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Interdiffusion and Self-Cross-Linking in Acetal-Functionalized Latex Films

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ABSTRACT: Poly(2-ethylhexyl methacrylate)-based latex particles were synthesized with an acetal-functionalized methacrylamide comonomer. The acetal function is stable at alkaline pH but can be deprotected under acidic conditions to form an intermediate that can undergo acid-catalyzed self-condensation to introduce cross-links into the polymer under ambient conditions. Studies of the kinetics of hydrolysis of the acetal groups showed that the hydrolysis occurred much faster than the subsequent self-condensation reaction. The evolution with time of the cross-link density and the film morphology were monitored as a function of pH and of functional comonomer content for films formed from acidified latex dispersions. Energy transfer experiments were used to follow the rate of polymer diffusion across the interparticle boundaries in the film, in competition with the cross-linking reaction. These experiments showed that under ambient conditions, the major contributor to polymer diffusion was the lowest molecular weight components of the latex polymer. These chains ultimately underwent reaction to become incorporated into the polymer network, yielding films with reasonable tensile properties and good solvent resistance. When the temperature was increased, the extent of mixing due to polymer diffusion increased, but remained incomplete when the competing chemical reaction was fast.

Introduction

The coating industry aspires to change from solvent-based formulations to more environmentally friendly options, which contain water as the main solvent. The challenge with those water-borne coatings, such as latex coatings, is to obtain film formation with little or no emission of organic compounds, while achieving good film properties. Therefore, polymer T_g should be sufficiently low with respect to the application temperature so that latex coalescence takes place without the need of any organic plasticizer; at the same time, the final film should exhibit a resistance comparable to that of a solvent-borne coating. Such an apparent contradiction can be overcome by introducing cross-links into a latex film after its application to the substrate, to increase its physical and chemical stability, as well as improve its tensile strength and abrasion resistance.[1−4]

Cross-linking can be accomplished during the film formation process via reactive groups, which are covalently incorporated into the latex particles using functional comonomers. Among the various possibilities, self-condensing comonomers are quite valuable and have been the subject of several articles in the past.[5−15] The main requirement is that the system should be chemically stable during polymerization and storage to avoid the loss of reactive groups by hydrolysis and to avoid premature cross-linking, which prevents efficient coalescence.[16,17] The chemical reaction leading to cross-link formation should only take place following film formation. To avoid early cross-linking in self-cross-linkable latexes, the chemical reaction is usually induced by an external parameter such as temperature, UV light, or a change in pH. In all cases, the ultimate properties are directly related to the rate, location, and extent of the chemical reaction as well as to the degree of chain interdiffusion.[3,16−27]

In this work, we chose to focus on the use of self-reactive chemical functions able to react at room temperature. For this purpose, various acrylamide monomers are available either with a *N*-methylol group such as *N*-methylolacrylamide or with a *N*-butoxymethyl substituent such as *N*-(butoxymethyl)acrylamide.[5,6,8,14] These groups do not react rapidly at room temperature. Other functional monomers bearing trialkoxysilane[12,15] or isocyanate[9,10,11] groups are much more reactive, but tend to be chemically unstable in latex dispersions. Monomers with an acetal functionality have also been proposed in the past as described below. They exhibit several advantages, which prompted us to select one of them as a good candidate for the application in cross-linkable latexes. For instance, previous articles reported the incorporation of acetal groups at the surface of latex particles and the use of these reactive particles, in acidic conditions at room temperature, as cross-linking agents for water-based coating resins containing poly(vinyl alcohol).[28,29] In other studies, the surface acetal groups were used as precursor for covalent binding of biological molecules for immunoassays.[30−33] Indeed, under acidic conditions the acetal group hydrolyzes into functions (typically aldehyde) able to react at room temperature either with diols or with amines. Aldehyde might also induce cross-linking reactions in polymer films, either by self-condensation (such as aldol condensation) or by reaction with a purposely added cross-linker. Special acetal-functionalized acrylamide monomers have also been used, because of their rich chemistry, to produce

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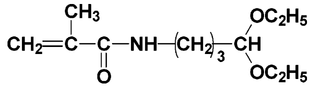
Scheme 1. Acetal Functional Monomer Used as a Cross-Linker in Water-Borne Films: *N*-(4,4-Diethoxybutyl) Methacrylamide (MABEA)



$CH_2{=}C(CH_3){-}C({=}O){-}NH{-}(CH_2)_3{-}CH(OC_2H_5)_2$

either post-cross-linkable polymer films via self-reaction in acidic conditions or substrate-reactive materials.[34−39] Such monomers induce cross-linking reactions without the formation of toxic side-products (such as formaldehyde in the case of *N*-methylolacrylamide).

In this work, we selected such an acetal-functionalized methacrylamide comonomer (Scheme 1). It was purposely synthesized and introduced into latex particles obtained via emulsion copolymerization with 2-ethylhexyl methacrylate. A methacrylate-based copolymer system was chosen to avoid branched chains and microgels, both generally observed in the emulsion polymerization of acrylate monomers.[40] In addition, poly(2-ethylhexyl methacrylate) exhibits a glass transition temperature close to −10 °C,[41] which is a good compromise, allowing film formation at ambient temperature without the need of an organic plasticizer, while avoiding the achievement of soft, sticky films.

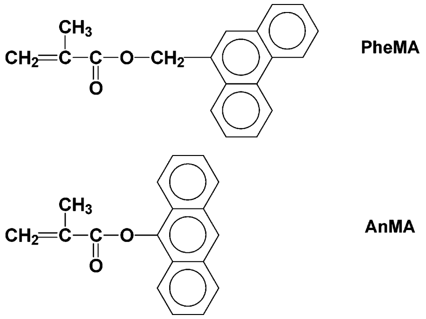
We performed emulsion polymerizations under alkaline conditions, to keep the acetal group stable and thus to prevent early cross-linking during polymerization and storage. The kinetics of hydrolysis of the acetal functions in the latex was studied in acidic conditions at various pH values. Films were formed at room temperature and annealed at 30 °C or at moderately elevated temperatures (60, 70, and 80 °C). Cross-link formation was induced by acidification of the latex prior to film formation. We studied the evolution with time of film cross-link density (swell ratio and gel content), morphology, and final mechanical properties as a function of the initial concentration of functional monomers and of the pH. Concomitant polymer chain interdiffusion was also studied by nonradiative energy transfer. This study gives a new insight into the behavior and properties of self-cross-linkable latex films, both at room temperature and at moderately elevated temperatures, and aims at answering the important issue of the degree of chain interdiffusion (interparticle mixing) versus the rate and extent of cross-link formation.

Experimental Section

Materials. The monomers 2-ethylhexyl methacrylate (2EHMA) and methyl methacrylate (MMA) were kindly provided by Atofina and used as received. The functional monomer, *N*-(4,4-diethoxybutyl) methacrylamide (MABEA), was synthesized from methacryloyl chloride (Aldrich, 97% purity) and 4,4-diethoxybutylamine (Aldrich, >90% purity) according to the procedure described below. Two fluorescent dye comonomers have been synthesized: the donor dye was 9-(methacryloyloxymethyl)phenanthrene (PheMA), and the acceptor dye was 9-(methacryloyloxy)anthracene (AnMA) (Scheme 2). Both were prepared according to previously described procedures.[42] For the emulsion polymerizations, a mixture of a nonionic (Disponil A3065 from Cognis) and two anionic (Disponil FES 771S from Cognis and Aerosol GPG from Cytec) surfactants was used. The initiator, sodium persulfate ($Na_2S_2O_8$ from Aldrich, 98% purity), and the buffer, sodium hydrogencarbonate ($NaHCO_3$ from Aldrich, 99.99% purity), were used without further purification.

Synthesis of the MABEA Monomer. Methacryloyl chloride and 4,4-diethoxybutylamine were first distilled before use. Methacryloyl chloride was then slowly added, under stirring, to an equimolar amount of the amine in dichloromethane solution, in the presence of a 14 N solution of sodium hydroxide (90/10 vol/vol, respectively). The temperature of the reaction medium was maintained below 10 °C by a water/ice bath. After addition was completed, the reaction medium was stirred for 1 h at room temperature. The organic layer was separated and washed twice with a saturated NaCl solution and once with a saturated KH_2PO_4 solution. It was then dried over calcium sulfate, filtered, and the solvent was evaporated.

Scheme 2. Fluorescent Dye Comonomers (PheMA and AnMA)



^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.16$ (1H, broad peak, NH); 5.59 and 5.22 (two s, 2 × 1H, $CH_2{=}$); 4.41 (t, 1H, CH acetal); 3.54 and 3.43 (q, 2 × 2H, CH_2 ethyl); 3.24 (m, 2H, CH_2 amide); 1.87 (s, 3H, methyl adjacent to double bond); 1.57 (m, 4H, $-CH_2-CH_2-$); 1.12 (t, 6H, CH_3 from acetal ethyl group).

^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 168.3$; 140.1; 119.0; 102.5; 61.3; 39.2; 30.9; 24.4; 18.6; 15.2.

A nonpolymerizable model of MABEA (PrABEA, *N*-(4,4-diethoxybutyl) propanamide) was synthesized starting from propanoyl chloride, according to the same procedure.

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.78$; 4.43; 3.61; 3.46; 3.22; 2.14; 1.57; 1.15.

^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 173.71$; 102.61; 61.29; 39.08; 30.97; 29.61; 24.50; 15.20; 9.83.

Synthesis and Characterization of the Latexes. Emulsion polymerizations were performed at 85 °C in a conventional thermostated glass reactor using a semi-continuous addition of a stable emulsion of the monomers 2EHMA and MMA, the functional comonomer MABEA, and/or the dye comonomer, either AnMA or PheMA. A small amount of methyl methacrylate was introduced in addition to 2EHMA to increase the rate of water phase initiation (2EHMA exhibits a too low water solubility) and hence to improve the nucleation step. Starve-feed conditions were applied to maintain a uniform copolymer composition throughout the polymerization. A 5 wt % portion of the monomer emulsion and a 10 wt % portion of the initiator solution were fed into the reactor, and the polymerization was allowed to proceed for 30 min. After this time, the remaining part of the emulsion was added over 4 h; the polymerization was then continued at 85 °C for a further hour after the addition was completed. The latex pH was carefully maintained above 7.0 during polymerization and storage by the addition of sodium hydrogen carbonate, to avoid premature hydrolysis of the acetal groups. A typical recipe is given in Table 1, and the latex characteristics are summarized in Table 2.

Analytical Techniques for Latex and Copolymer Characterization. Proton and carbon 13 NMR spectra were recorded in $CDCl_3$ solution at room temperature using a Bruker AC200 spectrometer operating at a frequency of 200 MHz for ^{1}H and 50.3 MHz for ^{13}C; the chemical shift scales were calibrated on the basis of the solvent peak (7.24 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR). This technique was applied to determine the structural quality and purity of the functional monomers and to verify the amount of incorporated MABEA into the latex copolymers. For the latter purpose, the latexes were cleaned by dialysis for 10 days (Spectra Por 2 membrane from Biovalley, cutoff at 12 kDa) against an alkaline $NaHCO_3$ water solution, changed every day. The copolymer was recovered from the latex by lyophilization and

Table 1. Typical Emulsion Polymerization Recipe[a]

	initial load (g)	added emulsion of the monomers (g)[b]	added solution of the initiator
deionized water	80.9	49.4	10.0
surfactants			
Disponil A3065	0.05	0.83	0
Disponil FES 771IS	0.38	2.25	0
Aerosol GPG	0	0.50	0
monomers		100	
2EHMA	0	$0.98 \times (100 - x)$	
MMA	0	$0.02 \times (100 - x)$	0
X[c]	0	x	0
$NaHCO_3$	0.08	0.375	0
$Na_2S_2O_8$	0	0	0.33

[a] The recipe is based on 100 g of monomers (1 L reactor); it was also applied to 300 g of monomers in a 3 L reactor. Temperature = 85 °C; stirring rate = 70 rpm. [b] Emulsion addition rate = 0.61 g min^{-1} (0.40 g min^{-1} of monomers; 4 h addition time). [c] MABEA and/or dye comonomer.

was analyzed by ^1H NMR. The molar fraction of incorporated MABEA was calculated from the area of the acetal CH peak (4.4 ppm) and the area of the broad peak at 3.1−4.2 ppm (related to the $O-CH_2$ and $O-CH_3$ of all of the monomers and the surfactants). A good agreement between the introduced and the measured amounts of MABEA was observed, indicating efficient incorporation via copolymerization.

The average particle diameters (D) were measured by dynamic light scattering (DLS) of the diluted latexes, using a Zetasizer4 from Malvern at an angle of 90° and a temperature of 25 °C.

The molar mass and molar mass distribution of the copolymers were analyzed by size exclusion chromatography (SEC) using tetrahydrofuran as an eluent at a flow rate of 1 mL min^{-1}. Separation was performed with two columns (PL-gel 10μ mixed, 60 cm; Shodex KF 805L, 30 cm). A differential refractive index detector was used, and molar masses were derived from a calibration curve based on polystyrene standards from Polymer Standards Service. This technique allowed us to determine M_n (the number average molar mass), M_w (the weight average molar mass), and M_w/M_n, the polydispersity index.

Kinetics of Hydrolysis of Acetal Groups in the Latex. The kinetics of hydrolysis of the acetal groups incorporated into the latex particles was studied at room temperature. The latex L8.6 (Table 2) was diluted to 30 wt % by the addition of D_2O. For three individual aliquots, the pH was then adjusted to 1.0, 2.0, and 3.0, respectively, by the addition of 1 N hydrochloric acid. The amount of ethanol released by the hydrolysis reaction performed at room temperature was monitored by ^1H NMR spectroscopy as a function of time (peak at 1.1 ppm corresponding to the methyl), by reference to a known amount of sodium *para*-toluenesulfonate (NaPTS, peak at 2.3 ppm corresponding to the methyl). The fraction of hydrolyzed MABEA was calculated with the expression:

$$f = \frac{1}{2} \cdot \frac{I(\mathrm{CH_3,ethanol})}{I(\mathrm{CH_3,NaPTS})} \cdot \frac{n(\mathrm{NaPTS})}{n(\mathrm{MABEA})} \tag{1}$$

$I(CH_3\text{,ethanol})$ and $I(CH_3\text{,NaPTS})$ are the integrals of the peaks corresponding to the methyl of ethanol and NaPTS, respectively; n(NaPTS) is the molar amount of NaPTS, and n(MABEA) is the molar amount of MABEA in the analyzed latex.

Film Formation and Characterization. Swelling Experiments and Mechanical Properties. First, latexes were diluted to 30 wt % by the addition of distilled water. For films to be annealed at room temperature, the pH of the latex was adjusted by the addition of a given amount of 1 N hydrochloric acid. For films to be annealed at higher temperatures, hydrochloric acid was replaced by *para*-toluenesulfonic acid (PTSA) to avoid evaporation of the acid. In that case, the amount of acid added was expressed in wt % of acid with respect to polymer (recalculated in mol % with respect to the acetal functions). For each film, the desired amount of latex (90 g) was cast onto a rectangular Teflon mold (12 cm × 22 cm). To obtain films with a smooth surface and without fissures, the freshly cast films were kept covered for the first 2 days at 20 °C to limit the rate of water evaporation. The films were then dried in a thermostated oven at atmospheric pressure. Time zero was taken as the beginning of the annealing process, when the films were placed in the thermostated oven at the selected temperature. The final film thickness was 1.2−1.5 mm.

To follow the evolution of cross-link density with annealing time, swelling experiments were performed periodically. For this purpose, film samples were weighed (weight w_0) and swollen for 24 h in chloroform at room temperature. Swollen films were then weighed (weight w_1) and carefully dried (weight of the dry film, w_2). For each film, the gel content ($\varphi = w_2/w_0$) and swell ratio ($\tau_s = w_1/w_2$) were calculated. The latter gives an indication of the film cross-link density (i.e., the lower τ_s, the higher the cross-link density). The evolution of gel content and swell ratio were monitored as a function of annealing time.

After a period of 50 or 60 days, the tensile properties were determined in the Atofina research center of Serquigny (CERDATO) using an Instron 4301 universal tensile testing machine at 23 °C and at a crosshead speed of 50 mm min^{-1}.

Fluorescence Decay Measurements. Thinner films were employed for the fluorescence nonradiative energy transfer experiments. For this purpose, the latexes were diluted to 10 wt % by the addition of distilled water. The pH of the latex dispersion was adjusted by the addition of a given amount of 1 N hydrochloric acid for films annealed at room temperature, or, for films annealed at high temperatures, by the addition of a given weight of *para*-toluenesulfonic acid (PTSA). A 0.25 g sample of a 50/50 wt/wt mixture of PheMA labeled latex and AnMA labeled latex was deposited onto a quartz plate (10 mm × 25 mm). For the first 2 days, as described above, water evaporation was limited by covering the films and keeping them at 20 °C. The films were then dried in a thermostated oven, under atmospheric pressure. Time zero was taken at the beginning of the annealing process. The final film thickness ranged from 80 to 100 μm.

Energy transfer measurements and data analyses were carried out at the University of Toronto as described in detail in several articles from the Winnik group.[14,43] For films formed from mixtures of donor- and acceptor-labeled latexes and aged or annealed for time t, the quantum efficiencies of energy transfer Φ_{ET} were calculated from the areas under the integrated donor fluorescence decay profiles ($I_{DA}(t')$) by comparison with the intensity decay profile of a film ($I_D(t')$) prepared from a donor-labeled latex in which [AnMA] = 0.

$$\Phi_{ET}(t) = 1 - \frac{\int_0^\infty I_{DA}(t')\,dt'}{\int_0^\infty I_D(t')\,dt'} = 1 - \frac{\mathrm{area}_{DA}(t)}{\mathrm{area}_D} \tag{2}$$

Here t' is the time scale of the donor fluorescence decay measurements. The $I_D(t')$ decay profiles were exponential, with PheMA lifetimes of $\tau_D = 44.5 \pm 0.1$ ns for latex PL0 and $\tau_D = 44.9 \pm 0.1$ ns for latex PL8.6.

A useful measure of polymer diffusion in the films is the extent of mixing parameter $f_m(t)$ using eq 3.

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

This equation describes the growth in $\Phi_{ET}(t)$ from its value in the newly formed film, $\Phi_{ET}(t = 0)$, to the value expected, $\Phi_{ET}(t = \infty)$, for complete randomization of the dyes in the film due to polymer diffusion. In films examined here $\Phi_{ET}(t = 0) = 0.15$ for latex L0 before annealing and $\Phi_{ET}(t = 0) = 0.13-0.14$ for latex L8.6. These values are higher than the value (0.05−0.07) one expects for a system in which no diffusion occurs

Table 2. Characteristics of the MABEA-Functionalized Latexes

latex	MABEA content (mol %)[a]	dye (content: 1 mol %)[a]	solids content (wt %)	D (nm)	M_w (kg mol^{-1})	M_w/M_n	$\bar{f}_n$[b]
L0	0	none	39	148	363	4.3	0
L2.5	2.5	none	39	145	335	4.3	10
L4.3	4.3	none	38	159	422	5.1	18
L8.6	8.6	none	40	159	403	4.9	36
AL0	0	AnMA	40	130	326	4.8	
AL2.5	2.5	AnMA	39	135	296	4.5	
AL4.3	4.3	AnMA	40	130	330	4.7	
AL8.6	8.6	AnMA	40	131	291	4.5	
PL0	0	PheMA	36	130	380	5.0	
PL2.5	2.6	PheMA	35	133	331	4.7	
PL4.3	4.3	PheMA	36	128	364	5.0	
PL8.6	8.6	PheMA	38	136	331	4.7	

[a] mol % with respect to the overall monomers. [b] $\bar{f}_n$ is the number average functionality of the copolymer chains in acetal functions.

during the film drying stage,[44] but are consistent with the small amount of unbound donor chromophore (ca. 8%) detected in SEC analyses of the donor-labeled latex.

$\Phi_{ET}(t = \infty) = 0.44$ for latex L0 in the case of fully mixed film (cast from THF solution of the latex film) and $\Phi_{ET}(t = \infty) = 0.48$ for latex L8.6 (the values obtained for latex L8.6 were systematically used for the other functionalized latexes). To parametrize the rate of polymer diffusion in these films, apparent diffusion coefficients, D_{app}, assuming a Fickian diffusion process,[45] were calculated as described in refs 46 and 47. These calculations make strong assumptions about the nature of the diffusion process which are often not fully warranted, but changes in D_{app} values with changes in temperature are consistent with the temperature dependence of viscoelastic properties of the polymer over the same temperature range.

Atomic Force Microscopy (AFM) Experiments. Films for AFM experiments were prepared on a mica substrate in a manner analogous to that used to prepare films for fluorescence nonradiative energy transfer experiments. Once dried, each film surface was washed with distilled water to eliminate the surfactants. AFM images were obtained with a Nanoscope IIIa Digital Instruments in the tapping mode with a silicon nitride cantilever at a resonance frequency of 280 ± 10 kHz (Olympus Optical Co.) and a scan rate of 1.2 Hz.

Results and Discussion

Film Formation and Cross-Linking at Room Temperature. Hydrolysis and Self-Reaction of the Acetal Group of the MABEA-Functionalized Monomer. Pinschmidt et al.[34−38] studied the hydrolysis of the acetal function of a monomer similar to MABEA. Under acidic conditions, they observed the formation of cyclic species (**C1** and **C2**, Scheme 3), resulting from an intramolecular reaction between the amide and the hydrolyzed acetal. The aldehyde form was strongly disfavored. We also carefully studied this reaction using a model for MABEA, the *N*-(4,4-diethoxybutyl) propanamide (PrABEA). The same products were identified by proton NMR at room temperature, and their proportion at equilibrium was quantified by integration of the CH peaks corresponding either to the acetal or to the derived products (see Table 3). In D_2O/d_6-DMSO mixed solvent (1:2, wt:wt; pH of the water phase = 1.1), **C1** and **C2** were found to be in equilibrium with a small amount of residual acetal, linear aldehyde, and hydrate, the **C2** form being predominant (approximately 80 mol % at equilibrium). In pure D_2O, the equilibrium was completely shifted toward the **C2** form and the cyclization reaction was very fast when the pH was below 3: The reaction was complete within 3 h at pH = 2.9, within 2 h at pH = 2.6, and in less than 10 min at pH = 2.0 and pH = 1.0. When the pH was above 3.5, however, the acetal was quite stable, because it remained unreacted for more than 13 days.

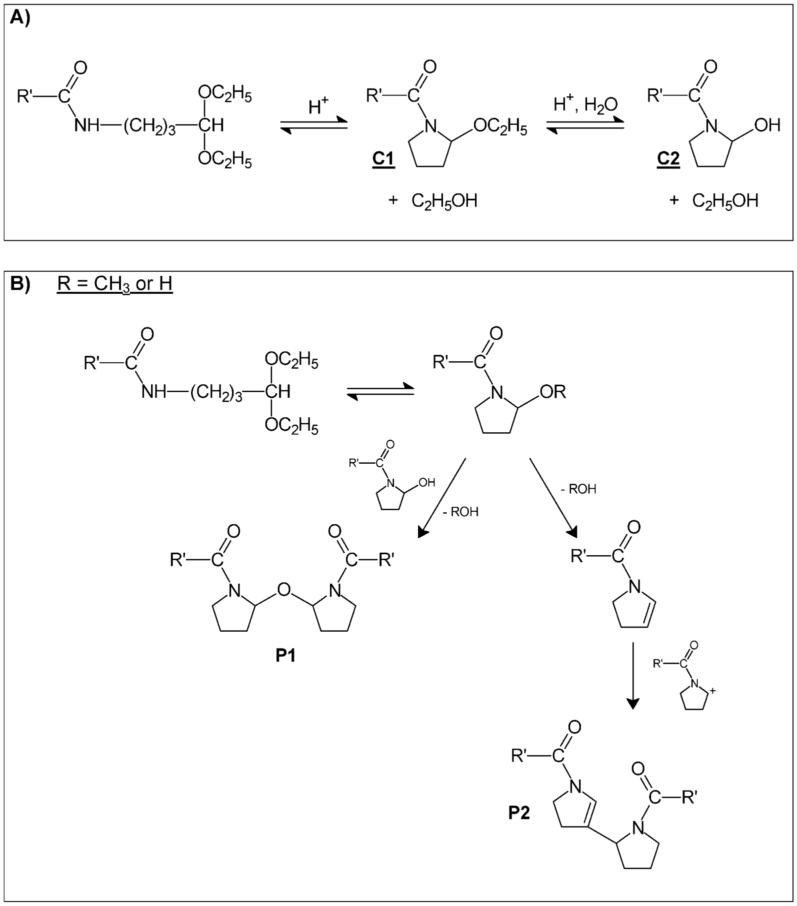
Self-condensation reactions that can occur at room temperature are presented in Scheme 3, according to the final products identified by Pinschmidt et al.[37] We noticed that the final **C2** cyclic form remained stable in acidic aqueous solutions for more than 1 month. Upon water evaporation (for 4 weeks at 30 °C), a light yellow product was obtained, the proton and carbon 13 NMR spectra of which were fully compatible with the condensation product **P1**. Under these conditions, **P2** was not detected.

Kinetics of Hydrolysis of the Acetal Groups in the Latex. The acidic hydrolysis reaction was also studied for the acetal groups incorporated into the latex particles. For this purpose, latex L8.6 (Table 2) was selected; the analytical conditions are described in the Experimental Section. Figure 1 shows the fraction of hydrolyzed MABEA (f) as a function of time for latex maintained at pH values of 1.0, 2.0, and 3.0. Deprotection was faster when the pH was lower. For all pH values, an initial fraction of essentially instantaneous hydrolysis could be seen, corresponding to approximately 40% of the acetal functions. It is likely that the acetal groups located at or near the particle surface were involved. Considering that the functional monomer was homogeneously distributed within the particle volume, the experimentally determined value of $f = 0.4$ corresponds to a depth of 15−20% of the particle radius, that is, a thickness of 12−16 nm. After the initial stage, the hydrolysis process was very slow, significantly slower than in solution, as shown in Figure 1. At the lowest pH values, however, complete deprotection could be achieved: At pH = 1.0, hydrolysis was complete within 2 days, and at pH = 2.0, it was complete within 6−8 days. In contrast, at pH = 3.0, acetal hydrolysis remained incomplete, and f appeared to reach a plateau of 0.7 after 20 days.

These results provide useful information regarding cross-linked film formation. (i) The fast initial deprotection leads to the formation of reactive functions near the particle surface, able to further react with each other to form cross-links. For one to obtain films with useful mechanical strength, it is necessary that the polymer interdiffusion process start within a very short time after deprotection, to avoid premature intraparticle condensation. (ii) With homogeneous distribution of the functional monomer in the polymer chains together with the possibility of complete deprotection, fully cross-linked films can be expected.

Scheme 3. (A) Products of Acidic Hydrolysis of the Acetal/Amide Function; (B) Products of Self-Condensation (According to Ref 37)

PrABEA: R' = CH_3-CH_2-; MABEA: R' = CH_2=CH-



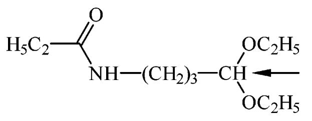
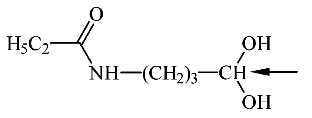
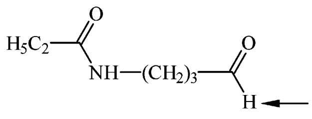
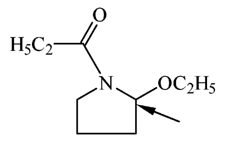
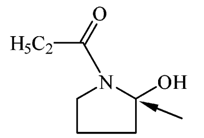
Parameters that Affect Film Cross-Link Density and Kinetics of Cross-Links Formation. Cross-link formation occurs in two main steps: deprotection of the reactive functionality under acidic conditions and self-condensation. Therefore, at a given temperature, two parameters should play an important role in the reaction kinetics and the cross-link density: the acid concentration in the film, as determined operationally by the pH of the latex prior to film formation, and the concentration of acetal groups in the latex.

Figure 2 shows the effect of pH for latex L2.5 containing 2.5 mol % MABEA in the copolymer. The evolution of cross-link density was examined over a period of 45 days annealing time via the film swelling properties, that is, the measurement of φ (the gel content) and τ_s (the swell ratio). Control experiments showed that none of the films formed a measurable amount of cross-links at alkaline pH (typically pH = 8, where hydrolysis did not take place). At a pH of 3.0, all films remained fully soluble, even though the acetal functions were partially hydrolyzed under these conditions. Branched polymer and microgels may have formed, but the gel point was not reached. Cross-linked films were only obtained at pH $\leq$ 2.0. Under these conditions, cross-link formation was faster when the pH was lower, and the gel point was achieved earlier. At pH 1.0, the film exhibited its final properties within 3–5 days, whereas at pH = 2.0, a continuous evolution was observed. The two systems reached the same cross-link density only after 45 days. At this stage, the gel content was between 80% and 90%, and the swell ratio was close to 10, indicating only moderately cross-linked films. This result was assigned to the rather low amount of functional monomer in this latex sample.

The effect of functional monomer concentration on the swelling properties was further studied at pH = 2.0, using latexes L2.5, L4.3, and L8.6 (see Tables 1 and 2). As displayed in Figure 3, a strong effect of the amount of acetal functions was observed. The increase in MABEA concentration had a very similar effect on the kinetics of cross-link formation as the decrease of pH. Films containing 4.3 and 8.6 mol % MABEA reached their final properties within 8 and approximately 3 days of annealing time, respectively, whereas the film with only 2.5 mol % MABEA continuously improved over the annealing time of 45 days. The final cross-link density was a function of the initial MABEA concentration. This was demonstrated by the lower final value of τ_s with the increase in [MABEA]: at 45 days with 8.6 mol %, $\tau_s = 5.0$, with 4.3 mol %, $\tau_s = 9.0$, and with 2.5 mol %, $\tau_s = 13.7$. In addition, the gel content also increased and reached values above 90% for the films derived from latexes L4.3 and L8.6. This increase in cross-link density improved the tensile properties of the films as illustrated in Figure 4, which shows the stress–strain curves measured after 50 days. Tensile strength increased with the initial concentration of MABEA, and the extension to break significantly decreased. This is typical of films with increasing cross-link densities.

To summarize, cross-linked films were obtained at room temperature from MABEA-functionalized latexes, under acidic conditions. The overall kinetics of cross-

Table 3. Structure of the Hydrolysis Products of PrABEA and Characteristic Chemical Shifts Allowing Identification and Quantitative Analysis

Structure	Chemical shift (ppm) of the acetal, hydrate, aldehyde or hemiamidal H
	4.47
	4.74
	9.53
	5.26 and 5.06
	5.42 and 5.31

link formation was enhanced both by the decrease in pH and by the increase in acetal content, while the final cross-link density was a function of the latter parameter only. Cross-linking was a two-step process: deprotection of the acetal groups and self-condensation. The kinetic study of both reactions suggested that these reactions were successive, deprotection being faster than condensation (see Figures 1 and 2).

Because our system is based on self-condensation, the chain interdiffusion between adjacent particles is not a requirement for reaction to take place; it is however critical for the achievement of cross-linked films with good cohesion. As demonstrated by the swelling experiments (good resistance to organic solvent) and the mechanical properties, this criterion was actually met for all cross-linked films. These results establish that formation of the network did not suppress chain inter-

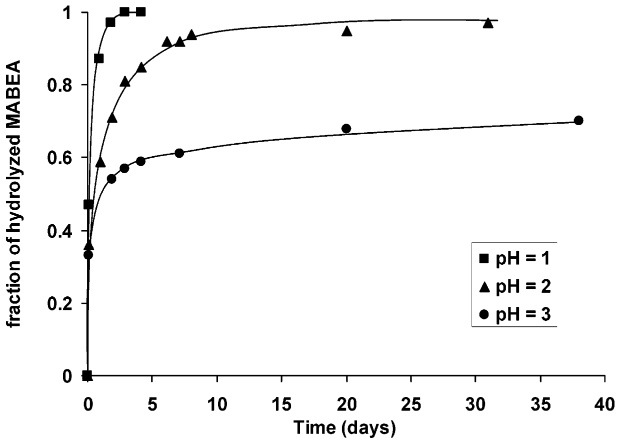


Figure 1. Hydrolysis of the acetal groups in latex L8.6 with 8.6 mol % of the MABEA functional comonomer at room temperature and at different pH values. The fraction of hydrolyzed MABEA versus time was followed by measuring the amount of released ethanol using ^{1}H NMR spectroscopy.

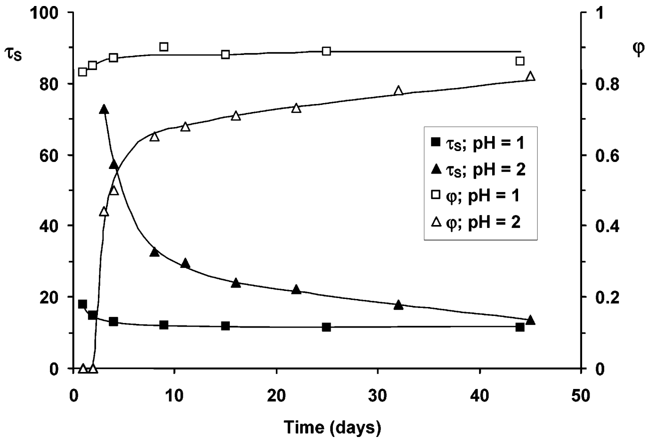


Figure 2. Effect of the pH on the swell ratio (τ_s) and gel content (φ) versus annealing time for films formed from latex L2.5, with 2.5 mol % of the MABEA functional comonomer, annealed at 30 °C. (Time zero corresponds to the beginning of the annealing time.)

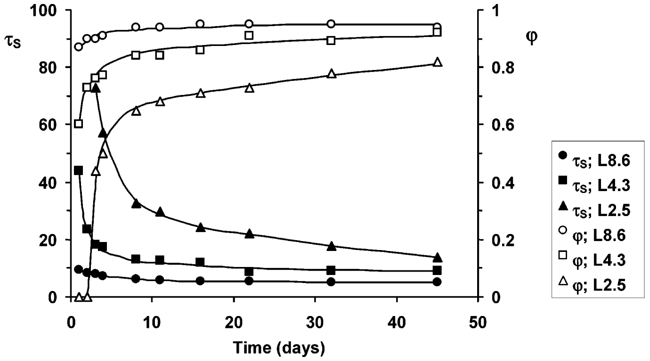


Figure 3. Effect of the MABEA concentration (latexes L2.5, L4.3, and L8.6) on the swell ratio (τ_s) and gel content (φ) versus annealing time for films formed at pH = 2.0 and 30 °C. (Time zero corresponds to the beginning of the annealing time.)

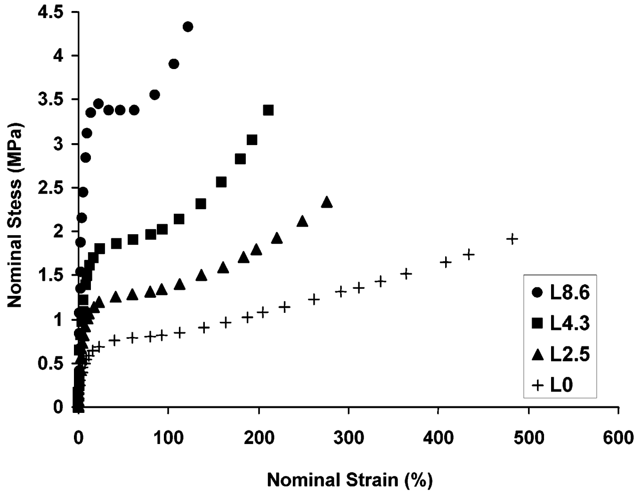


Figure 4. Effect of MABEA concentration (Latexes L0, L2.5, L4.3, and L8.6) on the tensile properties (measured at 23 °C) of the films annealed for 50 days at 30 °C and pH = 2.0.

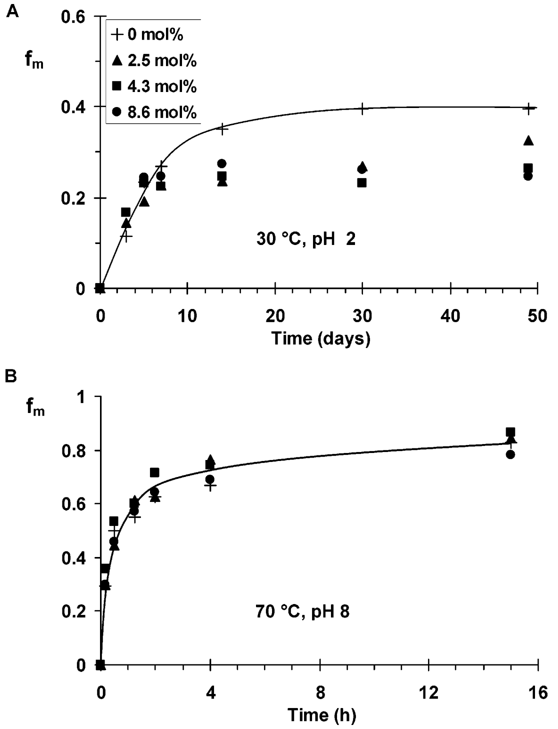


Figure 5. (A) Effect of MABEA concentration on the extent of mixing, f_m, versus the annealing time at 30 °C and pH = 2.0 for latexes AL0 + PL0, AL2.5 + PL2.5, AL4.3 + PL4.3, and AL8.6 + PL8.6. (B) Plot of f_m versus annealing time at 70 °C for films prepared at pH = 8.0 for the same latex samples.

diffusion between the cells, either because both processes took place simultaneously or because diffusion was faster than the chemical reaction. The kinetics of chain interdiffusion as well as its extent are thus important parameters to consider for a better understanding of the system.

Kinetics of Polymer Interdiffusion and Extent of Mixing at 30 °C. Nonradiative energy transfer experiments were used to follow polymer chain interdiffusion in the films. For this purpose, MABEA-functionalized latexes containing 1 mol % of a fluorescent dye were prepared, one set of latexes labeled with the donor dye (phenanthrene-based comonomer, latexes PL in Table 2), and the other set labeled with the acceptor dye (anthracene-based comonomer, latexes AL in Table 2). The extent and kinetics of chain interdiffusion were studied for 1:1 mixtures of AL and PL latexes, both containing the same molar concentration of MABEA. Results on films annealed at elevated temperatures will be presented later in the paper. Here, results are presented for films prepared at pH = 2.0 and annealed at 30 °C, from latexes containing 0, 2.5, 4.3, and 8.6 mol % MABEA. For these films, plots of the extent of mixing, f_m, as a function of annealing time are shown in Figure 5A. Films of the MABEA-containing polymers, cast from dispersions at pH 8, show a plot of f_m versus time at 30 °C similar to that of the top curve (0% MABEA) in Figure 5A, indicating the absence of effect of MABEA on polymer mixing in the absence of cross-linking.

At this low temperature, for the film lacking the acetal functionality, the f_m values increased over 8 days to a value of ca. 0.25, and more slowly afterward, reaching an apparent plateau of ca. 0.4 after 50 days. There is no reason to suspect that polymer diffusion has ceased in this sample, but rather it has slowed considerably at this temperature. To put this result in context, we compared the rate of polymer diffusion for this sample at 70 °C with that of films containing 2.5, 4.3, and 8.6 mol % MABEA but cast from dispersions at pH 8, where no cross-linking should occur. This comparison is meaningful, because the mean molar masses and molar mass distributions of these samples were similar. As shown in Figure 5B, at this temperature, f_m values for all of these samples increased monotonically from 0 to 0.8 over a period of 16 h. The samples behaved as expected for linear polymers, and the diffusion rates, as inferred from the rate of increase of f_m values, were the same for all four polymers. From these experiments, we learned that there is nothing unusual about the nature of the latex polymer in the film lacking reactive functionality to indicate that the diffusion of this polymer would cease at an f_m value of ca. 0.4 at 30 °C. What is more likely is that the broad molar mass distribution of the polymer led to an even larger distribution of molecular diffusion rates in the film.[48,49] Polymer molecules of relatively high diffusivity contributed to the growth of Φ_{ET} over the first 20 days at 30 °C. The higher molar mass components of the samples, subject, for example, to the constraints of entanglements, took much longer to diffuse across the interparticle boundaries in the film.

For the functional films, prepared at pH 2, the condensation reaction at 30 °C competed with polymer diffusion. Over the first few days of annealing, the influence of the reaction on the polymer diffusion rate was negligible. After 8−10 days, a sufficient fraction of branched polymer and network polymer had formed that the polymer diffusion appeared to cease, with a limiting f_m value on the order of 0.25. The extents of diffusion seen over the first 8 days of annealing for these functional latex films prepared at pH 2 were at first glance in apparent contradiction to the results on the growth rate of gel content as depicted in Figure 3. To appreciate the origin of these two independent results, one has to take into account that the relationship between gel formation and functional group content depends on both the molar mass of the functional polymer and its polydispersity[50] (see Table 2). High molar mass polymer can reach the gel point when only a fraction of its acetal groups condense. A low molar mass polymer can contribute to gel formation only if it contains a minimum of two functional groups per chain. With one functional group, it can become connected to the network. From this perspective, we obtained the important result that most of the chains that contributed to the gel content seen in Figure 3 were also the chains that underwent negligible diffusion at 30 °C. According to the model of Aradian et al.,[26,27] the chains that contribute to the growth in strength of the interface in cross-linked latex films are the chains which diffuse across the interparticle boundaries and form cross-links that anchor the chains on opposite sides of the interface. From the data in Figure 5A, we infer that these are the low molar mass chains that contributed to f_m during the first 6−8 days of sample annealing at 30 °C.

Film Surface Morphology. The AFM images (Figure 6A) and the surface roughness profile (Figure 6B) provide important information about the influence of the cross-linking reaction on the evolution of the surface morphology of the latex films. On the left-hand side of Figure 6A, one sees images of a film formed from latex L0 without reactive functionality, aged at 30 °C. In

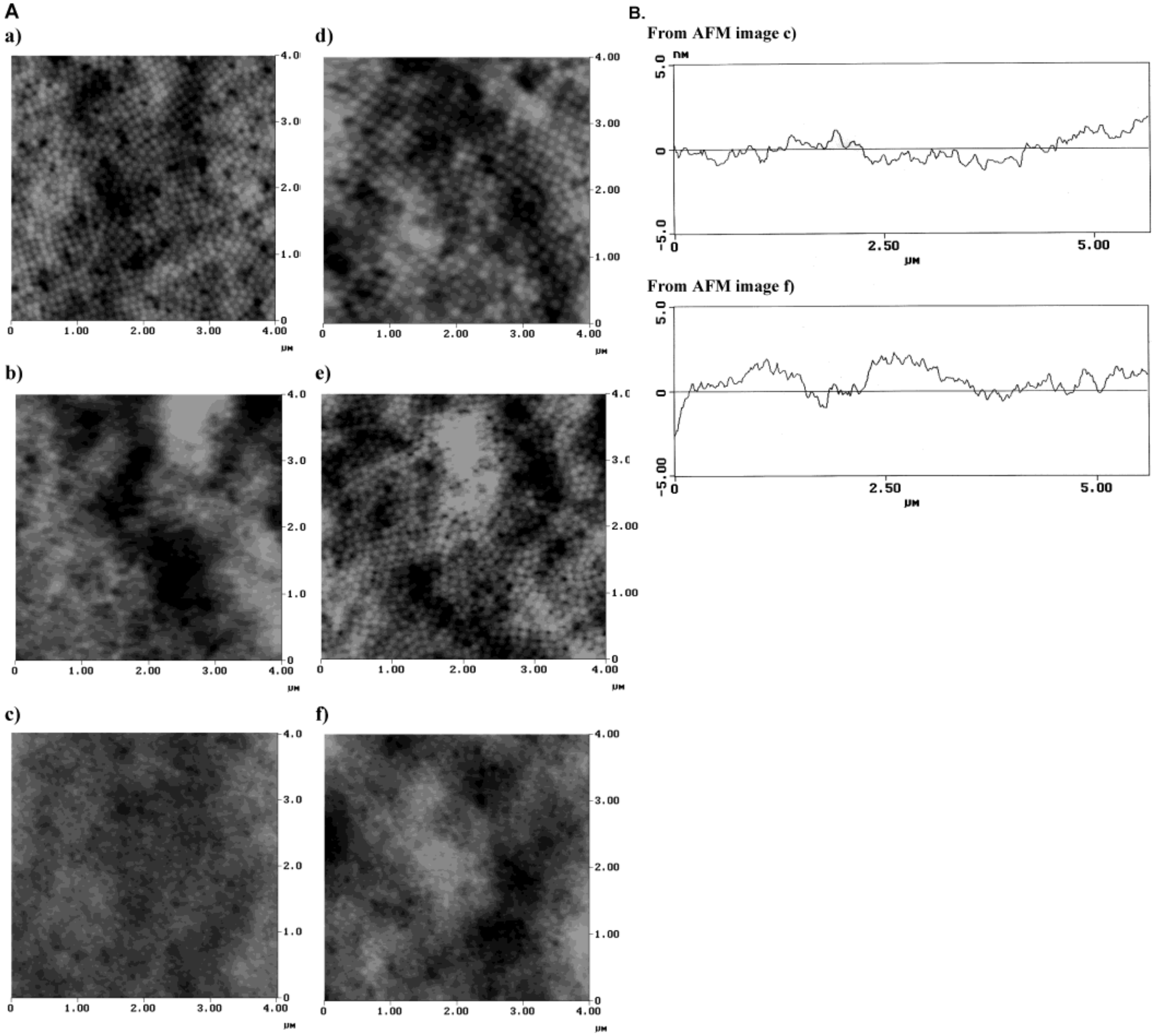


Figure 6. (A) Atomic force microscopy (AFM) of latexes L0 and L4.3 annealed for 24 h to 50 days at 30 °C and pH = 2.0 (conditions are reported in the experimental part). Vertical range: 0−35 nm (from dark to light) for images a and d; 0−10 nm for images b, e, c, and f. (a) 24 h, L0; (b) 7 days, L0; (c) 50 days, L0; (d) 24 h, L4.3; (e) 7 days, L4.3; (f) 50 days, L4.3. (B) Surface roughness profile at 50 days (corresponding to the AFM images c and f).

image a taken after 24 h, the particle boundaries remain sharp, but after 7 days (image b), there is a loss of definition associated with polymer flow and diffusion. After 50 days (image c), the film surface is smooth and flat (see Figure 6B). In contrast, the film formed from latex L4.3 at pH 2 shows a preservation of film surface structure. After 7 days (image e), many of the particle boundaries in the film remain distinct. This effect is much less pronounced after 50 days at 30 °C as seen in image f (see also Figure 6B). While the leveling of the film surface as seen in images a, b, and c has been interpreted in terms of diffusion of the polymers near the film surface,[51] it is more appropriate to describe the effect in terms of polymer flow, that is, relaxation of the polymer in the terminal region of the viscoelastic spectrum of relaxation rates. The formation of branches and the increase in molar mass will have a large influence on retarding these relaxation rates, and gel formation will suppress the terminal relaxation. Because the longest chains in the sample contribute to this relaxation, whereas the shortest chains contribute to the growth of Φ_{ET} in the fluorescence nonradiative energy transfer experiment, one can expect a more pronounced effect of the condensation reaction on the preservation of film surface morphology than on the extent of polymer diffusion inferred from energy transfer experiments.

Film Formation and Cross-Linking at High Temperature. Effect of Temperature on the Interdiffusion Process in the Absence of Cross-Linking Reaction. Poly(2-ethylhexyl methacrylate) exhibits a glass transition temperature that is below 0 °C. Although film formation occurs readily at room temperature, the polymer interdiffusion process at this temperature was shown to be rather limited. To help us understand the influence of temperature on the rate of polymer diffusion with this particular polymer, a series of energy transfer experiments were carried out at 60, 70, and 80 °C on films formed from a 1:1 mixture of the

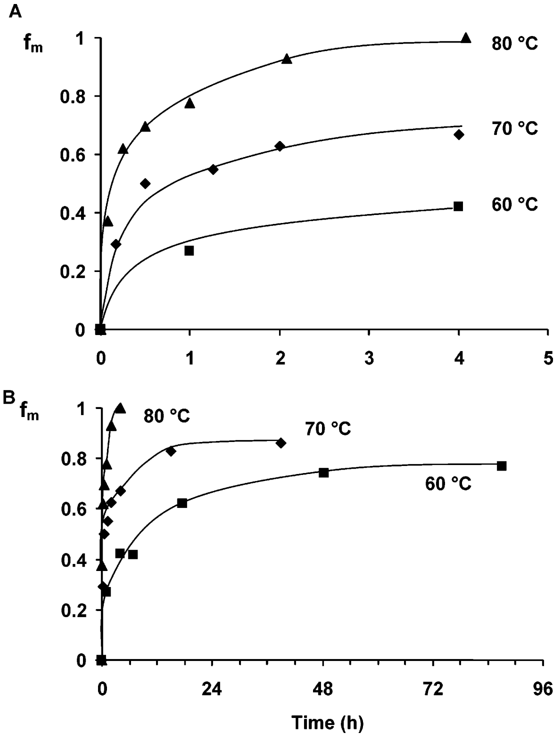


Figure 7. Fraction of mixing (f_m) versus annealing time at 60, 70, and 80 °C, for the 1:1 mixture of the labeled latexes AL0 and PL0. (A) Short-time behavior; (B) long-time behavior.

labeled latexes AL0 and PL0, which did not contain reactive functionality. The short-time behavior is shown in Figure 7A, whereas the polymer diffusion on a much longer time scale is presented in Figure 7B. These results show that the chain interdiffusion process was strongly enhanced by a moderate increase in temperature. At 80 °C, f_m increased to 1.0 over about 4 h, whereas at lower temperatures, f_m values appeared to level off at lower extents of mixing. As we emphasized in our discussion of the reference L0 film in Figure 5, the polymer diffusion rates of the high molar mass components of the film were slow, and at intermediate temperatures, these polymers took a very long time to diffuse sufficiently to contribute to the growth in Φ_{ET}.

Apparent diffusion coefficients (D_{app}) were calculated as described in refs 46 and 47. The strengths and weaknesses of this approach were examined in detail in a recent publication by Ye et al.[52] These D_{app} values are plotted as a function of the fraction of mixing in Figure 8. The D_{app} values decreased with increasing f_m. For example, for the film at 60 °C, the D_{app} values decreased by an order of magnitude for f_m values between 0.25 and 0.75. Because D_{app} is a mean cumulative value, the decrease in the instantaneous diffusion coefficients of polymers at increasing values of f_m is more pronounced than the data in Figure 8 would indicate.[14,42,53] Even larger changes in D_{app} are associated with a change in temperature. Analysis of the data obtained at 60, 70, and 80 °C led to an effective activation energy for polymer diffusion of ca. 200 kJ mol^{-1}, independent of the extent of mixing. This value was close to the activation energy E_a = 180 kJ mol^{-1} determined earlier by Liu et al.[14] for a poly(methyl methacrylate-*co*-*n*-butyl acrylate) in the 50−80 °C range, exhibiting a glass transition temperature of 12 °C.

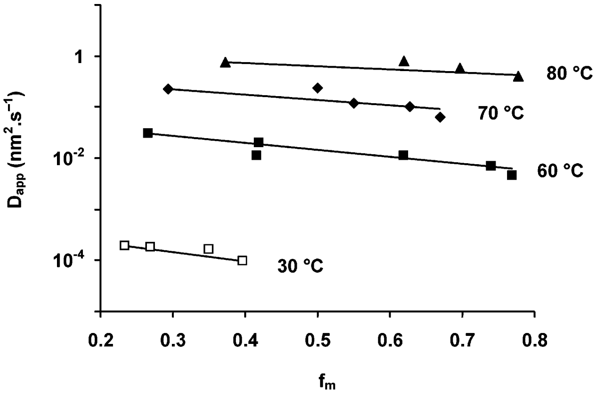


Figure 8. Apparent diffusion coefficient (D_{app}) versus the fraction of mixing (f_m) for the process of chain interdiffusion in the absence of cross-link formation (1:1 mixture of the labeled latexes AL0 and PL0).

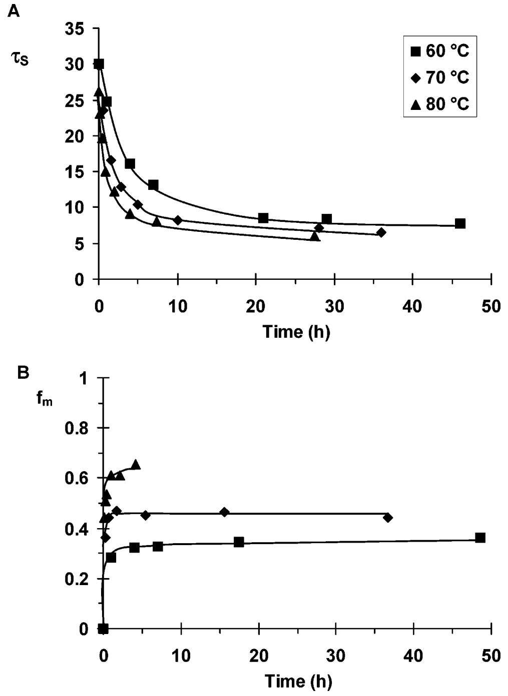


Figure 9. (A) Swell ratio (τ_s) and (B) fraction of mixing (f_m) versus annealing time for films prepared at 60, 70, and 80 °C from latex L4.3 in the presence of 2.0 wt % PTSA (with respect to polymer; i.e., 0.46 mol/mol MABEA).

Cross-Link Formation and Chain Interdiffusion Process at Elevated Temperatures. Similar experiments were carried out at 60, 70, and 80 °C on films formed from the functional latex L4.3 with 4.3 mol % MABEA. These films were prepared in the presence of 2.0 wt % PTSA (with respect to polymer; i.e., 0.46 acid mol/mol MABEA). In these films, the condensation reaction occurred in competition with polymer diffusion. Cross-link formation was monitored by swelling experiments. The gel content reached a plateau at 90−92% for all films, within 4 h at 80 °C, within 5 h at 70 °C, and over about 20 h at 60 °C. Note that these time scales are much shorter than those for films annealed at 30 °C. The evolution of the swell ratio over time for these films is presented in Figure 9A. The experimental data indicate that the higher the temperature, the faster the cross-linking reaction and the higher the cross-link density at a given time. In addition, the swell ratios appear to converge toward the same final value similar to that obtained at longer times for films of this polymer annealed at 30 °C. This type of result is expected, because only the rate of the condensation reaction and not the final cross-link density should be a function of temperature.

Energy transfer experiments were carried out in parallel, using the labeled latexes AL4.3 and PL4.3, to monitor the rates of polymer diffusion in these films. In Figure 9B, the extent of mixing f_m is plotted as a function of time for films annealed at 60, 70, and 80 °C. Over the first hour of annealing, a significant amount of polymer diffusion occurred at all three temperatures. As compared to the data in Figure 7 for the films in which no cross-links were formed, one sees that gel formation led to pronounced limits on the extent of polymer interdiffusion. As a consequence of extensive gel formation, f_m reached maximum values of 0.34 at 60 °C, 0.46 at 70 °C, and 0.65 at 80 °C. As in the nonreactive systems, higher temperatures led to faster polymer diffusion rates and larger degrees of mixing over a given period of time. In the nonreactive system, however, all components of the system remain able to diffuse, and values of f_m will continue to grow if one waits a sufficient length of time. In the reactive system, gel formation leads to components for which diffusion is limited to dangling ends at the edges of the network. As the cross-link density increases, as reflected in the decrease in swell ratio, these dangling ends become shorter, and no further intermixing of donor- and acceptor-labeled polymer can occur. At intermediate cross-link densities, well past the gel point but for gel contents less than 50−70%, the sol component is still able to diffuse. The efficiency of energy transfer in the system will continue to increase as Phe-labeled sol polymer diffuses out of cells formed by donor-labeled polymer to be replaced by An-labeled polymer originating in cells formed by acceptor-labeled polymer.

The higher limiting values of f_m obtained at 80 °C as compared to 70 °C, and at 70 °C as compared to 60 °C, emphasize an important feature of the competition between the polymer diffusion rate and the chemical reaction rate. The polymer diffusion rate depends on two factors, $(T - T_g)$, which is a measure of the temperature dependence of the microscopic friction coefficient, and chain length. For long chain polymers, particularly those well above the entanglement length, polymer diffusion can take place at reasonable rates at temperatures well above T_g. Over a limited range of temperatures, changes in the polymer diffusion rate will fit an Arrhenius analysis, characterized by an effective activation energy $E_{a,eff}$. For values of T not too far from T_g, the magnitude of $E_{a,eff}$ will be substantially larger than the activation energy of normal bimolecular chemical reactions. Thus, an increase in temperature will have a more pronounced effect on increasing the rate of polymer diffusion than it will have on the cross-linking reaction rate.

Effect of Acid Concentration. The condensation reaction that leads to cross-link formation is acid catalyzed. Thus, the rate of this reaction should be sensitive to the amount and strength of the acid present in the films. To investigate this effect, without modifying the rate of the polymer interdiffusion process, a series of films were studied at a common temperature (70 °C), with the same MABEA content (4.3 mol %) but various acid concentrations: 0.7, 1.0, and 2.0 wt % PTSA (0.0046, 0.046, and 0.46 mol acid/mol MABEA, respectively). As expected, the rate of cross-link formation, as inferred from the growth in gel content and the decrease in swell ratio, was enhanced by the increase in acid concentration (see Figure 10). For this series of films, the increase in acid content had an even more pronounced impact on the rate of increase in f_m and the limiting extent of mixing achieved in the system. For example, the film in the presence of 0.7 wt % PTSA reached $f_m = 0.8$ after 55 h at 70 °C, which may not be the limiting value for this film. In contrast, an essentially identical film containing 2 wt % PTSA reached its limiting value of $f_m = 0.48$ within the first hour of annealing, with no further growth in f_m. These results illustrate the strong impact of branched and cross-linked chains on the polymer interdiffusion process.

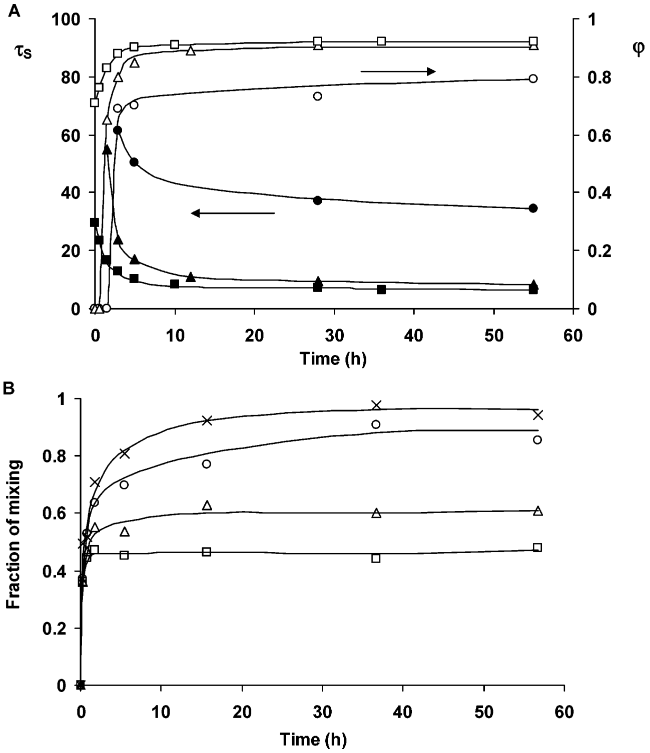


Figure 10. (A) Swell ratio (τ_s), gel content (φ), and (B) fraction of mixing (f_m) versus annealing time for films prepared from latex L4.3 in the presence of various amounts of PTSA. PTSA content: □, ■ 2.0 wt %; △, ▲ 1.0 wt %; ○, ● 0.7 wt %; × 0 (in wt % with respect to the polymer).

Discussion about the Film Morphology. The latex particles described in this paper had a statistical distribution of functional monomer units along the polymer backbone and a globally uniform distribution of acetal groups throughout the latex particles. When these particles formed films in the presence of an acid catalyst, a condensation reaction occurred that led to cross-link formation. Because the cross-links were formed within the film by the self-condensation of homogeneously distributed functional groups, a high gel content and high cross-link densities could be achieved. Over time, the network formed occupied a large volume fraction of the polymer film. The yield of the chemical reaction was independent of the extent of mixing of the polymer chains from different particles. Good film cohesion requires chains to span the interface between cells, connecting cross-links on either side. Thus, a sufficient extent of polymer diffusion between adjacent cells must occur before gel formation becomes too advanced. In this system, for a given concentration of MABEA (i.e., a selected final cross-link density), the extent of mixing, and hence the film morphology, could be adjusted by varying two different parameters. The amount of acid had a strong influence on the rate of cross-link formation, whereas changes in temperature had a much stronger influence on the polymer diffusion rate than on the cross-link formation rate. We have shown, for example, that, for a given amount of acid present in the films, an increase in temperature led to an increase in the limiting extent of mixing in the film. This was explained by the high activation energy of the interdiffusion process. In all cases, however, the films obtained exhibited excellent cohesive strength and good resistance to solvent.

Conclusions

Cross-linked films were obtained from MABEA-functionalized latexes, under acidic conditions. The kinetics of cross-link formation was enhanced by both a decrease in the pH of the latex dispersion and an increase in acetal function content. The final cross-link density was a function only of the acetal content, because hydrolysis of the acetal groups was rapid and efficient. Thus, all of the acetal groups in the latex polymer became available for the cross-linking reaction. In all cases, the films obtained exhibited good resistance to organic solvents, as well as good mechanical properties, as determined by the growth in tensile strength. Polymer chain interdiffusion occurred simultaneously with the chemical reaction, but the chemical reaction limited the extent of polymer mixing due to diffusion. Even at 30 °C, where this effect was most pronounced, sufficient polymer diffusion across cell boundaries occurred to reinforce the film. From these results, we conclude that cross-linking involved the entire film volume made up of cells formed from individual particles, but only the outer part of each individual cell was involved in polymer mixing through diffusion. When the temperature was increased, the extent of mixing due to polymer diffusion increased, but remained incomplete when the competing chemical reaction was fast. At any given temperature, the chemical reaction rate was controlled by the strength and the amount of acid present. Thus, both the film annealing temperature and the amount of added acid could be used as external parameters to control the extent of mixing.

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Note Added After ASAP Posting

This article was released ASAP on 7/9/2004. The last sentence of reference 50 has been revised. The correct version was posted on 7/16/2004.

References and Notes

(1) Provder, T.; Winnik, M. A.; Urban, M. W. Film formation in water-borne coatings. *Am. Chem. Soc. Symp. Series* **1996**, 648.
(2) Provder, T.; Urban, M. W. Film formation in coatings. Mechanisms, properties, and morphology. *Am. Chem. Soc. Symp. Series* **2001**, 790.
(3) Winnik, M. A.; Pinenq, P.; Krüger, C.; Zhang, J.; Yaneff, P. V. *J. Coat. Technol.* **1999**, *71*, 47.
(4) Tamai, T.; Pinenq, P.; Winnik, M. A. *Macromolecules* **1999**, *32*, 6102.
(5) Grawe, J. R.; Bufkin, B. G. *J. Coat. Technol.* **1978**, *50*, 67.
(6) Zosel, A.; Hekman, W.; Ley, G.; Maechtle, W. *Makromol. Chem. Suppl.* **1990**, *35/36*, 423.
(7) Hidalgo, M.; Guillot, J.; Cavaillé, J.-Y. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1991**, *49*, 103.
(8) Hidalgo, M.; Cavaillé, J. Y.; Guillot, J.; Guyot, A.; Perez, J.; Vassoille, R. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 1995.
(9) Mohammed, S.; Daniels, E. S.; Klein, A.; El-Aasser, M. S. *J. Appl. Polym. Sci.* **1996**, *61*, 911.
(10) Mohammed, S.; Daniel, E. S.; Sperling, L. H.; Klein, A.; El-Aasser, M. S. *J. Appl. Polym. Sci.* **1997**, *66*, 1869.
(11) He, Y.; Daniels, E. S.; Klein, A.; El-Aasser, M. S. *J. Appl. Polym. Sci.* **1997**, *64*, 1143.
(12) Chen, M. J.; Ramdatt, P. E.; Cai, W. *Eur. Coat. J.* **1998**, *7/8*, 532.
(13) Soares, C.; Charleux, B.; Vairon, J. P.; Vergé, C.; Loyen, K. Film formation in coatings: mechanisms, properties, and morphology. *Am. Chem. Soc. Symp. Series* **2001**, *790*, 157.
(14) Liu, R.; Winnik, M. A.; Di Stefano, F.; Vanketessan, J. *Macromolecules* **2001**, *34*, 7306.
(15) Bourgeat-Lami, E.; Tissot, I.; Lefebvre, F. *Macromolecules* **2002**, *35*, 6185.
(16) Pham, H. H.; Winnik, M. A. *Macromolecules* **1999**, *32*, 7692.
(17) Zosel, A.; Ley, G. *Macromolecules* **1993**, *26*, 2222.
(18) Guinot, P.; Charleux, B.; Vairon, J.-P. *Macromol. Symp.* **2000**, *152*, 55.
(19) Misra, S. C.; Pichot, C.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci.* **1983**, *21*, 2845.
(20) Park, Y.-J.; Kim, J. H. *Colloids Surf., A* **1999**, *153*, 583.
(21) Pham, H. H.; Farinha, J. P. S.; Winnik, M. A. *Macromolecules* **2000**, *33*, 5850.
(22) Pham, H. H.; Winnik, M. A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 855.
(23) Pham, H. H.; Winnik, M. A. *Am. Chem. Soc. Symp. Series* **2001**, *790*, 88.
(24) Yeliseeva, V. I. *Br. Polym. J.* **1975**, *7*, 33.
(25) Makuuchi, K.; Katakai, A.; Nakayama, H. *J. Coat. Technol.* **1983**, *55*, 29.
(26) Aradian, A.; Raphael, E.; de Gennes, P.-G. *Macromolecules* **2000**, *33*, 9444.
(27) Aradian, A.; Raphael, E.; de Gennes, P.-G. *Macromolecules* **2002**, *35*, 4036.
(28) Kjellqvist, K.; Rassing, J.; Wesslen, B. *J. Appl. Polym. Sci.* **1994**, *51*, 1063.
(29) Kjellqvist, K.; Rassing, J.; Wesslen, B. *J. Appl. Polym. Sci.* **1995**, *57*, 1381.
(30) Peula, J. M.; Hidalgo-Alvarez, R.; De las Nieves, F. J. *J. Colloid Interface Sci.* **1998**, *201*, 139.
(31) Santos, R. M.; Forcada, J. *J. Mater. Sci.: Mater. Med.* **2001**, *12*, 173.
(32) Gibanel, S.; Heroguez, V.; Gnanou, Y.; Aramendia, E.; Bucsi, A.; Forcada, J. *Polym. Adv. Technol.* **2001**, *12*, 494.
(33) Forcada, J. *Recent Res. Dev. Polym. Sci.* **2000**, *4*, 107.
(34) Pinschmidt, R. K., Jr.; Davidowich, G. E.; Burgoyne, W. F.; Dixon, D. D.; Goldstein, J. E. *Polym. Mater. Sci. Eng.* **1987**, *56*, 780.
(35) Pinschmidt, R. K. Jr.; Davidowich, G. E.; Burgoyne, W. F.; Dixon, D. D.; Goldstein, J. E. *Polym. Mater. Sci. Eng.* **1987**, *56*, 785.
(36) Pinschmidt, R. K., Jr. *Polym. Mater. Sci. Eng.* **1988**, *59*, 1156.
(37) Pinschmidt, R. K., Jr.; Burgoyne, W. F.; Dixon, D. D.; Golstein, J. E. Crosslinked Polymers: chemistry, properties and applications. *Am. Chem. Soc. Symp. Series* **1988**, *367*, 453.
(38) Pinschmidt, R. K., Jr.; Burgoyne, W. F.; Dixon, D. D.; Golstein, J. E. Crosslinked Polymers: chemistry, properties and applications. *Am. Chem. Soc. Symp. Series* **1988**, *367*, 467.
(39) Soares, C.; Charleux, B.; Vairon, J.-P.; Verge, C.; Loyen, K. *Am. Chem. Soc. Symp. Series* **2001**, *790*, 157.
(40) Plessis, C.; Arzamendi, G.; Leiza, J. R.; Schoonbrood, H. A. S.; Charmot, D.; Asua, J. M. *Macromolecules* **2000**, *33*, 5041.
(41) Pham, H. H. Ph.D. Thesis, University of Toronto, 2000.
(42) Zhao, C.-L., Z.; Wang, Y.; Hruska, Z.; Winnik, M. A. *Macromolecules* **1990**, *23*, 4082.
(43) Odrobina, E.; Winnik, M. A. *Macromolecules* **2001**, *34*, 6029.
(44) Farinha, J. P. S.; Martinho, J. M. G.; Yekta, A.; Winnik, M. A. *Macromolecules* **1995**, *28*, 6084.

(45) Crank, J. *The Mathematics of Diffusion*; Clarendon Press: Oxford, UK, 1975.

(46) Kim, H. B.; Winnik, M. A. *Macromolecules* **1994**, *27*, 1007.

(47) Kim, H. B.; Winnik, M. A. *Macromolecules* **1995**, *28*, 2033.

(48) Wang, Y.; Winnik, M. A. *J. Phys. Chem.* **1993**, *97*, 2507.

(49) Boczar, E. M.; Dionne, B. C.; Fu, Z.; Kirk, A. B.; Lesko, P. M.; Koller, A. D. *Macromolecules* **1993**, *26*, 5772.

(50) For example, Flory has shown for reversible reactions that the soluble fraction of polymer in equilibrium with the gel is related to the polydispersity of the polymer and the cross-link density: Flory, P. J. *J. Am. Chem. Soc.* **1947**, *69*, 30. For a more recent discussion of this point, see: Taylor, J., Winnik, M. A. *JCT Res.* **2004**, *1*, 163.

(51) Goh, M. C.; Juhué, D.; Leung, O.; Wang, Y.; Winnik, M. A. *Langmuir* **1993**, *9*, 1319.

(52) Ye, X.; Farinha, J. P. S.; Oh, J. K.; Winnik, M. A.; Wu, C. *Macromolecules* **2004**, *37*, in press.

(53) Hahn, K.; Ley, G.; Schuller, H.; Oberthur, R. *Colloid Polym. Sci.* **1986**, *264*, 1092.

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