborne Crosslinkable Latexes

*Iñigo González, José M. Asua, José R. Leiza**

Summary: Chain crosslinking through the different stages of the production of acetoacetoxy ethyl methacrylate (AAEMA) containing acrylic latexes was studied; namely, during the synthesis step, after latex neutralization and after crosslinking with diamines. The gel content of the latex increased with increasing amounts of the functional AAEMA monomer likely due to dimethacrylate impurities contained in the monomer. Moreover, the neutralization of the latex with ammonia had important implications in the microstructure of the polymer. A base catalyzed Michael addition reaction between acetaocetoxy groups and terminal double bonds present in the polymer particles produced chain pre-crosslinking that affected the further crosslinking reaction with diamines. The compatibility of the diamines with the polymer matrix and the ratio diamine/acetoacetoxy used to crosslink the latex during film formation also played an important role in the crosslinking efficiency as evaluated by solvent resistance of crosslinked films.

Keywords: acetoacetoxy; crosslinking; emulsion polymerization; mechanical properties

Introduction

A major problem using crosslinkers in latex formulations is that particle-particle coalescence is hindered during film formation. Due to the highly crosslinked network generated, chain interdiffusion is impeded yielding weak films with a poor cohesive strength performance. This issue has been traditionally faced by using two component reactive formulations (e.g., epoxy-diamine, melamine- formaldehyde and epoxy-isocyanate) containing low molar mass species.[1–3] In these systems, the crosslinking reaction takes place during mixing (right before application) and application, thus densely crosslinked networks are generated. However, these so-called *"Two-pot"* systems require the separation of the two components during storage to avoid a premature crosslinking reaction. A further improvement in this crosslinkable formulations are *"One-pot"* systems which are more convenient because of the simplicity of using a single formulation. These systems are characterized by containing the two components, which yield the crosslinking reaction, coexisting in the same pot. Usually they are blends of two types of polymer particles each of them containing one of the crosslinking functionality. The particles are kept separated by sterical repulsions and crosslinking only takes place once polymer particles come into contact during film formation.[4] However, although these systems are considered *"One-pot"*, they still are *"Two-Pack"* systems, which require the blending of two different latexes.

Currently, the technical challenge is the development of "*One-pack in One-pot*" ambient cure systems, which do not require blending of different latexes produced in different stages. These systems are claimed to show a balance on properties such as long-term storage stability and good film

---

Institute for Polymer Materials, POLYMAT and Grupo de Ingeniería Química, Dpto. de Química Aplicada. Facultad de Ciencias Químicas. The University of the Basque Country P.O Box 1072, 20080 Donostia-San Sebastián, Spain
Telephone: (+34) 943015329. Fax: (+34) 943015270
E-mail: jrleiza@ehu.es

properties (e.g., early hardness or fast crosslinking, scratch resistance, and water and alcohol resistance). Polymers containing active hydrogen atoms, such as acetoacetoxy, diketo and acetoacetamide do not crosslink by themselves, but crosslink rapidly at room temperature in the presence of diamines. A successful approach to achieving this balance of properties involves polymers containing the reactive monomer acetoacetoxy ethyl methacrylate (AAEMA, Scheme 1).[5–11]

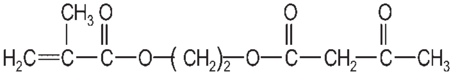
An important feature of this crosslinkable monomer compared to epoxy, aziridine or isocyanate curing systems is its relatively low toxicity[4] which makes it especially attractive for high-performance, environmentally friendly, non hazardous coatings. In addition, these systems permit the inhibition of the crosslinking reaction by using inhibiting volatile species, which retard the crosslinking reaction until film formation.

This article investigates the microstructure of AAEMA containing acrylic copolymers through the different stages of the latex preparation and application; namely, during synthesis and neutralization for storage and after crosslinking with diamines during film formation.

Experimental Section

Materials

MMA and BA (Quimidroga), AAEMA (Lonza), MAA (Aldrich) and DVB (Aldrich) were used as received. Sodium lauryl sulfate (Aldrich) was used as emulsifier in the seed preparation and ABEX2005 (Rhodia) in the semicontinuous experiments. Sodium bicarbonate (PANREAC) was used as buffer in the preparation of the seed. Potassium persulfate (FLUKA Chemika) was used as initiator. Jeffamine XTJ 504 (Huntsman) and trimethylene hexadiamine (Aldrich) were used as crosslinking diamines.



$$H_2C{=}\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-O-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

Scheme 1.
Chemical structure of AAEMA.

Emulsion Polymerizations

All the semicontinuous reactions were seeded. The poly(MMA-co-BA) seed used in the semicontinuous experiments was prepared batch-wise following the formulation shown in Table 1 in a stainless steel reactor fitted with a sampling device, N_2 inlet, and a stainless steel impeller rotating at 350 rpm. The reaction was carried out at 65 °C for 1 hour and it was kept overnight at 90 °C with the aim of decomposing the unreacted initiator.

The seeded semicontinuous emulsion polymerizations were carried out in a 1 L glass jacketed reactor fitted with a reflux condenser, sampling device, N_2 inlet, two feeding inlets and a stainless steel anchor stirrer equipped with two blade impellers rotating at 230 rpm. Table 2 summarizes the formulation used in the semicontinuous experiments.

The experimental procedure was as follows: First, the polymer seed (dp = 67 nm and 20.1 wt % solids content) and a part of the emulsifier were added into the reactor. When the temperature was 0.5 °C below the reaction temperature set point, half of the initiator was added to the reactor. When the desired reactor temperature was reached, the rest of the ingredients were fed in three hours. Upon finishing the addition, the reaction was kept batch-wise for 60 min. After cooling, a 30% water solution of ammonia was added up to pH = 9 to protect AcAc groups against hydrolysis; finally, the diamine was added under constant agitation.

Table 1.
Formulation used to prepare the seed.

Ingredient	Amount (g)
Methyl methacrylate	125
Butyl acrylate	125
Water	1000
SLS	5
$NaHCO_3$	1.25
$K_2S_2O_8$	1.25

Table 2.
Formulation used in the seeded semicontinuous emulsion polymerization of MMA/BA/MAA with different amounts of AAEMA.

Ingredient	Initial charge (g)	Stream 1 (g)	Stream 2 (g)
Seed polymer	32	–	–
Water[a]	160	27	207.64
ABEX2005	3.68	–	14.72
Methyl methacrylate	–	–	180.00
Butyl acrylate	–	–	180.00
Methacrylic acid	–	–	2.82
AAEMA	–	–	3.68–92.00
$K_2S_2O_8$	0.69	0.69	–

[a] Includes the water contained in the seed.

Characterization

Monomer conversion was determined by gravimetry. The instantaneous conversion, X_i, was defined as the amount of polymer divided by the amount of monomer and polymer in the reactor. The overall conversion was the amount of polymer divided by the total amount of monomer plus polymer in the formulation.

The gel fraction was determined by extraction with THF. The process consisted in a 7 hours continuous extraction with THF under reflux in a 2L glass reactor. This process was considered long enough as after 2 hours, almost 90% of the soluble fraction was extracted. After the extraction, the samples were dried and the gel content was calculated as the ratio between the dry polymer remaining after the extraction and the initial amount of dry polymer. Each sample was measured twice and an error lower than 5% was obtained in all the cases.

The sol molecular weight was determined by size exclusion chromatography (SEC,Waters). The setting consists in a pump (Waters 510), a Waters 2410 differential refractometer and three columns in series (Styragel HR2, HR4 and HR6; with a pore size from 10^2 to 10^6 Å). The analysis were performed at 35 °C and THF was used as solvent at a flow rate of 1mL/min. A previously dried latex film was directly added to THF and it was kept on a shaking bath at 50 °C for 3 days. Then, the soluble part was filtered (polyamide filter $\phi = 0.45\ \mu m$) and the sample was injected in the equipment.

The dynamic mechanical behavior of the films was investigated using a Polymer Labs MKIII viscoelastometer. The storage modulus (G') and the loss tangent ($\tan\delta$) over a range of temperature from −50 to 125 °C was measured. A sinusoidal tensile force of 1Hz was applied to the sample while rising the temperature at 5 °C/min. Diluted latex (to favor ammonia evaporation in order to avoid bubbles in the samples) plus diamine mixtures were poured into a Teflon capsule controlling the thickness of the film by means of the amount of latex added, as the solids content was fixed to the same value (25%). The films were dried for 1 week at 50 °C into a ventilated oven.

Results and Discussion

Figure 1 shows the evolution of the instantaneous conversion of the latexes synthesized with different AAEMA concentrations as measured by gravimetry. It can be observed that the process proceeded under rather starved conditions in all cases. Moreover, the addition of AAEMA had no remarkable effect on the polymerization kinetics.

Figure 2 presents the values of the final gel content of the latex after polymerization. It can be observed that, the higher the amount of AAEMA in the formulation the higher the gel content.

Figure 3 displays the evolution of the gel content through the reaction time. The formation of gel started at conversions

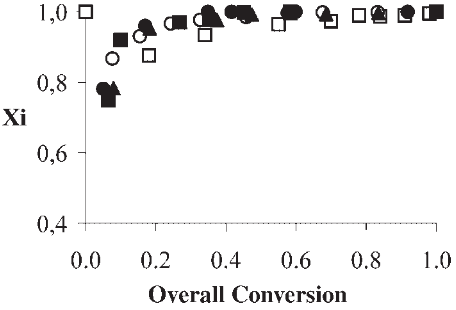


Figure 1.
Evolution of the instantaneous conversion in the seeded semicontinuous emulsion copolymerization of MMA/BA/MAA (55/44/1) carried out at 80 °C and with different AAEMA concentrations. ***Legend***: (□) 0wt%; (▲)1wt%; (○)2.5wt%; (■)5wt%; (●)10wt%.

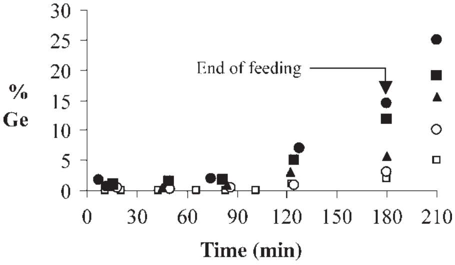


Figure 3.
Evolution of the gel content on the seeded semibatch experiments carried out with different AAEMA concentrations. ***Legend:*** (□)0wt%; (○)1wt%; (▲)2.5wt%; (■)5wt%; (●)10wt%.

about 70% for the reactions with 2.5, 5 and 10 wt% of AAEMA. A possible explanation for the increase of the gel content when the amount of AAEMA is increased in the formulation can be found in the dimethacrylate impurities that AAEMA contains. Bouvier-Fontes et al.[12] have shown that 0.23 mol % of diacrylates added in the polymerization of BA led to an increase of the gel content from 60% (without diacrylate) to 80%. According to the supplier of AAEMA, a 0.1% of dimethacrylate species is present as impurity in the monomer, and hence this might cause the increase of the gel content. However, the use of diacrylates should increase the gel content from the beginning of the reaction[12] because the reactivity of the methacrylate group of the divinyl monomers is very similar to other methacrylate monomers. This was not observed in these polymerizations. The low concentration of dimethacrylates made that the number of pendant double bonds per polymer chain was very low. Therefore, the linkage of macromolecules by means of polymerization of these double bonds was a slow process. Actually, Figure 4a), which displays the GPC traces of latex samples taken at 40 and 70% conversion during the polymerizations with different amounts of AAEMA, shows that at relatively low overall conversions (Xo = 0.4), the GPC trace was not affected by the AAEMA content.

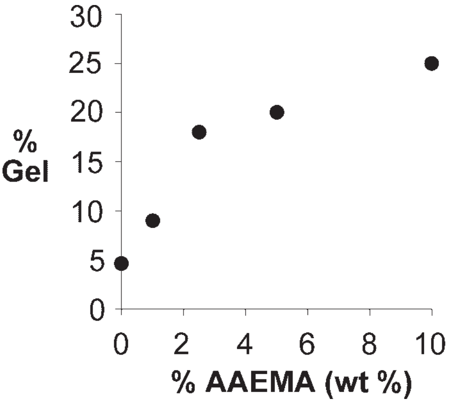


Figure 2.
Final gel content of MMA/BA/MAA latexes produced with different amounts of AAEMA.

However, at higher conversions (Xo = 0.7, see Figure 4b)) the GPC trace showed the presence of shoulders at low elution times (high molecular weights) most likely formed by the linkage of macromolecules by polymerization of pendant double bonds. The shoulders are significant for the samples containing higher amounts of AAEMA; namely higher amounts of dimethacrylate. Further polymerization of the pendant double bonds of these high molecular weight polymers led to gel formation during the last stages of the process.

The gel content of the latexes was also measured after adding ammonia with the aim of protecting the AcAc groups from

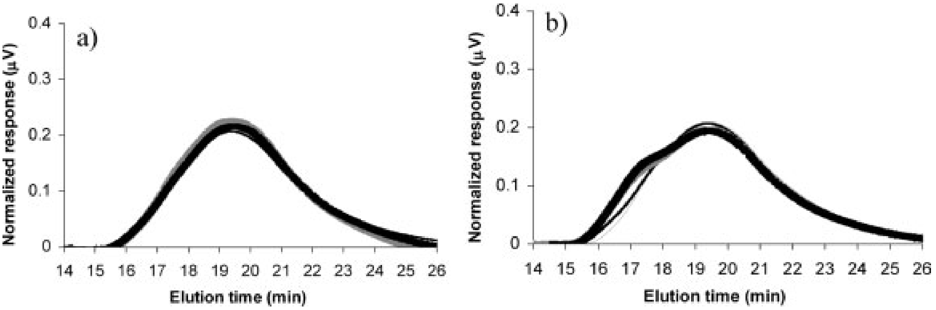
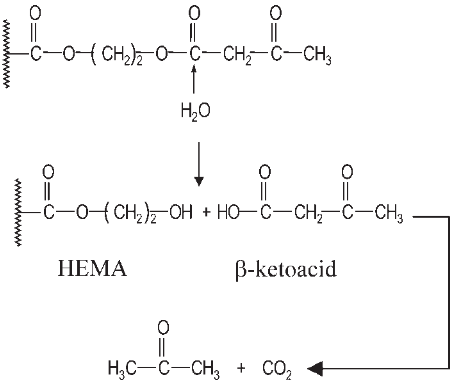


Figure 4.
Normalized GPC traces of the samples withdrawn from the reactor at a) 40% and b) 70% of overall conversion.
Legend: (—) 1wt%;(—) 2.5wt%;(▬) 5wt%;(▬) 10wt% of AAEMA.

hydrolysis. The use of this functional monomer in waterborne systems presents an important drawback which is the hydrolysis of the AcAc functional group (Scheme 2), which takes place during storage[13] and throughout polymerization at temperatures higher than 90 °C,[14] and which yields the definitive loss of AcAc functionality.

The hydrolysis can be avoided by forming an enamine group[10,13,15,16] by adding a volatile amine, i.e., ammonia[6,10,17] to the latex after the completion of the emulsion polymerization (Scheme 3).

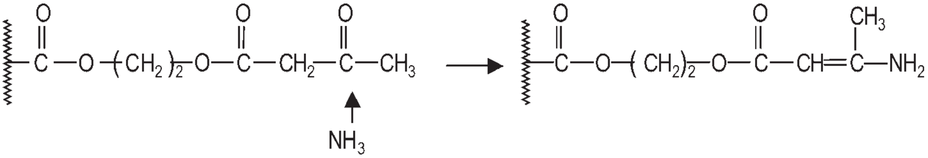
During film formation ammonia is released upon drying and the AcAc groups are regenerated becoming available for crosslinking reactions, i.e., with diamines (Scheme 4).



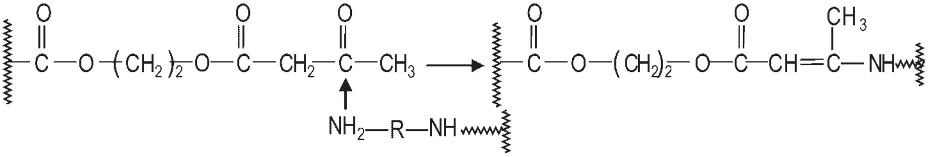
Scheme 2.
Hydrolysis reaction of AAEMA.

As Figure 5 displays, the addition of ammonia significantly increased the gel content of the latex, this result being not expected because ammonia does not present bifunctional activity. A base catalyzed Michael addition reaction between AcAc groups and terminal double bonds (Scheme 5) has been proposed to explain the increase of the gel content upon addition of ammonia (or other bases) to the latex.[18]

The base abstracts a hydrogen between the carbonyls of the AcAc group generating a carbanion which might react with an electron deficient species; for instance a terminal (meth)acrylate vinyl group. Potential sources of these terminal (meth)acrylate vinyl groups in the free radical polymerization of (meth)acrylates are: i) termination by disproportionation, ii) β-scission and iii) chain transfer to monomer. The probability for chain transfer to monomer during the polymerizations carried out in this work was low because of the low monomer concentration (the instantaneous conversion was always above 90%, see Figure 1). Therefore, the amount of terminal double bonds produced by this mechanism was relatively low. The contribution of chain transfer to polymer followed by β-scission was also dismissed because β-scission has not been reported to be significant at temperatures lower than 110 °C, except for extremely low monomer concentrations.[19] Otherwise, its effect on



Scheme 3.
AcAc group protection against hydrolysis reaction of AAEMA.



Scheme 4.
Crosslinking of AAEMA reaction with a generic diamine.

the MWD should have been observed (see Figure 4). Thus, termination by disproportionation was considered the most probable source of terminal (meth)acrylate vinyl groups, which has been reported as the main termination process in the polymerization of methacrylate monomers.[20]

Figure 6 shows the mechanical properties of two latex films cast with diamines. One of the latex was neutralized with ammonia while the other was not. It can be observed that lower crosslinking densities (the storage modulus was lower in the rubbery state plateau above the T_g) were achieved in the case of crosslinked films produced with an ammonia containing latex. The increase of gel due to the Michael addition affected the chain interdiffusion during particle coalescence and hence the crosslinking reaction occurred faster than interdiffusion. Consequently, the AcAc groups present in the interior of the polymer particle remained unreacted, and hence a lower overall crosslinking density was achieved, which in turn yielded a lower T_g of the polymer (Figure 6 right).

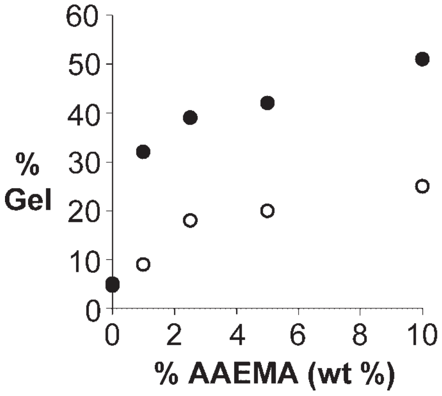
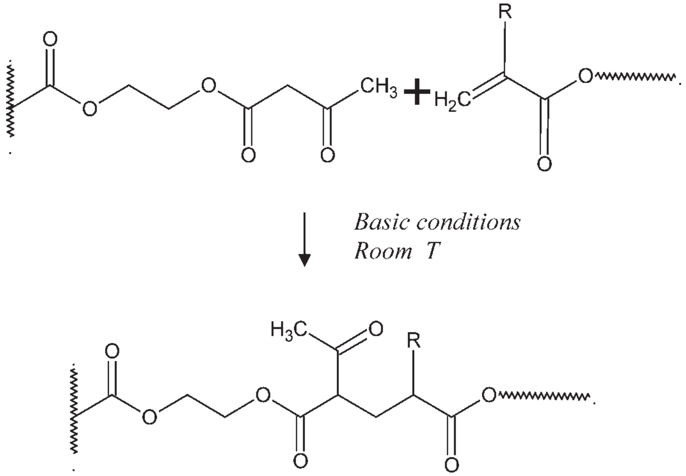


Figure 5.
Final gel content of the latexes of MMA/BA/MAA produced with different amounts of AAEMA measured before diamine addition. ***Legend:*** (○) Before NH_3 addition; (●) After NH_3 addition.

Figure 7 shows the DMA experiments performed to films crosslinked with diamines[10,16,17,21] with different amounts of AAEMA. No rubbery state plateau was observed for formulations containing less than 1% of AAEMA; namely, these films did not present any elastic properties above the T_g. On the other hand, for values above 2.5% of AAEMA, a plateau was observed. Moreover, the value of the storage modulus in the rubbery state plateau increased as the amount AAEMA increased and hence, the crosslinking density increased as it was expected.

The crosslinking density was also evaluated by performing solvent resistance tests (ASTM D1308-87) to crosslinked films.



Scheme 5.
Michael addition between AcAc functional groups and terminal double bonds.

Table 3 summarizes the results obtained for solvent resistance and it can be observed that, in general, the higher the AAEMA amount the higher the resistance to softening and lifting (swelling).

However, although the results for non polar solvents (xylene and gasoline) were good, it is worth pointing out that the crosslinked films showed a severe weakness against polar solvents. This weakness to polar solvents can be explained by a low crosslinking efficiency achieved during film formation and due to the non-crosslinked nature of the seed used during the synthesis of the latexes. The low crosslinking efficiency was a consequence of the hydrophilicity of the diamine and the presence of AcAc groups buried within the polymer particle that do not participate in the crosslinking reaction. Thus, the diamine used in the crosslinking of the AAEMA containing latex was a Jeffamine XTJ 504 (Huntsman). This is a poly(ethylene oxide) based diamine, which is completely water soluble. Therefore, the crosslinking reaction likely took place at the surface of the particles. Because part of the AcAc functional groups might be buried during

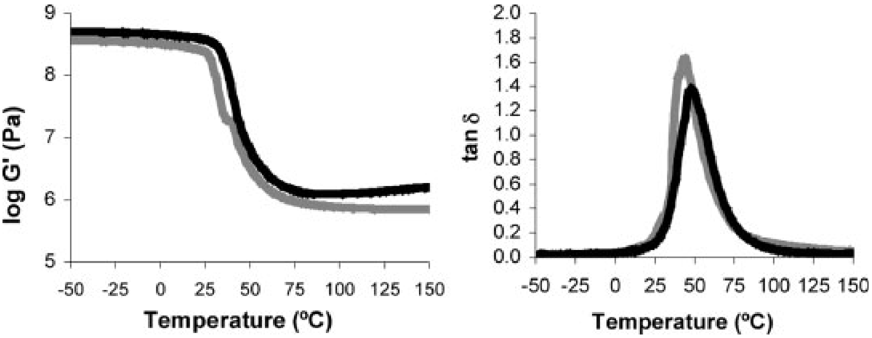


Figure 6.
Typical isochronal temperature dependence of the storage modulus G′ (left) and the loss tangent (tanδ) (right) of diamine crosslinked MMA/BA/MAA/AAEMA films (AAEMA = 5wt%). ***Legend:*** (——) latex without ammonia ;(——) latex with ammonia.

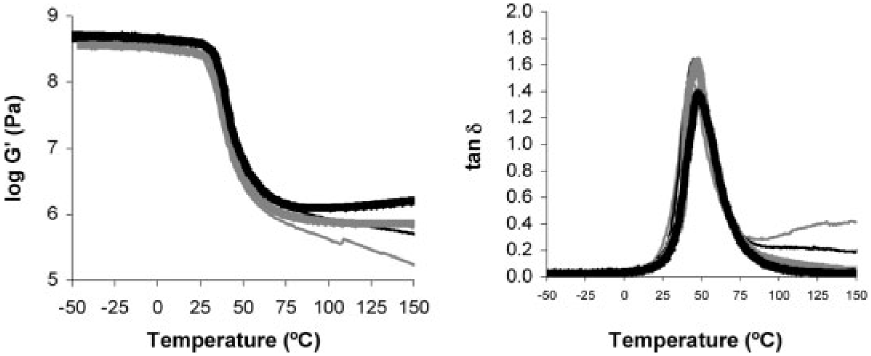


Figure 7.

Typical isochronal temperature dependence of the storage modulus G′(left) and the loss tangent (tanδ) (right) of **diamine** crosslinked MMA/BA/MAA/AAEMA co-polymer latexes with different amounts of AAEMA. ***Legend:*** (—) 0wt%; (▬) 1wt%; (▬) 2.5wt%;(▬) 5wt%.

Table 3.

Solvent resistance tests (ASTM D1308-87) performed to crosslinked latex films containing different amounts of AAEMA and cast onto glass sample pads. L = Lifting; S = Softening. 0 (no damage) – 4 (failure).

Wt % AAEMA	Water	Ethanol	Xylene	Gasoline
0	L3/S3	L4/S4	L2/S3	L2/S3
1	L3/S3	L3/S4	L2/S2	L2/S2
2.5	L3/S3	L3/S4	L1/S2	L1/S2
5	L2/S3	L2/S4	L1/S2	L1/S2

particle growth, the relative AcAc/diamine ratio at the surface of the particles was lower than the stechiometric (2:1) ratio employed in the formulation. Thus, an excess of diamine might be generated, and hence AcAc-Diamine coupling is favored versus AcAc-Diamine-AcAc coupling that yields crosslinking (see Figure 8 for a qualitative illustration). Consequently, the crosslinking efficiency decreased. The use of a higher AcAc/diamine ratio favored AcAc-Diamine-AcAc coupling and, as it is

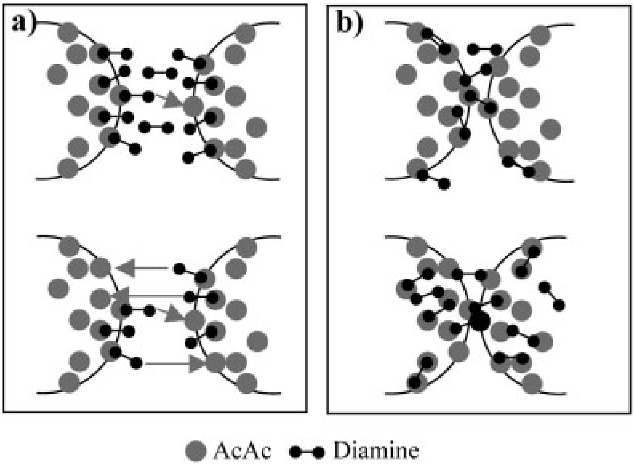


Figure 8.

Qualitative illustrations of the effect on the crosslinking efficiency of a) the use of a hydrophilic diamine in the stechiometric AcAc/diamine ratio (top) and in a higher ratio (bottom) and b) of the use of a hydrophilic diamine (top) and a more hydrophobic diamine (bottom).

Table 4.
MFFT results obtained for 5 wt% AAEMA containing latex - diamine mixture with different diamines and AcAc/diamine molar ratios.

AcAc/Diamine	XTJ504/TMHD**	MFFT (°C)
2/1*	100/0	10.4
2/0.75	100/0	11.9
2/0.5	100/0	11.3
2/1	0/100	12.3
2/1	20/80	15.4
2/1	40/60	15.4

* Stechiometric ratio.
** TMHD = Trimethylen Hexadiamine.

Table 5.
Solvent resistance tests (ASTM D1308-87) performed to crosslinked latex films (20/80 XTJ 504/TMHD) synthesized using a non-crosslinked and a crosslinked seed. L = Lifting; S = Softening.0 (no damage) – 4 (failure).

	Water	Ethanol	Xylene	Gasoline
Non-crosslinked Seed	L2/S3	L2/S4	L1/S2	L1/S2
Crosslinked seed*	L1/S2	L1/S2	L0/S0	L0/S0

* 1.5 wt % of divinyl benzene based on monomer was used in the formulation of Table 1 to prepare the seed.

summarized in Table 4, yielded higher crosslinking densities as can be inferred from the measurement of the minimum film formation temperature (MFFT).

In order to get the buried AcAc groups involved in the crosslinking reaction, a more hydrophobic diamine was used; namely trimethylene hexadiamine. Table 4 shows that the addition of trimethylene hexadiamine, more hydrophobic than XTJ504, led to higher values of the MFFT. This might be explained by the higher compatibility of the more hydrophobic diamine with the polymer matrix that may favor the penetration of the diamine within the particle, and hence the crosslinking of AcAc groups buried within the polymer particle (Figure 8). In addition, the results of Table 4 also show an increase on the MFFT when different mixtures of both diamines were used. It seems that there is a synergetic effect of both diamines; however, the reason of this effect is not well understood at the present time. The more hydrophobic diamine might tend to crosslink the polymer chains within the polymer particle, whereas the hydrophilic diamine may be prone to crosslink polymer chains from adjacent particles. Therefore a mixture of both diamines might contribute to chain crosslinking in both the particle surface and the core of the particle.

The nature of the seed used in the synthesis of the latex might also explain the weakness to polar solvents. The polymer latexes were synthesized by seeded emulsion polymerization and the seed used had no crosslinkable agent in the formulation (see Table 1). Therefore, the use of this seed might generate non-crosslinked micro-domains in the polymer film that might lead to the formation of weak spots in terms of solvent resistance.

Table 5 shows the solvent resistance tests performed to films cast from latexes produced from non crosslinked and crosslinked seeds (1.5% of divinyl benzene with respect to the monomers was added to produce the crosslinked seed polymer). The use of a crosslinked seed for the preparation of AcAc functionality containing latexes improved the resistance to both polar and non polar solvents by depleting the presence of soluble micro-domains in the film.

Conclusions

The polymer microstructure in the emulsion polymerization of MMA/BA/MAA/AAEMA was studied. The effect of the addition of the specialty monomer AAEMA on the polymer microstructure in the different stages of the latex production and after crosslinking was investigated. The addition of AAEMA to the formulation increased the gel content of the latexes likely due to the presence of divinyl species as impurities in the AAEMA monomer. In addition, surprisingly, the protection of the AcAc functionality with ammonia had an important effect on the polymer microstructure; namely, the gel content was doubled upon the addition of ammonia. A Michael addition reaction was proposed as responsible for the increase observed on the gel content. Moreover, this chain crosslinking was found to hinder chain interdiffusion leading to poorer mechanical properties of the crosslinked polymer films with diamines.

The mechanical properties of the film improved after polymer crosslinking with diamines. However, the resistance to polar solvents of the crosslinked films was still poor. The unavailability of the AcAc groups buried inside the polymer particles to react with the water soluble diamine made the AcAc/diamine ratio to be lower than the stechiometric ratio (2/1) at the surface of the particles. Thus, AcAc-Diamine coupling in spite of AcAc-Diamine-AcAc coupling, which yields crosslinking, was favored. This led to lower crosslinking densities. In addition, the use of a hydrophilic diamine hindered the diamine penetration within the particle, avoiding the crosslinking of AcAc in the particle core. The use of a more hydrophobic diamine increased the crosslinking of the inner polymer chains enhancing the crosslinking efficiency. Moreover, the polymer films cast from latexes produced with a non crosslinked seed showed solvent sensitivity due to the presence of soluble microdomains in the crosslinked film. The use of a crosslinked seed avoided these weak spots and hence, solvent resistance was further increased.

Acknowledgements: The authors thank the financial support provided by the Industrial Liaison Program in Polymerization in Dispersed Media of Polymat (Nuplex Resins, Dow Chemical, Arkema, Euroresin, Rohm and Haas, Wacker Chemie and Cytec Surface Specialties).

[1] W. Kubitza, *Surface Coatings International* **1992**, *75*, 340.
[2] M. Okubo, Y. Nakamura, T. Matsumoto, *J. Polym. Sci. Part A: Polym. Chem.* **1980**, *18*, 2451.
[3] S. Magnet, J. Guillot, A. Guyot, C. Pichot, *Prog. Org. Coat.* **1992**, *20*, 73.
[4] J. M. Geurts, S. van Es, A. L. German, *Prog. Org. Coat.* **1996**, *29*, 107.
[5] U.S. Patent 4,894,397, S.C. Johnson, **1990**.
[6] U.S. Patent 5002998. ICI, **1991**.
[7] U.S. Patent 5494975, Rohm and Haas, **1996**.
[8] U.S. Patent 5536784, Air Products and Chemicals, **1996**.
[9] U.S. Patent 5663266, Eastman Chemical Co., 1997.
[10] R. J. Esser, J. E. Devona, D. E. Setzkem, L. Wagemans, *Prog. Org. Coat.* **1999**, *36*, 45.
[11] A. Noomen, *Prog. Org. Coat.* **1997**, *32*, 137.
[12] L. Bouvier-Fontes, R. Pirri, J. M. Asua, J. R. Leiza, *Macromolecules* **2005**, *38*, 1164.
[13] P. J. A. Geurink, T. van't Veer, R. Buter, I. Rood, J. Schlief, L. Van der Ven, R. Leijzer, *Prog. Org. Coat.* **2003**, *48*, 153.
[14] L. Van der Ven, R. R. Camping, P. J. A. Geurink, L. van Dalen, *FATIPEC conf.* **1994**, Budapest, Hungary, 105–118.
[15] P. J. A. Geurink, L. van Dalen, L. van der Ven, Camping, *Prog. Org. Coat.* **1996**, *27*, 73.
[16] W. Schubert *Prog. Org. Coat.* **1993**, *22*, 357.
[17] J. Feng, H. Pham, P. McDonald, M. A. Winnik, J. M. Geurts, H. Zirkzee, S. van Es, A. L. German, *J. Coat. Technol.* **1998**, *70*, 57.
[18] I. Gonzalez, G. Arzamendi, J. M. Asua, J. R. Leiza. *Accepted in Macromol. Mat. Eng.* **2006**.
[19] J. Chiefari, J. Jeffery, R. T. A. Mayadunne, G. Moad, E. Rizzardo, S. H. Thang *Macromolecules* **1999**, *32*, 7700.
[20] A. K. Chaudhuri, S. R. Palit, *J. Polym. Sci, Part: A Polym. Chem.* **1968**, *6*, 2187.
[21] Y. J. Park, M. J. Monteiro, S. van Es, A. L. German *European Polym. J.* **2001**, *37*, 965.