Formation and Crosslinking of Latex Films through the Reaction of Acetoacetoxy Groups with Diamines under Ambient Conditions

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We investigated the processes of film formation, polymer diffusion, and crosslinking of latex films at ambient temperature, using low T_g methacrylate latex bearing acetoacetoxy groups, and curing the systems with 1,6-hexanediamine as the crosslinker. The addition of diamine induces floc formation, which modifies the rheological properties of the dispersion and increases its drying rate when coated onto a substrate. The crosslinking reaction between diamine and acetoacetoxy groups occurs at a rapid rate, even in the dispersed state. Although the crosslinking reaction precedes polymer diffusion in the two systems we examined, latex films with relatively good solvent resistance are obtained.

INTRODUCTION

Polymer latex particles bearing functional groups at the particle surface or within the particles have many practical applications. The functional groups can provide a latex with specific properties such as improved colloidal stability, modified rheological behavior, enhanced binding capacity for biomolecules or surface active substances, better adhesion to a given substrate, as well as increased mechanical performance of the films obtained from these latex samples.[1] When the functional groups are chemically reactive, they are capable of participating in various post-polymerization reactions.[2] Increasing attention is being paid to utilizing these reactive latex polymers to form crosslinkable films for their applications in waterborne paints, coatings, and adhesives. Although latex coatings reduce the amount of volatile organic emissions compared to solvent-based coatings and display excellent performance in many areas of applications, thermoplastic latex films lack tensile strength, abrasion resistance, chemical resistance, and general durability. These film properties can be greatly improved by introducing crosslinks in the systems.[3]

Reactive latex particles which can form crosslinkable films are conventionally prepared by copolymerizing the base monomers with a functional monomer during the emulsion polymerization process. Carboxyl and hydroxyl functionalities are frequently introduced into latex systems, particularly at the particle surface, with the use of monomers such as methacrylic acid and 2-hydroxyethyl methacrylate.[1] An example of an application of this kind of functional latex is the use of multistage acrylic latex, with surface carboxyl and hydroxyl functional groups, in automotive basecoat.[4] Crosslinking can be achieved by reacting the hydroxyl groups with a melamine crosslinker at a high curing temperature (normally 140-160°C). Of the various reactive monomers, N-methylol(meth)acrylamides [N-M(M)AA] are commonly used to develop crosslinking emulsions.[3,5] The methylol groups of N-M(M)AA can self-condense or cross-condense with -OH groups upon conventional thermal curing (e.g., at 200°C). Ethers of N-methylolacrylamide [e.g., N-(iso-butoxymethyl)-acrylamide)] have also been used

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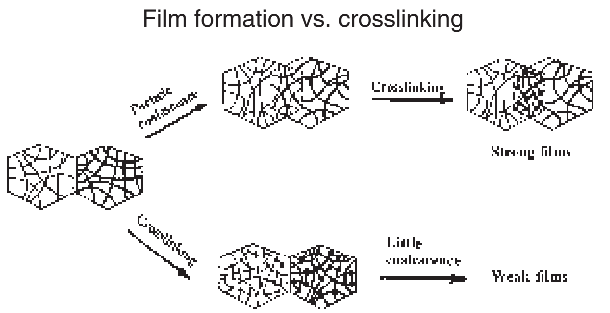


Figure 1—A drawing showing schematically the two competitive processes: polymer diffusion (or film coalescence) vs. crosslinking. The formation of a mechanically strong film requires that a significant amount of interdiffusion is achieved before crosslinking.

as functional monomers to prepare crosslinkable latex, by self-condensation or reacting with amines, hydroxyls, and carboxyls, under thermal treatment.[2,6,7] Glycidyl (meth)acrylates (GA or GMA) are very useful reactive monomers. They contain both an epoxy group and an unsaturated group and can be used in either nucleophilic substitution reactions or radical reactions.[8] These monomers can copolymerize with unsaturated monomers to produce latex particles bearing epoxy groups, preferably at low polymerization temperature, to preserve the epoxy content.[9-11] Films formed from these particles can be cured with reactive substances such as carboxylic acids at elevated temperature.[8,12] Thiirane-functional monomers, e.g., 2,3-epithiopropyl methacrylate, have also been used to produce crosslinkable emulsions and the reactivity of the thiirane group has some differences compared to oxiranes introduced via GMA.[13]

An important goal for novel latex-based coatings is to be able to cure the films at ambient temperature. This requires very reactive crosslinking functional groups. An interesting type of reactive monomer is acetoacetoxyethyl methacrylate.[14,15] The functional (acetoacetoxy) groups can be easily incorporated into an acrylic latex, and crosslinking can be achieved at ambient temperature by reaction with difunctional amines to form enamines, with aldehydes, and with electron-deficient olefins via Michael addition. In this sense, the acetoacetoxy functionality offers unique versatility to the coatings formulator. Other reactive systems include maleimide-containing emulsions prepared with 6-(3-chloromaleimido) hexyl acrylate.[16] The maleimide unsaturation may be able to react with nucleophiles such as amines by addition reactions at ambient temperature. Epoxy-containing latex prepared with GMA may also crosslink with diamines at temperatures close to room temperature.[12,17] Another type of application of GMA employs the double bond as the reactive functionality.[8,18] Latex particles bearing carboxylic acid groups at the surface may be prepared first. After post-reaction of the carboxyl groups with GMA, an unsaturated latex is obtained, and its films can be crosslinked under ambient conditions[18] using a curing procedure similar to that employed for unsaturated oils or alkyd resins. Film curing based on hydrazone formation between a carbonyl and a hydrazine residue has also been widely investigated.[19] Other strategies involve esterification between carboxylic acid and oxazoline,[20] and Schiff-base formation between primary amine and C=O groups.[21]

While heat-curable latex systems have been described in both the patent literature and in scientific journals, there have been very few reports systematically examining films prepared from reactive latex that are curable at room temperature. We are interested in examining both film formation and crosslinking processes occurring at ambient temperature. As a start in this direction, we have prepared latex samples containing the acetoacetoxy functionality and examined its reaction with diamines. Another approach involves preparing films with unsaturated functionality and curing the films in air. In this paper we present our results for systems with the acetoacetoxy functionality.

For latex films the crosslinks need to be formed in a special way: one needs interdiffusion and entanglement between polymer molecules from adjacent latex particles to generate adhesion strength. Crosslinks between polymers originating in the same latex particles will only make the film weaker. The technology depends on a proper balance between the rate of polymer diffusion to generate interpenetration (or entanglements), and the rate of crosslinking to lock the penetration in place. There is very little known about the rates of interdiffusion and crosslinking in these systems. This issue of the rate of polymer diffusion across an interface, in competition with the rate of the crosslinking reaction, which retards the diffusion rate, is a topic of intense interest. In *Figure* 1, we depict schematically these two competitive processes and the influence of their relative rates on the final film strength. In the following we will describe a system in which we measure both rates, which are important for the development of mechanical properties of the films. In this way we hope to obtain a deeper understanding of the curing process in latex films.

Table 1—Recipes for the Preparation of AA-PBMA and AA-PEHMA Latex Samples

	AA-PBMA	AA-PEHMA
Recipe		
BMA (g)	85.50	—
EHMA (g)	—	85.33
AAEMA (g)	8.60	8.53
Water (g)	847.5	850.4
$Na_2S_2O_8$ (g)	2.316	2.364
$NaHSO_3$ (g)	1.040	1.06
$CuSO_4$.EDTA[a] (µ mol)	1.50	1.50
SDS[b] (g)	2.883	2.887
$NaHCO_3$ (g)	0.804	0.804
Temp (°C)	20	20
Time (hr)	24	20

(a) EDTA: ethylene diamine tetraacetic acid, tetrasodium salt; b. SDS: sodium dodecyl sulfate.

Table 2—Recipes for the Preparation of Labeled AA-PEHMA Samples

First Stage		Second Stage	
EHMA (g)	2.8	EHMA (g)	22.5
AAEMA (g)	0.28	AAEMA (g)	2.5
DM (ml)	0.075	DM (ml)	0.60
Water (ml)	60	FLM (mol%)[a]	1
$K_2S_2O_8$ (g)	0.062	Water (ml)	26
SDS (g)	0.15	$K_2S_2O_8$ (g)	0.060
$NaHCO_3$ (g)	0.080	SDS (g)	0.60
Temp (°C)	80	Temp (°C)	80
Time (hr)	1	Time (hr)	7

(a) FLM: fluorescent monomer. For labeling with Phe, 1 mol% 9-vinyl phenanthrene, based on total moles of monomers, was added into the monomer feed. For labeling with An, the FLM was (9-anthryl) methacrylate.

EXPERIMENTAL

Latex Sample Preparation and Characterization

The reactive latex samples used here contain acetoacetoxy (AA) functionality. These are copolymers of either butyl methacrylate (BMA), or 2-ethylhexyl methacrylate (EHMA), with 10 wt% acetoacetoxyethyl methacrylate (AAEMA), referred to as AA-PBMA or AA-PEHMA. Many of these samples were prepared by emulsion copolymerization at 20°C using a redox initiation system ($Na_2S_2O_8/NaHSO_3/CuSO_4.EDTA$) by a batch process. The recipes are described in *Table* 1.

Some AA-PEHMA samples were labeled with a small amount of phenanthrene (Phe), and some with anthracene (An), referred to as Phe-AA-PEHMA and An-AA-PEHMA. One pair of labeled polymers was poly(butyl methacrylate), without AA groups, referred to as Phe-PBMA and An-PBMA. These labeled samples were prepared at 80°C, using potassium persulfate as the initiator and dodecyl mercaptan (DM) as the chain transfer agent, via a semi-continuous process. The recipes for the preparation of labeled AA-PEHMA latex are presented in *Table* 2. The conditions for preparing labeled PBMA samples were essentially identical to those of PEHMA. One mol% of dye co-monomer was used in each polymer sample. Nearly 100% of dye fraction was reacted and randomly incorporated into polymer chains, as analyzed by a technique described previously based on gel permeation chromatography (GPC) measurements.[22] We found in our experiments that it was difficult to obtain efficient and uniform dye labeling when polymerizations were carried out at 20°C using the redox initiators, either via a batch or via a semi-continuous process.

Particle sizes and size distributions were measured by dynamic light scattering employing a Brookhaven BI-90 Particle Sizer. The glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7), with a heating rate of 10°C/min and under N_2 atmosphere. Molecular weight and molecular weight distributions were determined by gel permeation chromatography (GPC), using two Ultrastyragel columns (500 + 10^4 Å) and THF as an eluent with a flow rate of 0.8 ml/min. The important characteristics for the latex are shown in *Table* 3.

The acetoacetoxy-functional groups in the latex polymers were quantitatively and qualitatively characterized by ^{1}H-NMR spectroscopy (Varian 200-MHz NMR spectrometer). The characteristic NMR peaks of the AA monomer, 3.6 ppm for the methylene group and 2.3 ppm for the methyl group, were used to quantify the AA content in the polymers. We found that the labeled AA-PEHMA samples prepared at 80°C with a total polymerization time of eight hours had a significantly lower (ca. 30%) AA content than the theoretical value, although a significant level of AA was still present, and the polymer was completely soluble in organic solvents. Storage of these latex dispersions at room temperature led to the loss of the functionality: ca. 35% functionality in the AA-containing latex was lost after six months. In addition, some intraparticle crosslinking occurred over this time.

Analysis of Film Properties

The solids content of the latex dispersion samples used here were in the range of 10-25 wt%, and it took two to five hours for them to dry in the open air (50-65% RH) to form films (typically 50 µm thick). For some dispersion samples, the drying rates were analyzed by gravimetric water loss measurements. Most of our latex polymers were chosen to have T_g values below or close to room temperature, and thus were able to form continuous films after drying in air at room temperature. For crosslinking the AA-functionalized films, a certain amount of 5 wt% aqueous solution of 1,6-hexanediamine, with a molar ratio $H_2N(CH_2)_6NH_2$:AA = 1:2, was added into the dispersions. A film was cast onto a solid substrate and allowed to dry, giving solid films. Some films were further aged in air for three days or a week.

The extent of crosslinking was characterized by solvent extraction and swelling measurements. A film specimen (weight: W_o, dimensions: 15 × 15 × 0.1 mm) was immersed in an excess of 1,4-dioxane for 72 h to promote swelling and dissolution equilibrium. The film specimen was then carefully removed from the solution, and the solvent on the surface was absorbed by touching it with a filter paper. The weight of the swollen film (W_1) was immediately measured. This procedure was completed within five seconds after removing the specimen from the solution to assure consistency in all measurements. The swollen film was then dried in a vacuum oven to a constant weight (W_2). The gel content (%) and

Table 3—Characteristics of Acetoacetoxy-Functionalized and Fluorescent-Labeled Latexes[a]

Latex	AA-PBMA	PBMA	AA-PEHMA	
Label	none	Phe- An- (1:1)	none	Phe- An- (1:1)
Diameter (nm)[b]	54.2	120	50.8	85
Polydispersity	0.082	0.02	0.078	0.02
T_g (°C)	33	21	—	-7
Solids (wt%)	10.6	26.0	10.5	24.5
Mw ($x10^4$)[c]	78	3.5	—	4.7
Mn ($x10^4$)[c]	28	1.7	—	1.6

(a) For each pair of Phe- and An- labeled samples, the T_g value, particle size, and average molecular weight were measured for 1:1 mixtures of the pair.
(b) From dynamic light scattering: z-averaged particle diameters.
(c) Nominal molecular weights based upon gel permeation measurements using poly(methyl methacrylate) standards.

swelling ratio are calculated from the following expressions:

$$\text{Gel content (\%)} = (W_2 / W_o) \times 100\% \quad (1)$$

$$\text{Swelling ratio} = (W_1 / W_2) \quad (2)$$

NMR and FTIR measurements were also used to characterize the latex films. For FTIR measurements, films were prepared by casting very dilute latex dispersions onto water-resistant IR plates and then placed in a sample chamber equipped with N_2 flow. ^{1}H-NMR measurements were performed for non-crosslinked polymers in d-chloroform and for slightly-crosslinked polymers in the swollen state with d-chloroform or a mixture of d-chloroform and d-toluene. For crosslinked films, ^{13}C solid-state high-resolution NMR spectra were measured in the laboratory of Prof. Peter Macdonald, employing various techniques including magic-angle spinning, cross-polarization, and decoupling to minimize the line broadening.

We then used direct non-radiative energy transfer technique as a means of measuring polymer interdiffusion. Fluorescence decay measurements were carried out for labeled films. The measurement conditions were similar to those used previously.[23]

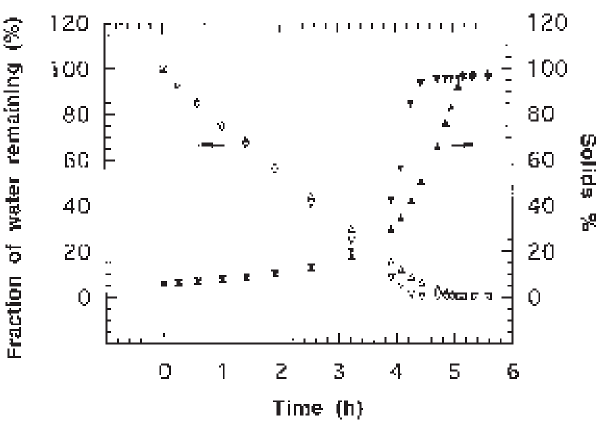


Figure 2—Plots of percent solids (%, filled symbols) and the fraction of water remaining (%, open symbols) as a function of drying time (in hr) for an AA-PBMA latex dispersion in the presence (∇t) and absence (∆s) of hexane diamine.

RESULTS AND DISCUSSION

The Film Drying Process

The AA-PBMA latex, having a high molecular weight (Mw = 7.8×10^5) with a T_g of 33°C, forms turbid films with large cracks after drying at room temperature (21±1°C). The lower T_g PBMA sample (Mw = 3.5×10^4, T_g = 21°C) can form continuous, clear films under slow drying conditions (drying time > two hours, either at high humidity or with a thick layer of dispersion). The AA-PEHMA latex can readily form soft, clear films at 21°C. These observations indicate that the minimum film-forming temperatures follow the trend of T_g values measured for the samples. To crosslink the AA-containing copolymer latex, hexanediamine was added into these dispersions, followed by air drying to give films. All the previously mentioned latex samples form crack-free films with the addition of diamine to the dispersions.

THE DRYING BEHAVIOR AND PSEUDOPLASTIC EFFECT: When the AA-containing latex samples were mixed with diamine in dispersion and air dried, a different drying behavior and a different appearance of the dispersions were observed. First, these dispersions had increased viscosity and turned into a nearly immobile state when the drying reached only about 15 wt% solids (in about 40 min). In contrast, the dispersions in the absence of diamine remained liquid-like until the end of the drying process. Second, from the very beginning of the drying process, dispersions with diamine exhibited much higher turbidity than those of the pure latex, implying the association of individual particles into flocs. We infer from these results that there may be interactions between the diamine molecules and particles, which causes association of the particles, leading to an increase in turbidity and viscosity. This high viscosity persists only under conditions of little mechanical disturbance or low shear rate. Under shear, the viscosity drops. This type of pseudoplastic behavior[24] is often useful for many coatings applications. Pseudoplasticity can arise from many different types of interactions, e.g., hydrogen bonding or association between polar or hydrophobic groups.[4] An example of such a system is a latex dispersion containing carboxylic acid and hydroxyl groups in the particle shell, which exhibits pseudoplastic behavior upon addition of melamine to the system.[4] In the present system, the interaction is likely the hydrogen-bonding between the amino groups and the acrylic ester groups or the polar groups at the particle surface. This is confirmed by a similar rheological effect observed for dispersions of PBMA without the AA-functional groups but in the presence of diamine.

In addition to the physical association between the amino groups in the diamine and the functional groups at the particle surfaces, the chemical reaction between the diamine and the acetoacetoxy groups can promote the viscosity increase. We found that the AA-containing PBMA dispersions became highly viscous over a shorter time (40 min) during drying than the AA-free PBMA samples (here 90 min), both in the presence of diamine and with the same initial solids content (10%) and particle size. Also, as will be pointed out in the following, the crosslinking reactions in the AA-containing system occur well before the dispersions are dried. This type of chemical bridging of particles leads to the formation of microgel, and unlike physical association, is an irreversible process. Note that the AA-PBMA latex (T_g = 33°C), which only formed powdery films upon drying at room temperature, produced continuous, highly transparent films when mixed with diamine and then dried. We did not observe a decrease of minimum film-forming temperature for AA-free PBMA with the addition of hexanediamine.

Another important phenomenon that we observed is that all of these latex dispersions (either AA-free or AA-containing), in the presence of hexanediamine, dry uniformly across the surface. Films obtained by spreading dispersions without diamine dry with a pronounced drying front, exhibiting a dry transparent film at the edge which grows towards the center. This type of drying front is common for films formed from normal latex dispersions. Front propagation is related to the flux of liquid water and particles in the plane of the substrate.[25] Our observations indicate that no macroscopic particle fluxes across the film plane are possible in the presence of diamine in the drying dispersions. This drying behavior is consistent with the high viscosity and the formation of crosslinks found for dispersions in the presence of diamine.

Drying Rates in the Presence or Absence of 1,6-Hexanediamine: Due to the large difference in drying behavior between dispersions with and without the diamine, we carried out experiments in which we monitored the drying rate of these samples. *Figure* 2 shows drying curves of an AA-PBMA latex dispersion in the presence and absence of the diamine. One sees that the presence of the diamine gives a noticeable increase in the drying rate. It takes less time (ca. 4.3 hr vs. 5 hr) for the amino-containing dispersion to reach 97% solids than for the dispersion without the diamine. When we compare the drying behavior of pure PBMA latex (no AA) in the presence and in the absence of hexanediamine, we observed a very similar behavior: the diamine-containing dispersions dry faster than the diamine-free dispersions. In our experiments some samples were ion-exchanged to remove ionic substances (e.g., surfactant) before addition of diamine, and some were examined without cleaning. The presence of surfactant and other ionic species alters slightly the rate difference between the amino-containing and amino-free dispersions. This, however, does not change the trend of drying rates: the presence of the diamine always facilitates drying. We attribute the fast drying rate in the presence of the diamine to the formation of flocs in the dispersion, leading to hydrophilic channels between particles in the film. These channels facilitate water transport as the film dries.

A somewhat similar mechanism has been suggested previously for the enhancement effect of surfactants on drying rate of latex dispersions.[25] Surfactants do not induce floc formation, nor do they suppress the drying front. They do appear to affect the interparticle spaces in the wet-dry boundary at the edge of the drying front to facilitate water transport and accelerate the drying rate for latex films. This effect is smaller than the effect described for diamine-induced floc formation.

Characterization of Film Crosslinking

Two major techniques were employed to characterize the crosslinking in the latex films. The swelling technique enables one to obtain the gel content and swelling ratio, both related to the extent of crosslinking. IR and NMR measurements provide information about structural changes related to the crosslinking reactions.

Characterization of Crosslinking by the Swelling Technique: Both pure AA-PBMA and pure AA-PEHMA latex samples give films soluble in organic solvents such as dioxane. This indicates that negligible crosslinking occurs during the preparation of the above two kinds of copolymer latex particles. The redox initiated low-temperature polymerization favors the production of linear polymers, avoiding thermal crosslinking reactions between functional groups and thermally enhanced hydrolysis of the AA group. In addition, the AAEMA content in the copolymers is sufficiently low to avoid gel formation during particle synthesis. We did find, however, that a homopolymer latex of acetoacetoxyethyl methacrylate, PAAEMA, prepared under similar low-

Table 4—Gel Contents and Swelling Ratios in Dioxane for Films Formed from AA-PBMA and AA-PEHMA Latex Samples With or Without Diamines and Aged for Different Times

Latex	AA-PBMA			AA-PEHMA			
		With amine			With amine		
	No amine	Fresh	3 days	No amine	Fresh	3 days	7 days
Gel content (%)	0	98	97	0	90	92	92
Swelling ratio	—	3.1	3.0	—	1.8	1.9	1.9

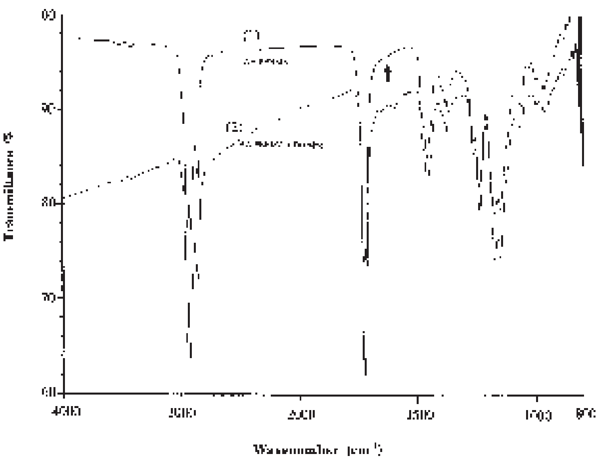


Figure 3—FTIR spectra for freshly dried AA-PEHMA films in the absence (curve 1) and presence (curve 2) of hexanediamine. The arrow indicates the absorption peak at 1632 cm^{-1} for curve 1, attributed to the enol double bond.

temperature conditions, was partially crosslinked. We also found that after long storage times, the AA-copolymer dispersions gave films with a measurable gel content.

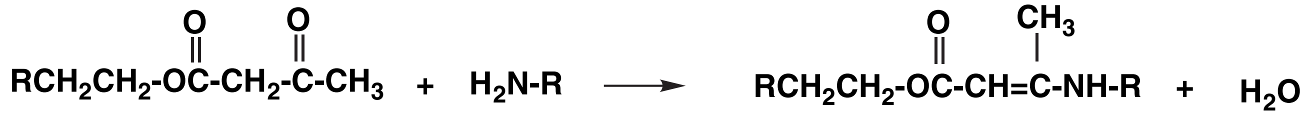
When hexanediamine was added to the AA-PBMA latex dispersions or to the AA-PEHMA latex dispersions, and films were cast, these films when dry did not dissolve in dioxane or in any other organic solvent. These results indicate that the reaction between the amino groups and the AA groups occurs rapidly, either in the dispersion or during air drying and aging, resulting in sufficient crosslink density in the latex films to resist organic solvents. The gel content and swelling ratio in dioxane were measured both for newly formed films and for aged films, allowing us to look at the crosslinking capacity of the reactive species in the films. *Table* 4 summarizes the results for these samples and also for films prepared in the absence of the diamine crosslinker.

The addition of diamine to both AA-PBMA and AA-PEHMA latex dispersions led to crosslinked films with only a small weight fraction extractable in a good solvent. The extractable part might include trace amounts of water, monomer, unreacted diamine, and a small amount of polymer. The major part of the film formed a stable network, swellable but not soluble in solvent. When comparing the AA-PBMA latex films with the AA-PEHMA films, the latter had a relatively lower degree of swelling. One would expect that the lower T_g AA-PEHMA copolymer would provide higher mobility for achieving a higher density of crosslinking than the relatively higher T_g AA-PBMA copolymer. A lower gel content observed for AA-PEHMA films compared to the AA-PBMA films could be explained by several possible reasons, e.g., higher compositional heterogeneity and lower miscibility of 1,6-hexanediamine in AA-PEHMA, and higher steric hindrance to the crosslinking reaction between AA-PEHMA and amine.

The results also show that there is virtually no significant difference between the newly formed films and those aged for three days or a week, for both AA-PBMA and AA-PEHMA latex samples in the presence of diamine. A possible explanation is that the crosslinking reaction takes place at a rapid rate. Thus after our films were dried (e.g., for three hours), the crosslinking reactions had already occurred to a large extent, and further aging does not increase significantly the crosslinking density. We will confirm this point in the following.

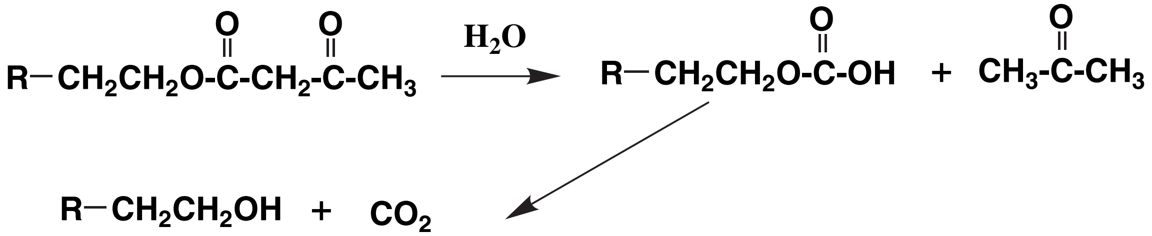
CHARACTERIZATION OF THE CROSSLINKING REACTION BY IR AND NMR SPECTROSCOPIES: The reaction mechanism between acetoacetoxy and amino groups is believed to be associated with the formation of enamino ester, as pointed out by Rector et al.[14] and Geurink et al.[15], and shown in *Scheme* 1.

The first spectroscopic technique we employed to characterize the crosslinking reactions was FTIR. Based on *Scheme* 1, the crosslinking reaction between an acetoacetoxy and an amino group should be characterized by the formation of a C–N bond and the cleavage of a C–O and a N–H bond. Unfortunately, in the IR spectra we obtained (*Figure* 3), the absorbance peaks for the C–N or C–O bonds largely overlap with those peaks from the base polymer and those from the added diamino compound. Yet, the characteristic peak at 3300 cm^{-1} for N–H bonds is always masked by the presence of trace amounts of water in the film or in the sample chamber, even when the films are stored under vacuum and examined in a nitrogen environment. One noticeable difference in the spectra in *Figure* 3 is that there is a peak at 1632 cm^{-1} for the film without the diamine, which becomes less pronounced when the diamine is present. We attribute this peak to the absorption of the enol double bond.[26] The reaction between AA and amine leads to the formation of an enamine. The enamine double bond should give an absorption band at 1606 cm^{-1},[27] which also overlaps with an absorption peak from pure 1,6-hexanediamine. Note that the IR spectra shown in *Figure* 3 are for films freshly prepared from a dispersion, and we obtained similar spectra when the films were aged for one to four days. This indicates that the enol structure vanishes rapidly prior to or during film formation when the diamine is added.



$$\mathrm{RCH_2CH_2\text{-}O\overset{\overset{\large O}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{\large O}{\|}}{C}\text{-}CH_3 + H_2N\text{-}R \longrightarrow RCH_2CH_2\text{-}O\overset{\overset{\large O}{\|}}{C}\text{-}CH{=}\overset{\overset{\large CH_3}{|}}{C}\text{-}NH\text{-}R + H_2O}$$

Scheme 1



$$R{-}CH_2CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \xrightarrow{H_2O} R{-}CH_2CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

$$R{-}CH_2CH_2OH + CO_2$$

Scheme 2

We also used high-resolution solid-state ^{13}C-NMR spectroscopy as a means of determining the extent of crosslinking with hexanediamine. *Figure* 4 shows ^{13}C-NMR spectra for a homopolymer of acetoacetoxyethyl methacrylate (PAAEMA) before and after mixing with the diamine in THF solution for 24 hr. The PAAEMA dispersion was prepared under conditions similar to the AA-PBMA and AA-PEHMA copolymers. The addition of hexanediamine to PAAEMA in this case should produce a model sample with a high extent of crosslinking, allowing us to observe clearly the changes associated with the reactions. In our assignment for each individual resonance shown, standard spectra of relevant compounds in references 28a and 28b were used for comparison.

In the spectrum of pure PAAEMA (*Figure* 4a), one can readily identify carbon resonances associated with the methacrylate backbone methyl (16 ppm), tertiary carbon (45 ppm), and carboxyl (178 ppm), although the backbone methylene (55 ppm) is obscured by other resonances. In particular, the ethoxy methylenes are expected to occur in the region of 63 ppm where there is a broad ill-resolved group of resonances. Likewise, the methylene of the acetoacetoxy, flanked by carbonyls, occurs in this region of the spectrum (50 ppm). The terminal methyl of the acetoacetoxy group is clearly resolved (30.3 ppm), as are the carboxyl carbonyl (168.2 ppm) and the ketone carbonyl (202.2 ppm) carbons. The peak at ca. 105 ppm probably arises from the unsaturated carbon in the enol structure. Because these ^{13}C-NMR spectra were acquired using cross-polarization, the resonance intensities cannot be interpreted quantitatively.

When the PAAEMA polymer is mixed with diamine to induce crosslinking, we observed some important changes in the ^{13}C-NMR spectra (*Figure* 4b). The resonances from the crosslinker hexanediamine itself appear in the region of 28-34 ppm for the methylenes beta and gamma to the amino groups, and at about 43 ppm for the alpha methylene, although the latter resonance cannot be resolved from the ethylene resonance occurring in the same region of the spectrum. Major changes in this spectrum include the decrease in intensity of the terminal methyl resonance at 30.3 ppm and the acetoacetoxy ketone resonance at 202 ppm. Their presence indicates that 100% crosslinking was not achieved. New resonances appear at 163.0 ppm, 82 ppm, and in the region of 95-105 ppm. By comparison with literature spectra for compounds of known structure, these peaks are assigned to the carbons in the enamine structure. These results indicate that ^{13}C-NMR is capable of detecting the reaction between acetoacetoxy and hexanediamine. In particular, the carbonyl region of the spectrum yields the most clear-cut information. Our results lend support to the reaction mechanism between acetoacetoxy and amine groups proposed previously (*Scheme* 1).[14,15] Unfortunately, when copolymers of BMA or EHMA with 10% AAEMA, after crosslinking with hexanediamine, were investigated by ^{13}C-NMR under the same conditions, we found that the resonances corresponding to the AAEMA units were too low in intensity to be useful as a means of quantifying the extent of crosslinking.

LOSS OF FUNCTIONALITY DURING STORAGE AND UPON HEATING: We noticed in our experiments that the AA-functionalized samples gradually lost their efficiency for crosslinking with diamine. *Table* 5 shows a comparison of crosslinking capacity with diamine between newly prepared AA-PEHMA latex and the same latex stored at room temperature for six months. One sees that in films prepared from aged dispersions, the gel content is somewhat decreased and the swelling ratio is considerably increased. We also observed that the AA-PEHMA films in the absence of diamine became partially crosslinked (gel content ca. 50% in dioxane) after storage for six months.

It has been proposed that the loss of functionality in such a system is mainly due to the hydrolysis of the acetoacetoxy group and a reverse Claisen condensation (*Scheme* 2), giving as decomposition products the hydroxyethyl group, acetone, and carbon dioxide.[29] Some coatings formulators try to add stabilizers such as ammonia, which converts the acetoacetyl group into an enamine, to slow down this hydrolysis during storage.[29]

Polymer Diffusion Rate vs. Crosslinking Rate

In the sections that follow, we examine the crosslinking rates and polymer interdiffusion rates in the AA-PEHMA and AA-PBMA latex films. Since the crosslinking reactions are very fast, we chose to prepare relatively small

Table 5—Gel Contents and Swelling Ratios in Dioxane for AA-PEHMA/Diamine Films Formed from Latex Dispersions Freshly Prepared and Stored for Six Months

	AA-PEHMA latex + Diamine	
Film	Fresh	Stored for 6 months
Gel content (%)	90-92	83-87
Swelling ratio	1.8-1.9	2.5-3.5

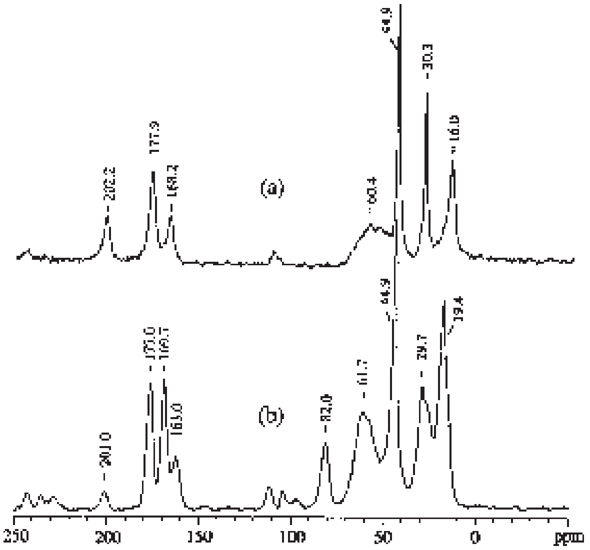


Figure 4—^{13}C high-resolution solid-state NMR spectra for samples of: (a) PAAEMA, and (b) PAAEMA crosslinked with diamine in THF and dried after reaction for 24 hr.

(50 to 80 nm diameter) latex particles (c.f., *Table* 3). Small particles form films with large interparticle surface area, and this offers the possibility that relatively small extents of polymer or polymer segment interdiffusion, coupled with interparticle polymer crosslinking, might still produce useful films. One result that we still find surprising is that even in the case of AA-PBMA, where we will infer that very little interparticle polymer diffusion takes place, we still obtain transparent films insoluble in organic solvents.

***Crosslinking Rate**:* To obtain information about crosslinking rates, we monitored the change of gel content of the polymer with reaction time. Since we observed that a high extent of crosslinking had occurred in the newly dried films, we began our measurements on samples in the dispersed state, well before drying was complete. An aliquot (ca. 0.3 g) of each dispersion, after a certain time of reaction, was removed and quickly freeze-dried (within about five minutes) at 0.06 mm Hg. The dried powder obtained in this way was placed into dioxane and stirred. Finally the suspension was centrifuged to sediment the insoluble gel, which was separated and weighed. *Figure* 5 shows the plot of gel content (%) as a function of time for an AA-PBMA latex mixed with diamine. Here the starting reaction time was chosen when the dispersion (latex + diamine) was placed onto a glass substrate, after the two reactive components had been mixed and stirred for five minutes. We see that rapid crosslinking occurs between the reactive moieties: the gel content exceeds 80% after about five minutes drying time (total 10 min after mixing the diamine with the latex). At a reaction time of 60 min, the gel content reached 95%, quite close to that (ca. 97%) for the dry film after 210 min.

Rapid crosslinking was also observed for the AA-PEHMA sample. A fast crosslinking reaction between acetoacetoxy and amino groups was also reported by Geurink et al.,[15] although the type of latex polymers and crosslinkers described by these authors were not the same as those used here.

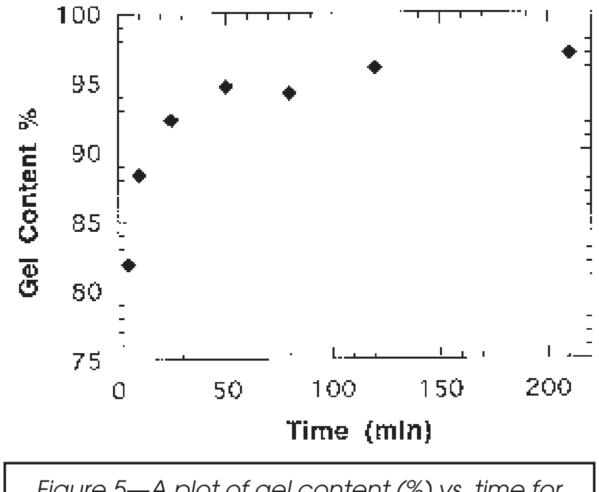


Figure 5—A plot of gel content (%) vs. time for an AA-PBMA latex polymer in dispersion mixed with hexane diamine as a crosslinker.

POLYMER DIFFUSION RATE AT AMBIENT TEMPERATURE: We monitored the polymer diffusion process by measuring changes in the extent of energy transfer between donors and acceptors attached to the polymers, originally separated in individual particles. Fluorescence decay measurements were carried out on our film samples as a means of assessing the extent of energy transfer and polymer diffusion as a function of aging history. *Figure* 6 shows an example of a series of donor decay profiles for film samples aged for different times. These films were prepared from a 1 : 1 mixture of Phe- and An-labeled AA-PEHMA samples (d = 85 nm, Mw = 4.7×10^4, T_g = -7°C) in the absence of diamine. Since the diffusion rate for this polymer is relatively rapid,[32] we prepared thick films (ca. 300 µm) to minimize the measurement time (ca. 5 min) needed for each decay profile. As seen in *Figure* 6, when the films are aged, the curvature of the decay profiles gradually becomes more pronounced. This indicates that molecular mixing has occurred between donor- and acceptor-labeled polymers and the extent of energy transfer is increased, leading to a faster decay of donor fluorescence.

To characterize the diffusion process, one approach that we have employed in the past is to try to estimate the extent of mixing from comparison of the fluorescence decay curves. A simple measure of the extent of mixing, $f_m(t)$, is the normalized growth in energy transfer efficiency,[23]

$$f_m(t) = \frac{\Phi_{ET}(t) - \Phi_{ET}(0)}{\Phi_{ET}(\infty) - \Phi_{ET}(0)} = \frac{\text{area }(0) - \text{area }(t)}{\text{area }(0) - \text{area }(\infty)} \qquad (3)$$

where $[\Phi_{ET}(t) - \Phi_{ET}(0)]$ represents the change in energy transfer efficiency between the initially prepared film and that aged for time t. In our experience, the most reliable way to obtain Φ_{ET} is from the area under the normalized fluorescence decay curve. To obtain an accurate area for each decay profile, we fit the profile to the decay function:

$$I_D(t_d) = A_1 \exp[-t_d/\tau_D^o - P(t_d/\tau_D^o)^{1/2}] + A_2 \exp(-t_d/\tau_D^o) \qquad (4)$$

The physical meaning of the fitting parameters (A_1, A_2, P) in equation (4) is not important here, but one can use these parameters to calculate the *area* under the normalized decay profile by integrating $I_D(t_d)$ from time zero to infinity. The $f_m(t)$ values are obtained by comparing the areas under the measured decay profiles for newly formed films [*area(0)*], films aged for certain times t [*area(t)*], and films aged for a sufficiently long time to approach a minimum value of the area [*area(∞)*]. Here we obtained the *area (∞)* by heating samples at 60 °C for four hours. The *area (∞)* values obtained in this way was also compared to that for a film prepared by solvent-casting, and similar values were obtained from the two types of samples.

From the f_m values, we also calculate the apparent mean diffusion coefficient (D_{app}) to characterize the rate of movement of the polymers across the interparticle interface in the samples. This involves fitting the f_m data obtained from energy transfer to a spherical Fickian diffusion model, as described previously.[23] The Fickian diffusion law is appropriate for polymers examined here which do not undergo crosslinking, since the polymers have molecular weights M_w lower than twice the entanglement molecular weight (M_e).[23,30,31] For the samples undergoing crosslinking, the diffusion process is likely to be much more complex, and the f_m data would be more useful than the D_{app} data. After the apparent diffusion coefficients are obtained, we can also estimate the interdiffusion distance d_{app} from the classical expression for diffusion distance for Fickian diffusion,

$$d_{app} = (6D_{appt})^{1/2} \qquad (5)$$

This estimate is very approximate, because of the many assumptions that go into the calculation of D_{app} values.

From the decay profiles, we analyze the diffusion rate for the labeled AA-PEHMA sample at 21°C. *Table* 6 shows the extent of mixing (f_m), the apparent diffusion coefficients (D_{app}), and the interdiffusion distance (d_{app}) at different times. We notice that this polymer diffuses to a significant extent ($f_m \approx 0.4$, $d_{app} \approx 25$ nm) over 30 min. The apparent diffusion distance per minute [$d(d_{app})/dt$] estimated for this sample is ca. 1 nm/min at early times and 0.4 nm/min at later times. For aging times as short as 10 min, a 10 nm interpenetration can be estimated. Thus, in this system, both polymer interdiffusion and crosslinking occur on a time scale of 10-30 min.

We carried out similar experiments in which the Phe- and An-labeled AA-PEHMA particles were mixed in the presence of diamine to produce films, in which both the growth of energy transfer efficiency and the crosslinking reactions occurred. Several donor decay profiles for such a film after aging for different times are shown in *Figure* 7, where curves 3 and 4 correspond to a film aged for 0 and 8 hr, respectively, and curve 5 is the decay profile for a film of the same composition obtained by solvent-recasting followed by aging for 20 hr. One sees that in addition to energy transfer from donors to acceptors causing the deviation of the decay profile from an exponential form, there is a very fast decay component at early times of the decay. The decay behavior of this component is much different from that due to energy transfer to anthracene, as seen in the profiles in *Figure* 6. This fast component is more pronounced for films aged for longer time and less pronounced for freshly-formed films. Since this decay behavior is not seen when we examine films prepared from latex without AA-functional groups but with the addition of diamine (curve 2), it is clear that it is related to chemical reactions occurring in the system. For example, some species produced from the reactions might act as a quencher for the donor fluorescence, or a short lived fluorescence impurity may be formed. Surprisingly, when we measure a film prepared from Phe-AA-PEHMA particles (no An-labeled particles) mixed with diamine, the donor decay rate is not influenced by the crosslinking reactions (curve 1, an exponential decay). We then suspect that the fast decay component would arise from cooperative action from both the An molecules and the crosslinking reaction products. This interaction may produce either a new short-lifetime fluorescent species or an efficient quencher to Phe-emission.

Table 6—The Extent of Mixing (f_m), Diffusion Coefficient (D_{app}), and Interdiffusion Depth (d_{app}) at 21 °C for Labeled AA-PEHMA (Mw = 4.7x10^4, d = 85 nm)

t (min)	f_m	D_{app}x10^{-2} (nm^2/s)	d_{app} (nm)
0	0	—	0
13	0.24	4.7	15
30	0.37	5.0	23
68	0.53	5.1	35
107	0.63	5.1	44
160	0.80	7.2	65

Table 7—f_m and Φ_Q Values for Films Prepared from 1 : 1 Phe- and An-labeled AA-PEHMA Particles in the Presence of Diamine and Aged for Different Times

Time (hr)	0	3	8	20
f_m	0	0.22	0.26	0.32
Φ_Q	0.59	0.65	0.74	0.82

Table 8—The Extent of Mixing (f_m), Diffusion Coefficient (D_{app}), and Interdiffusion Depth (d_{app}) at 21 ± 1 °C for Labeled PBMA (Mw = 3.5 x 10^4, d = 120 nm)

t (hr)	f_m	D_{app}x10^{-4} (nm^2/s)	d_{app} (nm)
0	0	—	0
12	0.14	6.4	13
40	0.21	4.2	19
72	0.28	4.3	25
90	0.31	4.3	29
264	0.58	5.9	58

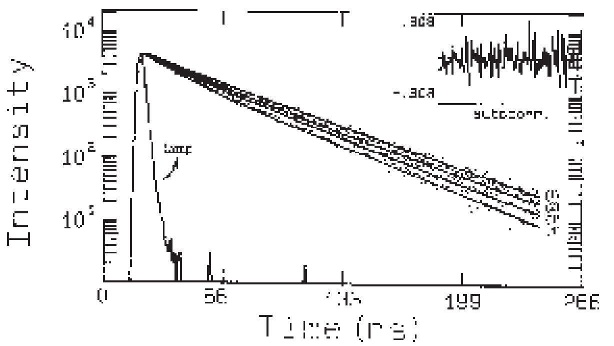


Figure 6—Donor fluorescence decay profiles for AA-PEHMA latex films (Mw = 4.7 x 10^4, d = 85 nm, Phe:An = 1:1) with diffusion time of: (1) 0, (2) 13, (3) 68, and (4) 160 min, respectively. These curves are integrated to obtain the areas under them in our data analysis. We also display the weighted residuals and their autocorrelation for curve 2 when fitted to equation (5).

The presence of the fast decay component complicates our data analysis for interdiffusion in competition with crosslinking. We believe, however, based upon the verification experiments described, that it serves as an indicator for the crosslinking reactions. Attempts were made to evaluate the contributions to the donor decay from this component associated with crosslinking reaction and that from the energy transfer in relation to polymer diffusion. Since the fast quenching component is only important at early times in the fluorescence decay, we estimate the efficiency of quenching (Φ_Q) by fitting the decay profile from 16 ns to 23 ns to equation (4) and then integrate the equation from time zero to infinity. Time 16 ns corresponds to the maximum donor fluorescence intensity, and near ca. 23 ns the two decay components crossover (*Figure* 7). Values for Φ_Q are obtained by comparing the integrated area for the fast quenching component, $Area_Q$, with that of the donor decay profile for a sample without quenching, the latter being numerically equal to the donor lifetime 45 ns.

$$\Phi_Q(t) = 1 - Area_Q(t)/45 \qquad (6)$$

The energy transfer efficiencies [$\Phi_{ET}(t)$] and hence the $f_m(t)$ values for these Phe- and An- containing AA-PEHMA films in the presence of diamine were analyzed in a similar way to that described previously, but here fitting to equation (4) for area integration was carried out from decay time 26 to 266 ns. We found that calculating the area of the long decay (energy transfer) component was not sensitive to the starting channel for the particular decay profiles here, even though this component represents less than 40% of the total fluorescence intensity.

Table 7 shows the Φ_Q and f_m values calculated from the donor decay data for films aged for different times t after drying. One sees that the f_m value increases with time, especially in the first three hours, but the increase is at a much slower rate than that for films without diamine. After 20 hr the f_m value is only 0.32, whereas in the diamine-free films, f_m reaches 0.8 at 160 min. This indicates that the presence of crosslinking retards significantly the diffusion of polymers. The mixing between the Phe- and An- bearing molecules is not entirely suppressed during this initial aging period, possibly related to the presence of residual low molar mass, non-gelled species. The Φ_Q value already has a high value (ca. 0.6) in the newly dried film, suggesting that a significant amount of crosslinked species has been formed. This is consistent with the results from solvent extraction and swelling experiments. The value of Φ_Q gradually increases to ca. 0.82 after aging for 20 hr, implying that the crosslinking reactions continue to some extent during this aging period, giving rise to enhanced quenching of donor fluorescence. More quantitative analysis about the crosslinking reactions is not possible at this time.

We also examined the diffusion rate for the higher T_g PBMA samples. We found that polymer diffusion is negligible at room temperature when the PBMA molecular weight is high (e.g., Mw > 3 × 10^5, T_g = 30-35°C). Such a high molecular weight is characteristic of many emulsion polymers. We have a pair of labeled PBMA samples with a much lower average molecular weight (Mw = 3.5 × 10^4, T_g = 21°C). By fluorescence energy transfer, we monitored the diffusion process for this polymer at 21 ± 1 °C.[32] *Table* 8 shows the results. For this PBMA sample, diffusion takes place effectively at room temperature, but on a time scale of days. As mentioned above, the crosslinking reaction for the AA-containing PBMA with diamine occurs on a time scale of minutes. From these results it appears that the PBMA diffusion rate is too slow to allow significant penetration before crosslinking, even for this low molecular weight sample.

By using these AA-free PBMA samples, we are also able to examine the effect of hexanediamine on the polymer diffusion rate itself. We observed equal diffusion

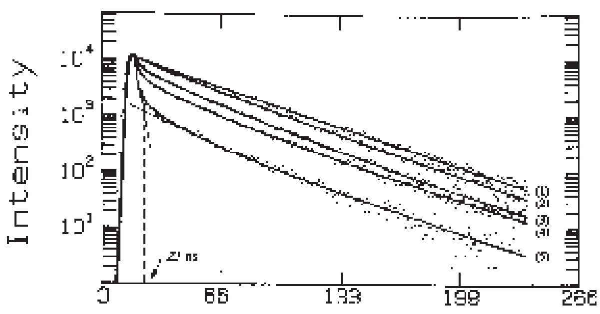


Figure 7—Donor decay profiles for AA-PEHMA films. Curve (1) is for a film prepared from Phe-AA-PEHMA particles (no An-labeled particles) mixed with diamine. Curve (2) is for a sample from 1:1 Phe- and An- labeled particles without AA-functional groups but with the addition of diamine. Curves (3), (4), and (5) are for films dried from 1:1 Phe- and An- labeled AA-PEHMA particles in the presence of diamine, followed by aging for 0, 8 hr, and by solvent-recasting, respectively.

rates (f_m and D_{app} at 21°C), within experimental error, in films with and without 5 wt% hexanediamine. This result indicates that hexanediamine has little plasticizing or diffusion-rate enhancing effects on the PBMA latex polymers at room temperature. It would be worthwhile to examine other diamines that are possibly more miscible with acrylic latex polymers to see if they act as coalescing aids for PBMA.

While the crosslinking strategy presented here based on acetoacetoxy/amino functionality provides an efficient way for film crosslinking, one can expect that the crosslinking reaction rate with 1,6-hexanediamine is too fast to form well-mixed, coherent latex films, although crack-free, transparent, and solvent resistant films are formed. The fact that a significant extent of crosslinking occurs before the dispersion is dried is particularly undesirable. Even for the AA-PEHMA sample which can diffuse a few nanometers in several minutes, crosslinking in the dispersed particles should have a strongly negative effect on the formation of films with good mechanical properties. We know from these and other experiments[32] that almost no interdiffusion occurs in the PEHMA films until they dry to a solids content of ca. 90 wt%, which under our drying conditions is 25 to 30 min before the films are completely dry. The fluorescence decay profile measured for a PEHMA film at 90 wt% solids (not shown) nearly overlaps with curve 1 in *Figure* 7. Thus the crosslinking reaction here is significantly faster than the polymer diffusion process.

To decrease the crosslinking rate, one can take advantage of several different strategies. One can reduce the AA content in the latex, prereact the AA group with ammonia or another primary amine to slow down the reaction with the diamine, or use a different diamine. Derivatives like Jeffamines™ that may remain in the water phase until the film dries will retard the rate of intraparticle crosslinking in the dispersed phase.

CONCLUSIONS

This paper describes our first results on the competition between polymer interdiffusion rates and crosslinking rates in latex films. Crosslinked films can be obtained at ambient temperature upon addition of 1,6-hexanediamine as the crosslinker to dispersions of latex polymers bearing acetoacetoxy (AA) groups. The presence of the diamine has a profound influence on the drying process for the dispersions. It induces floc formation, which in turn has a strong effect on the dispersion rheology. At solids contents as low as 15 wt%, the dispersions become pseudoplastic. The enhanced low-shear viscosity of the wet dispersion when spread on a substrate suppresses the drying front common to most latex films as they dry. It also increases the drying rate of the films. This effect occurs even for latex dispersions lacking AA groups, but is more pronounced when the AA groups are present.

The crosslinking rate for the present system is rapid. It occurs within the particles in the dispersion, and we find that a high gel content (> 80%) is obtained within several minutes after the diamine is added to the dispersion. The crosslinking rate is also compared with the interparticle diffusion rate of the polymers, as analyzed by fluorescence energy transfer measurements. We found that an AA-PEHMA copolymer, having a molecular weight of $Mw = 4.7 \times 10^4$ and a T_g of -7°C, can diffuse over significant distances on a time scale of 10-30 min at room temperature. In latex films prepared from a higher T_g (21°C) PBMA polymer having molecular weight similar to those of PEHMA, diffusion is much slower, on the time scale of days. In these systems, the rate of crosslinking reaction is substantially faster than the rate of polymer diffusion. While the latex films obtained may not have ideal mechanical properties, we nevertheless obtain transparent films with substantial resistance to organic solvents.

ACKNOWLEDGMENTS

We thank the Environmental Science and Technology Alliance Canada and NSERC Canada for their financial support.

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