Macromolecules **2006,** *39,* 1425−1435

Polymer Interdiffusion vs Cross-Linking in Carboxylic Acid−Carbodiimide Latex Films. Effect of Annealing Temperature, Reactive Group Concentration, and Carbodiimide Substituent

Hung H. Pham and Mitchell A. Winnik*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6

Received July 29, 2005; Revised Manuscript Received December 7, 2005

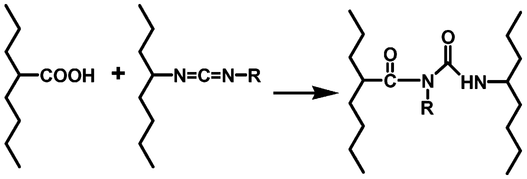
ABSTRACT: This article describes the results of experiments examining the competition between the polymer interdiffusion and a cross-linking reaction in poly(2-ethylhexyl methacrylate) latex blend films in which the reactive groups (carboxylic acid and carbodiimide groups) are present in separate latex particles. In this system, polymer diffusion is necessary to bring the reactive groups into proximity, but the reaction creates long chain branches and gel that retard or inhibit further polymer diffusion. To enable measuring polymer diffusion rates by the energy transfer method, the methacrylic acid-containing particles were also labeled with a donor dye, and the −NCN-containing particles were labeled with an acceptor dye. Along with the extent of polymer diffusion, we monitored the growth in gel content as well as the consumption of carbodiimide groups. High gel content in the final film was promoted by factors that maximize the rate of polymer diffusion relative to the rate of the cross-linking reaction: high annealing temperature, low functional group content, and less reactive carbodiimide groups.

Introduction

Environmental considerations are driving the coatings industry to modify or replace existing technology. The goal is to reduce and eventually eliminate volatile organic compounds (VOCs) from coatings formulations because VOCs lead to smog formation. Waterborne coatings, along with high solids and powder coatings, represent attractive solutions to these problems. Waterborne coatings, including those based upon aqueous dispersions of latex particles, however, still contain a significant amount of VOCs. The organic solvents added to latex coatings formulations serve two functions: to lower the modulus of hard latex polymers so that transparent films can form at the application temperature and to promote polymer interdiffusion across particle−particle boundaries to yield mechanically coherent films. Soft latex particles can form films in the absence of VOCs, but because of the low T_g of the polymer, the films are soft and tacky. To remove the tackiness and improve the chemical resistance and mechanical performance of these films, one can introduce chemistry into the components to undergo cross-linking following application of the coating to a substrate.[1]

We are interested in latex coatings containing reactive functionality. Thermoset latex coatings are not a new topic. Many new developments have occurred since the classic review papers by Bufkin and Grawe in 1978.[2] Many of these new ideas and new cross-linking chemistries can be found in a recent review paper.[3] Various strategies exist for the formulation of these types of coatings. In most commercial coatings, the latex and a second component, a catalyst or a polyfunctional reactant, are mixed immediately before use, and the coating is applied during the useful “pot life” of the mixture. These types of coatings are called “two-pot” or “2K” coatings. One-pot coatings exist, and they undergo ambient cure induced by oxygen in the air. A particularly attractive type of coating would be a “two-pack in one-pot” coating. In this strategy, one would mix two latex dispersions containing complementary reactive functionality. As long as the reactive groups were confined to separate latex particles, as they would be in the aqueous dispersion, they could not react with one another. In principle, these mixtures could be stored for long periods of time before use. In the film, however, polymer diffusion across interparticle boundaries would bring the reactive groups into contact and allow them to react.

Chart 1



In this paper, we consider a candidate system consisting of a carbodiimide-containing (−NCN−) latex plus a carboxylic acid-containing latex. In polymer films, these two groups react to form an *N*-acylurea.[4] One of the attractive features of this chemistry is that it converts the polar and protic −COOH group into the much less polar *N*-acylurea, as shown in Chart 1. In this way one hopes that the chemical reaction will not only introduce cross-links into the matrix but also reduce the number of −COOH groups and thereby lower the sensitivity of the coating to moisture.

We are interested in how the conditions of film formation and aging affect the rate and extent of polymer diffusion across the boundaries of the cells formed by these latex particles upon drying. In the freshly formed film, as shown in Figure 1, the reactive particles are randomly distributed, and the reactive groups are still confined within their own cells. The reaction between the −NCN− and −COOH groups occurs only at the boundary of different cells, while at the boundary of identical cells there is no chemical reaction. One can imagine that if the chemical reaction is faster than polymer interdiffusion, a cross-linked membrane will form at the interface of different cells. As a result, the cross-linked membrane will suppress further diffusion of polymer molecules across it. On the other hand, if

---

* To whom correspondence should be addressed. E-mail: mwinnik@chem.utoronto.ca.

10.1021/ma051685w CCC: $33.50

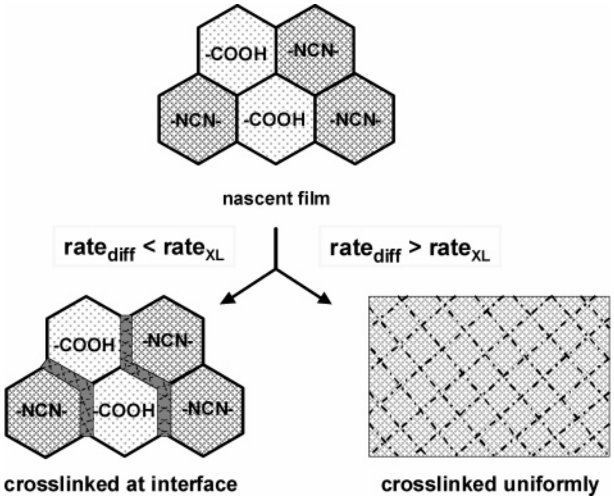


Figure 1. Competition between the rate of polymer diffusion and the rate of cross-linking reaction in films formed from a blend of carboxylated latex and carbodiimide-containing latex. When the polymer diffusion rate is slower than the cross-linking rate, a barrier membrane forms at the interface between the two types of polymer. When the polymer diffusion rate is rapid, the polymers fully mix before the film gels.

polymer diffusion is much more rapid, complete intermixing of the two polymers will occur before a substantial amount of reaction takes place. Under these circumstances, one expects to obtain a uniformly cross-linked polymer film similar to that cast from a solution of the two polymers. In previous publication,[5] we compared the rates of polymer diffusion and cross-linking for films of a carboxyl plus a *tert*-butyl-NCN-containing latex annealed at 60 °C. For the films described here, we examine these processes as they are influenced by annealing temperature, reactive group concentration, and the substituent on −NCN− moiety.

Experimental Section

The syntheses of *tert*-butylcarbodiimidoethyl methacrylate (tBCEMA), cyclohexylcarbodiimidoethyl methacrylate (CCEMA), 9-phenanthrylmethyl methacrylate (PheMMA) and 9-anthryl methacrylate (AnMA) are described elsewhere.[6−9] 2-Ethylhexyl methacrylate (EHMA, Aldrich) was distilled prior to use. 1-Dodecyl mercaptan ($C_{12}SH$, Aldrich), potassium persulfate (KPS, Aldrich), sodium dodecyl sulfate (SDS, Fisher Scientific), aqueous ammonia (NH_3(aq), Fisher Scientific), sodium bicarbonate ($NaHCO_3$, Aldrich), and methacrylic acid (MAA, Aldrich) were used as received. Water was collected from a Milli-Q Water System.

Particle sizes were determined by dynamic light scattering at an angle of 90° and at 22 °C, employing a Brookhaven BI-90 particle sizer. Polymer molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) at 30 °C, using an instrument equipped with two Styragel columns (HR 3 and 4) and tandem refractive index and fluorescence detectors. Linear poly(methyl methacrylate) standards were used to calibrate the columns. Fourier transform infrared (FTIR) measurements were carried out using a Perkin-Elmer spectrometer 1000 with resolution of 4 cm^{-1}.

Preparation of Latex Dispersions. All fluorescently labeled PEHMA latexes were prepared by a two-stage emulsion polymerization from a common seed with fluorescent and reactive comonomers being introduced only in the second stage under monomer-starved conditions.[6,10]

Stage 1. To a 1 L three-neck round-bottom flask equipped with a mechanical stirrer, a condenser, a nitrogen outlet, and a nitrogen inlet, EHMA (40.0 g), SDS (2.52 g), $NaHCO_3$ (0.5 g), and H_2O (740 g) were added. The flask was then heated to 80 °C in an oil bath while the solution was bubbled with nitrogen gas under mechanical agitation. After the solution was allowed to stabilize for half an hour at 80 °C, a solution of potassium persulfate (0.75 g in 10 g of H_2O) was then injected via a syringe. The solution became milky white in a few minutes. The reaction mixture was allowed to stir at 80 °C for another 2 h. The flask was then cooled to room temperature, and the aqueous solution was transferred to a 1 L bottle for future use.

Table 1. Representative Recipes in the Second Stage of Emulsion Polymerization to Prepared Labeled Latex

	D-MAA-11	A-tBCEMA-5.2
PEHMA seed dispersion[a] (g)	120.0	60.0
EHMA (g)	66.50	33.14
MAA (g)	3.50	
tBCEMA (g)		1.92
PheMMA (g)	0.77	
AnMA (g)		0.47
n-$C_{12}SH$ (g)	0.61	0.32
KPS (g)	0.12	0.07
SDS (g)	1.29	0.70
$NaHCO_3$ (g)		0.31
H_2O (g)	55.00	27.06
temp (°C)	80	60
feeding rate (mL/min)	1.24	0.56

[a] 5.5% solids content.

Stage 2. To a 250 mL three-neck round-bottom flask, equipped with a mechanical stirrer, a condenser, a nitrogen outlet, and a nitrogen inlet, a PEHMA seed dispersion (60.0 g) was added. The flask was heated to 80 °C under mechanical agitation with a gentle flow of nitrogen gas. After 10 min, an aqueous solution containing water-soluble reagents and an organic solution containing a monomer or a mixture of monomers and a chain transfer reagent were fed into the flask at a controlled rate via feed pumps (The FMI Lab Pump, model RP-G6). Both lines were fed in at the same time, but the aqueous line was adjusted so that the addition finished about 15−30 min after the organic line. When the addition of the aqueous solution was complete, the flask was allowed to stir for an additional hour at the reaction temperature before it was cooled to room temperature. Table 1 lists the recipes used in the second stage to prepare two types of labeled latex particles, D-MAA-11 and A-tBCEMA-5.2. D-MAA-11 represents latex polymers labeled with fluorescent donor (D), copolymerized with 11 mol % of methacrylic acid (MAA). The other carboxylic acid-containing latexes, D-MAA-5 and D-MAA-20, were also prepared from the recipe in the second column of Table 1, but with 5 and 20 mol % of MAA, respectively. These MAA-containing particles were prepared at 80 °C in the presence of a chain transfer reagent (1 wt %) and the fluorescent donor (1 mol %). Note that the amount of seed particles and ingredients used to prepare these MAA-containing latexes are doubled compared to that used to prepare the −NCN-containing particles.

The recipe shown in the last column was used to prepare acceptor-labeled latexes containing 5.2 mol % of tBCEMA, abbreviated as A-tBCEMA-5.2. Here A (acceptor) refers to the fluorescent dye, tBCEMA refers to the reactive comonomer, and the number 5.2 refers to the amount (in mol %) of the tBCEMA used in the recipe. The other acceptor-labeled latex containing −NCN− groups were also prepared using this recipe. The A-tBCEMA-11 latex dispersion was prepared with 11 mol % of tBCEMA, whereas the recipes for A-CCEMA-3.2 and A-CCEMA-4.6 contained 3.2 and 4.6 mol % of CCEMA, respectively. These −NCN-containing particles were prepared at 60 °C in the presence of $NaHCO_3$ buffer, chain transfer reagent (1 wt %), and the fluorescent acceptor (1 mol %).

Preparation of Latex Films. Films were prepared on quartz plates for energy transfer (ET), gel content, and swell ratio measurements and on CaF_2 disks for FTIR measurements. To ensure the results obtained from different methods were comparable, films were prepared from the same mixture of reactive latex.

For each mixture of reactive latex dispersions, a carboxylic acid-containing latex was first neutralized with aqueous ammonia to pH

8 and then mixed with a carbodiimide-containing latex. The dispersion mixture was then divided into two portions. One portion of the latex mixture was used to prepare films cast from an organic solvent, and the other was cast directly from an aqueous mixture. We shall refer to films obtained from the mixed aqueous latex as "dispersion-cast" and those obtained from an organic solution as "solvent-cast".

Preparation of Solvent-Cast Films. One portion of the latex mixture was freeze-dried for 1 h to yield a solid powder. A portion of the freeze-dried powder was mixed with KBr powder and pressed into a thin pellet. The pellet was examined by FTIR to determine the −NCN− group content of the sample. We assume that this mild treatment results in a negligible loss of carbodiimide groups. Another portion of the freeze-dried powder was dissolved in tetrahydrofuran (THF). An aliquot of this solution was cast on a quartz plate and allowed to dry rapidly in the open air. Fluorescence decay measurements were carried out, and then these films were also annealed at 60 °C for a various lengths of time.

Preparation of Dispersion-Cast Films. Another portion of the mixed aqueous latex was cast directly onto quartz plates and onto CaF_2 disks. The disks and plates were then placed under an inverted Petri dish at 22 °C so that the films would dry in a reproducible 100% humidity atmosphere. The drying time ranged from 5 to 7 h. All films were transparent and crack-free. Films on quartz plates were typically 0.1−0.5 mm thick, whereas those on CaF_2 disks were about 1−2 μm thick. We began the first ET, FTIR, and gel content and swell ratio measurements about 1 h after the last visible trace of the wet spot in the center of the films disappeared. We arbitrarily refer to this time as t_0.

Energy Transfer (ET) Measurements and Data Analysis. Fluorescence decay measurements were carried out by the single photon timing technique[11] with an excitation wavelength of 300 nm and an emission wavelength of 350 nm. An interference filter for the emission at 350 ± 5 nm was placed in front of the emission monochromator to reduce scattering light and to remove emission from the An chromophore. For these measurements, the quartz plate supporting a polymer film was placed in quartz tube and flushed with N_2 gas, and the quartz tube was placed in the sample cell of the fluorescence decay instrument. After each measurement, the quartz plate was removed from the tube and placed directly on a preheated aluminum plate under a Petri dish in a forced-air oven. The quartz plates were periodically removed from the oven, cooled to room temperature, and remeasured under a N_2 atmosphere. We analyzed the diffusion process in terms of the area under the donor fluorescence decay profiles $I_D(t)$. To obtain these areas, we fitted each decay curve to an empirical equation as described in our previous publications[12] and then evaluated the integral from the magnitude of the fitting parameters.

The quantum efficiency of energy transfer $\Phi_{ET}(t_n)$ for a sample annealed for a time t_n is defined by the middle term of the expression

$$\Phi_{ET}(t_n) = 1 - \frac{\int_0^\infty I_{DA}(t_n,t)\,dt}{\int_0^\infty I_D(t_n,t)\,dt} = 1 - \frac{\text{area}_{DA}(t_n)}{\text{area}_D} \qquad (1)$$

Here $\text{area}_{DA}(t_n)$ is the area under the normalized fluorescence decay curve of donor in the presence of acceptor after an annealing a time t_n, and area_D is the corresponding area for a sample in the absence of acceptor. The integral corresponding to area_D is equal to the unquenched donor lifetime τ_D and remains constant for samples that are annealed. For the phenanthrene−anthracene pair examined here, the Forster distance $R_0 = 2.3$ nm.[13]

As a measure of the extent of polymer diffusion in latex films, we evaluate the fraction of mixing parameter f_m.

$$f_m = \frac{\Phi_{ET}(t_n) - \Phi_{ET}(t_0)}{\Phi_{ET}(t_\infty) - \Phi_{ET}(t_0)} = \frac{\text{area}_{DA}(t_0) - \text{area}_{DA}(t_n)}{\text{area}_{DA}(t_0) - \text{area}_{DA}(t_\infty)} \qquad (2)$$

The term f_m represents the fractional growth in energy transfer efficiency in the system. $\Phi_{ET}(t_0)$ represents the contribution of energy transfer across the interparticle boundaries before any polymer diffusion takes place. In other systems comprised of particles of similar dimensions and with a similar dye content, values of $\Phi_{ET}(t_0)$ are found in the range of 0.05−0.07.[14] In the experiments described below, we often find larger values of $\Phi_{ET}(t_0)$, which we interpret to mean that some polymer diffusion across interparticle boundaries occurs as the films dry. To quantify the extent of this diffusion, we assume a value of $\Phi_{ET}(t_0) = 0.06$ in evaluating eq 2. We also require a value for $\Phi_{ET}(t_\infty)$. Experiments based upon solvent-cast films of PEHMA homopolymer latex with a similar dye content lead to a value of $\text{area}_{DA}(t_\infty)$ of 21.5 ns, which in conjunction with $\tau_D = 44.9$ ns leads to $\Phi_{ET}(t_\infty) = 0.52$.[6,10] As discussed in a later section of this paper, this value is more appropriate than the value obtained from a solvent-cast film formed from functional latex for the calculation of f_m values.

Table 2. Typical Characteristics of the Labeled Latex Polymers

sample name[a]	diam (nm)	solids content (%)	M_w, M_w/M_n	pH	−NCN− (%)[b]
D-MAA-5	98	30.5	68 000, 2.34	5	
D-MAA-11	101	31.2	41 000, 1.95	5	
D-MAA-20	113	31.0	50 500, 2.35	5	
A-CCEMA-3.2	97	31.7	69 500, 2.24	8	77
A-CCEMA-4.6	107	32.1	86 000, 2.05	8	80
A-tBCEMA-5.2	106	31.9	63 000, 3.15	8	98
A-tBCEMA-11	102	31.7	45 500, 2.39	8	98

[a] The number following the comonomer designation (MAA, CCEMA, tBCEMA) refers to the mol % of this comonomer in the second-stage reaction feed. [b] −NCN− content (%) = (moles of −NCN− in the polymer/moles of −NCN− monomer used in the synthesis) × 100, as determined by FTIR.

FTIR Measurements and Analysis. We employed FTIR measurements (a) to quantify the −NCN− content of the latex particles remaining after emulsion polymerization, (b) to determine the amount of −NCN− groups lost during the drying of blends of the −NCN-containing latex dispersion with the carboxyl latex into solid films, and (c) to follow the consumption of −NCN− groups as these blend films were aged or annealed.

To determine the −NCN− content of −NCN-containing latex particles, a small amount of a carbodiimide-containing latex dispersion, for example A-tBCEMA-5.2 latex dispersion, was first freeze-dried, weighed in a test tube, dissolved in a known amount of $CHCl_3$, and then transferred to a NaCl cell with a 1.0 mm path length for FTIR measurements. The spectrum of the pure solvent was subtracted from that of the sample solution, and then the intensity of the −NCN− absorbance at 2128 cm^{-1} was measured relative to the spectrum baseline at 2070 cm^{-1}. The −NCN− content of the latex polymer was calculated using the Beer−Lambert law assuming that the extinction coefficient (ϵ) of the carbodiimide group was the same as that for tBCEMA monomer ($\epsilon_{tBCEMA} = 1340$ L mol^{-1} cm^{-1}). From these experiments, we learned that for the carbodiimide monomer introduced into the emulsion polymerization 98% of the −NCN− of tBCEMA survived hydrolysis and became incorporated into the latex, whereas for CCEMA ($\epsilon_{CCEMA} = 2134$ L mol^{-1} cm^{-1}) a greater amount of hydrolysis occurred. We introduced 3.2 mol % CCEMA (of the total weight monomer in the second stage) and found an −NCN− content corresponding to only 77% of the total monomer was incorporated into the latex. The −NCN− content remaining after the particle synthesis of the four −NCN-containing latex samples is also shown in Table 2.

To determine the amount of −NCN− group lost during water evaporation of a dispersion-cast film, we compared the I_{-NCN-}/I_{1380} ratio in newly formed latex blend films with that in a KBr pellet containing the pure −NCN− latex polymer. I_{-NCN-} is the absorbance of the −NCN− peak (2125−2130 cm^{-1}). The intensity of this peak can decrease either through reaction with −COOH groups or by hydrolysis. I_{1380} is the intensity of a reference peak due to a C−H bending vibration of the polymer.[15,16] Its intensity does not change with consumption of carbodiimide groups. The

Table 3. Carbodiimide Group Survival during Particle Synthesis and Following Formation of Latex-Blend Films

	−NCN− content in the recipe (mol)[a]	−NCN− content of the latex itself (mol)[b] [%][c]	−NCN− content of latex blend films (mol)[d] [%][e]
A-CCEMA-3.2	3.2	2.5 [77]	1.7 [52] D-MAA-5
A-CCEMA-4.6	4.6	3.7 [80]	2.5 [54] D-MAA-11
A-tBCEMA-5.2	5.2	5.1 [98]	4.2 [80] D-MAA-11
A-tBCEMA-11	11.0	10.8 [98]	9.1 [82] D-MAA-20

[a] Mol % of −NCN− groups based on total weight of monomers in the second stage. [b] Mol % of −NCN− groups that survived after the synthesis of −NCN-containing particles. [c] From column 6 of Table 2. [d] Mol % of −NCN− groups that remained after the latex blend dispersions dried to solids films. [e] % of −NCN− groups remaining in the newly formed latex blend films compared to the amount used in the synthesis of the −NCN− latex.

results for −NCN− group loss during drying and film formation for the four reactive blends are listed in the last column of Table 3.

We then monitored the consumption of −NCN− in solid films annealed at different times. Following the FTIR measurement on the newly formed film, which corresponds to t_0, the entire sample holder containing the CaF_2 disk was removed from the spectrometer and placed in a preheated forced-air oven for various periods of time (t_n). The holder was then cooled to room temperature before the next measurement in the series. We characterize the extent of carbodiimide reaction in a latex film after various extents of annealing in terms of the expression

$$-\mathrm{NCN}-\text{ remaining (\%)} = \left(1 - \frac{(I_{-\mathrm{NCN}-}/I_{1380})_{t_0}}{(I_{-\mathrm{NCN}-}/I_{1380})_{t_n}}\right) \times 100 \tag{3}$$

where $(I_{-\mathrm{NCN}-}/I_{1380})_{t_0}$ and $(I_{-\mathrm{NCN}-}/I_{1380})_{t_n}$ are the ratios respectively of the absorbance intensity of −NCN− group to that of the reference peak at 1380 cm^{-1} of the freshly formed film (t_0) and of the same film annealed for a time t_n.

Gel Content and Swell Ratio Measurements. Gel content and swell ratios were determined gravimetrically. Films were prepared on quartz plates and annealed for various times in a preheated oven. Individual samples were removed, cooled to room temperature, weighed (W_0), and then immersed in excess 1,4-dioxane for at least 24 h to allow the un-cross-linked component to dissolve. The films were then removed from the solvent, touched with a dry filter paper to remove liquid solvent on the film surface, weighed (W_1), and then allowed to dry further in air for at least another 24 h to remove the remaining solvent. The weight of this dry polymer is W_2. The gel content is calculated as

$$\text{gel content (\%)} = \left(\frac{W_2}{W_0}\right) \times 100 \tag{4}$$

Neglecting the slight difference in density between dioxane and the polymer, the swell ratio is given by

$$\text{swell ratio} = \frac{W_1}{W_2} \tag{5}$$

Results

Latex Synthesis and Characterization. All latex particles were synthesized by seeded emulsion polymerization, with the fluorescent and functional comonomers being introduced only in the second stage under monomer-starved conditions. The seed particles have a mean diameter of about 48 nm and consist of high molecular weight PEHMA homopolymer ($M_w = 700\,000$, $M_w/M_n = 2.5$).

From these seed particles, we prepared seven batches of labeled latex. Three batches of latex were labeled with phenanthrene, the fluorescent donor, and contained different amounts of −COOH groups. Four batches of latex were labeled with anthracene, the acceptor chromophore, and contained different −NCN-containing comonomers, either CCEMA or tBCEMA. The polymer compositions of the individual latex samples are listed in Table 2, along with their abbreviated names. These abbreviated names contain information about the dye, the nature of the functional comonomer, and its mol % of the monomer mixture used in the emulsion polymerization. Because these reactions were run under monomer-starved conditions, we assumed that the copolymer composition remained constant throughout the reaction. In addition, the absence of significant amounts of acid in the serum[17] indicates that the MAA content of the latex is very similar to that in the feed. Thus, D-MAA-11 refers to a donor (Phe)-labeled PEHMA latex containing 11 mol % MAA. A-CCEMA-4.6 refers to an acceptor (An)-labeled PEHMA containing 4.6 mol % CCEMA in the original recipe. Similarly, A-tBCEMA-5.2 refers to an acceptor (An)-labeled PEHMA containing 5.2 mol % tBCEMA in the original recipe. Note that in each batch of latex dispersion we used 1 wt % of 1-dodecanthiol as a chain transfer reagent and 1 mol % of fluorescent comonomer, either AnMA or PheMMA.

Table 2 summarizes the characteristics of the reactive particles. All carboxylated latexes prepared in the absence of $NaHCO_3$ result in acidic dispersions with almost identical solids content, particle size and narrow size distribution, and similar polymer molecular weight and molecular weight distributions. For each sample, the polymer molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) using an instrument equipped with tandem fluorescence (FL) and refractive index (RI) detectors.[18] From the FL and RI chromatograms, we infer that all fluorescent dyes, either Phe or An, are randomly distributed and fully incorporated into the polymer chains, as well as uniformly distributed throughout each particle.

Table 2 also provides information about the measured −NCN− group content of the latex polymer compared to that in the reaction feed. The carbodiimide functionality is known to react with water. We found that during emulsion polymerization the rate of hydrolysis depended on the pH of the aqueous medium, the temperature of the polymerization, the hydrophobicity of the base polymer, and the steric hindrance of the substituent on the carbodiimide group.[6,7] Almost all of the carbodiimide groups (98%) survived the reaction when the latex particles containing carbodiimide groups were prepared in the presence of $NaHCO_3$ buffer at 60 °C, using EHMA as the base monomer and tBCEMA as the carbodiimide comonomer.

To prepare latex blend films for ET and FTIR measurements, a sample of carboxylated latex was neutralized with aqueous ammonia to pH 8, mixed with a known amount of a −NCN-containing latex. The mixture was then immediately cast on a substrate and allowed to dry at 22 °C under an inverted Petri dish, which slowed the water evaporation rate, so that the film formed at 100% relative humidity under easily reproducible conditions. The drying process took about 5−7 h. ET and FTIR measurements began at 1 h after the last visible wet spot on the film disappeared. We found that some of the −NCN− groups reacted during the drying process for these mixed dispersions. The results are shown in the fourth column of Table 3. The extent of −NCN− remaining does not depend on the

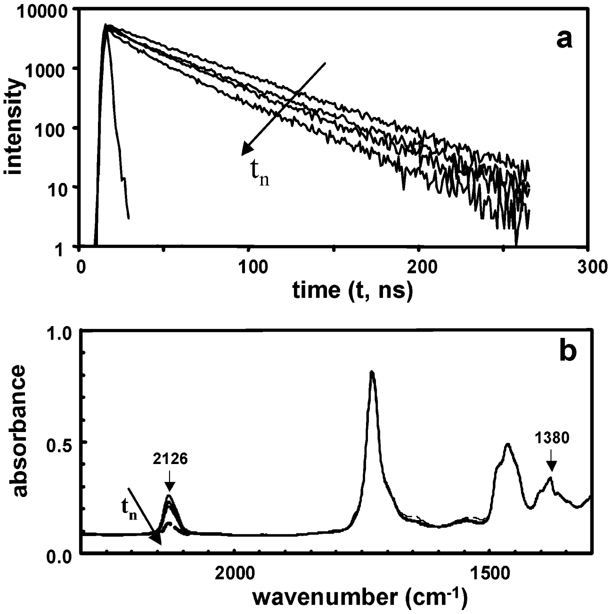


Figure 2. Representative (a) donor fluorescence decay profiles and (b) FTIR spectra, monitored as a function of annealing times for a latex film prepared from a 1:1 mixture of the D-MAA-11/A-tBCEMA-5.2 samples. The films were prepared at 22 °C and annealed at 60 °C.

concentration of −COOH in the complementary latex but does depend on the alkyl substituent of the −NCN− moiety (CCEMA vs tBCEMA). In control experiments, in which samples of only A-tBCEMA-5.2 or A-CCEMA-4.6 latex were allowed to dry into a film, no significant loss of −NCN− groups (3% for CCEMA and 2% for tBCEMA) was detected by FTIR.[6,7] The reference point for this calculation was the FTIR signal of −NCN− groups relative to the 1380 cm^{-1} peak in KBr pellets of freeze-dried samples. The absorbance at 1380 cm^{-1}, attributed to a C−H bending mode,[15,16] serves as a useful internal reference peak, since it was observed not to change during sample drying and annealing. The significant loss of −NCN− groups in the films formed from mixed latex is likely due to the chemical reaction between −COOH and −NCN− groups at the particle−particle boundaries. The reaction occurs to a greater extent when the substituent of the −NCN− moiety is the cyclohexyl group.

D-MAA-11/A-tBCEMA-5.2 Latex Blend. As the first example of a reactive blend, we examine a latex film formed from a dispersion containing a mixture of an equal amount of ammonia-neutralized D-MAA-11 and A-tBCEMA-5.2 and annealed at 60 °C. The molar ratio of −COOH/−NCN− is about 2. Representative fluorescence donor decays, measured as a function of annealing time, are shown in Figure 2a. In the newly formed film, examined 1 h after the drying was complete at 22 °C, we found $\Phi_{ET}(t_0) = 0.11$, consistent with a small extent of polymer diffusion across the particle−particle boundary during drying. The film was then annealed for various periods of times. The areas under the donor fluorescence decay curves decreased, indicating a growth in ET due to polymer diffusion.

Figure 2b shows the FTIR spectra of a dispersion-cast film, freshly prepared from the same dispersion mixture and annealed at the same temperature. Here we found that 18% of the −NCN− groups reacted during the drying process. As the annealing time increased, the intensity at 2128 cm^{-1}, associated with the −NCN− group, decreased. When a film of the A-tBCEMA-5.2 latex alone was annealed under similar conditions, the peak intensity at 2128 cm^{-1} remained constant.[6,7]

Of the various products that can form in the reaction between a carboxylic acid and a carbodiimide group, only *N*-acylurea formation (Chart 1) will lead to stable cross-linking. In our system, latex films are prepared at room temperature from a 1:1 mixture of ammonia-neutralized carboxylic acid-containing latex particles and carbodiimide-containing latex particles. Upon drying, the ammonia evaporated to regenerate the carboxyl group in its protonated form. These films were then annealed at elevated temperature. The growth in gel content and the decrease in swell ratio that we observed as the films were annealed provide support for the idea that *N*-acylurea groups were formed in this reaction.

We analyze the diffusion process by calculating f_m values and monitor the cross-linking reaction by determining the percentage of −NCN− groups remaining in the sample. We plot these results in Figure 3a. In the newly formed film, examined 1 h after the last visible trace of the wet spot had disappeared, we found $f_m = 0.11$. This value is somewhat larger than that expected for films in which the only contribution to ET is on opposite sides of the interparticle boundary. As a consequence, we believe that both local interdiffusion and cross-boundary ET contribute to this value. Because the films were formed at 22 °C, 20−30 °C above the glass transition temperature ($T_{g,PEHMA} = -10$ °C) of these latex polymers, it is not unreasonable that some polymer diffusion takes place during the drying process. We assign a range in $T - T_g$ values because the presence of the comonomers, particularly −COOH groups from MAA, has an influence on the T_g of the copolymers. According to the Fox equation,[19] incorporation of 11 mol % MAA into PEHMA should result in an increase in the polymer T_g from −10 °C to −4 °C.

In Figure 3a, the f_m plot at time zero starts at 0.11, and the percentage of −NCN− remaining begins at 82%. As the annealing time increased, the f_m values increased while the percentage of −NCN− remaining decreased. The increase in f_m indicates more donor and acceptor mixing due to polymer diffusion. A decrease in the percentage of −NCN− remaining shows that more −NCN− groups have reacted. At early times (<4 h), f_m increased rapidly to 0.65 over 1 h and then to 0.87, while over this time, the percentage of −NCN− remaining decreased from 82% to 55%; i.e., only 27% of −NCN− groups reacted. This result indicates that the rate of molecular mixing due to diffusion occurs much faster than that of the cross-linking reaction. The instantaneous rate is represented by the slope of each plot for a given period of times. The steeper the slope, the faster the rate. As the annealing time increased (>4 h), the slope flattened, and f_m values increased slowly from 0.87 to 0.98 over 12 h, while the percentage of −NCN− remaining decreased from 55% to about 30% over the same time. These observations at late times indicate that polymer diffusion had slowed to such an extent that the chemical reaction rate became faster than the polymer diffusion rate. Once the magnitude of f_m reached 0.98, the donors and acceptors in the film were essentially fully mixed. Further diffusion will not lead to any change in ET signal. We note that finding a limiting value of $f_m = 1.0$ is consistent with a proper choice of $\Phi_{ET}(t_\infty)$. This value was obtained from a solvent-cast film prepared from a 1:1 mixture of An- and Phe-labeled PEHMA homopolymer latex with a similar dye content and lacking reactive functionality.[10]

In Figure 3b, we show plots of f_m and the amount of −NCN− remaining for films formed from the same dispersion at 22 °C but annealed at 40 °C. In the newly formed film, the initial value of f_m was 0.17 and the percentage of −NCN− remaining was 82%. Here we see that the growth in f_m and the rate of

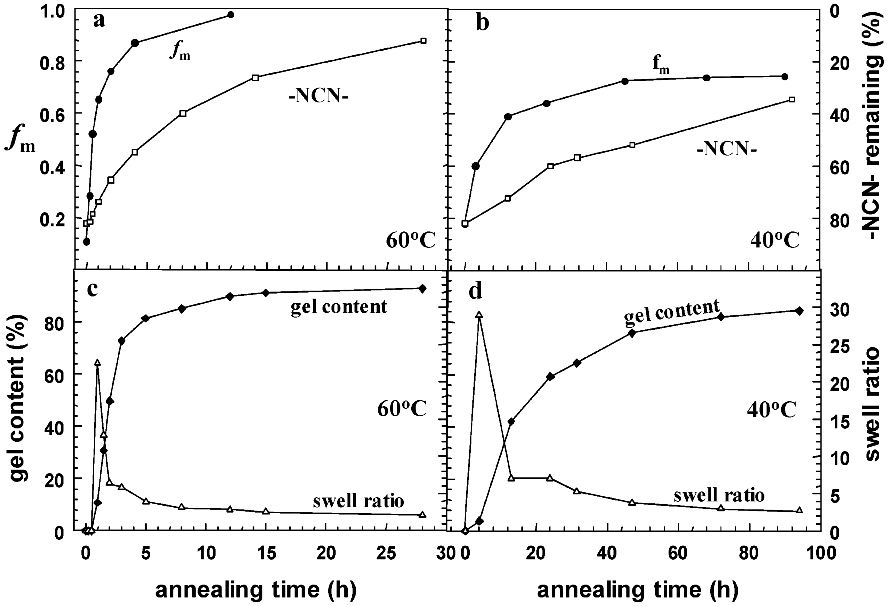


Figure 3. Plots of f_m (●) and the percentage of −NCN− groups remaining in the sample (☐) vs annealing times of latex films annealed at (a) 60 °C and (b) 40 °C for latex films prepared from a 1:1 mixture of the D-MAA-11/A-tBCEMA-5.2 samples. Plots of the growth in gel content (◆) and decrease of the swell ratio (△) vs annealing times at (c) 60 °C and (d) 40 °C.

disappearance of the carbodiimide band in the IR spectrum are slower than at 60 °C. As at the higher temperature, at early annealing times (<12 h), the rate of polymer diffusion was faster than that of the cross-linking reaction. At longer annealing times, one sees a marked decrease in the growth of f_m, which appears to cease for annealing times >45 h. These results suggest that the polymer diffusion rate is more sensitive than the chemical reaction rate to the reduction in temperature.

We follow the growth in the extent of cross-linking at 60 and 40 °C by measuring the gel content and the swell ratio of films prepared from the same mixture of labeled latex particles. The results are plotted in parts c and d of Figure 3, respectively. At 60 °C, no gel was detected until 1 h of annealing, when we found 11% insoluble polymer. During this time only 8% of the −NCN− groups present in the original latex underwent reaction. We obtain this value of 8% by taking the difference between the 82% of −NCN− groups that remained in the initial film and the 74% remaining after 1 h annealing at 60 °C. Over this time, f_m reached 0.65.

After 3 h annealing at 60 °C, the gel content increased to 77%, accompanied by a drastic decrease in the swell ratio to 5. During this time, f_m reached 0.80, while the amount of −NCN− remaining decreased from 74% to 60%. Upon longer annealing (15 h), the swell ratio decreased to 2, and the gel content increased to 92%. Theoretically, this is the value expected for full gel formation, since the linear polymer in the seed polymers represents 8% of the polymer mass. The seed polymer does not contain reactive groups and thus does not become part of the cross-linked network. The result of the gel content measurements is a strong indication that polymer diffusion is complete, because in order for the system to reach 100% gel, every polymer chain containing −COOH and −NCN− groups must be close enough for these group to react. We found that when the gel formation reached its full extent, f_m was greater than 0.98. Of the −NCN− groups present at the time of film formation, 28% of these remain unreacted after 15 h annealing.

At 40 °C, the gel content and swell ratio measurements show different results. No gel formation could be detected until the films were annealed for 4 h, and the amount of gel detected at that point was very small (4%). During this time, only about 2% of the original −NCN− groups reacted, while f_m increased to about 0.4. Upon longer annealing, the gel content slowly increased to 60% over 21 h and then to 77% over 48 h. During this time, f_m reached 0.70, and the amount of −NCN− remaining decreased to 52%, whereas the swell ratio dropped below 10 and decreased slowly after that. With further annealing (to 98 h), there was no significant increase in the measured gel content, even though the amount of −NCN− remaining decreased to 47%. During this time, there was no significant change in f_m.

It is useful to compare the rate of polymer diffusion in this reactive latex film to a film that does not have reactive groups, where no cross-linking can occur. In a previous publication, we described the preparation of donor-labeled PEHMA (PEHMA-D) and acceptor-labeled PEHMA (PEHMA-A) latex dispersions.[6,10] To capture the early stages of polymer diffusion, these films were prepared at 4 °C in a cold room because we had prior evidence that polymer diffusion in acetoacetoxy-containing PEHMA copolymer latex films takes place at a significant rate at room temperature (22 °C).[20] For films prepared at 4 °C, we obtain $\Phi_{ET}(0) = 0.06$. These films were then annealed at either 40 or 60 °C. We plot the values of f_m obtained at various annealing times in Figure 4. Polymer diffusion is more rapid here than in the films containing reactive functionality. Over a time scale of minutes, f_m values reach unity, whereas in the D-MAA-11/A-tBCEMA-5.2 latex films (Figure 3a,b), polymer diffusion takes hours.

D-MAA-20/A-tBCEMA-11 Latex Blend. We next examine what happens to the polymer diffusion rate and the extent of cross-linking when we doubled the amount of the reactive comonomers in individual latex samples, from 11 to 20 mol % for MAA and from 5.2 to 11 mol % for tBCEMA. We plot the f_m data for these films in Figure 5a, along with the percentage of −NCN− remaining. These films were prepared at 22 °C from the blend of (D-MAA-20 + A-tBCEMA-11) latex and then annealed at 60 °C. The molar ratio of −COOH/-NCN− in this blend is also about 2. We see that the initial value of f_m (0.03) was much smaller than that (0.11) in the films of (D-MAA-11 + A-tBCEMA-5.2) described above. The percentage of −NCN− remaining in the initial film was similar to that of the (D-MAA-

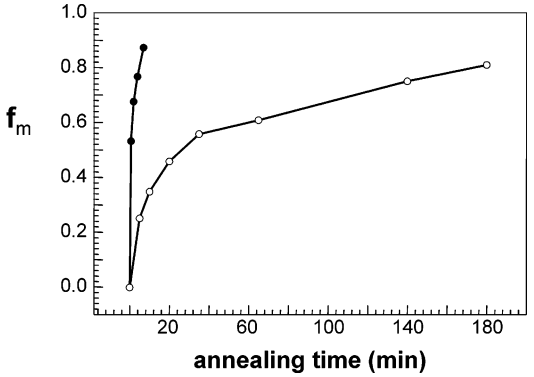


Figure 4. Plots of f_m vs annealing time of a latex film prepared from a 1:1 mixture of the PEHMA-D/PEHMA-A latex dispersions and annealed at 60 °C (●) and 40 °C (○). The latex dispersions were dried to a continuous film in the cold room at 4 °C, and the $t = 0$ measurement was taken immediately after the sample was dry.

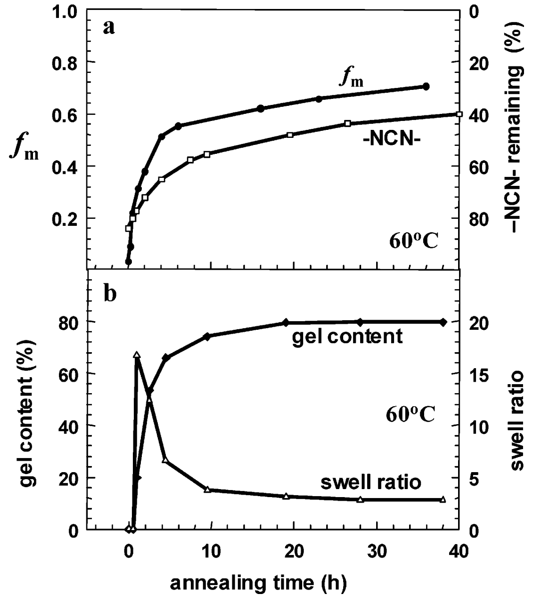


Figure 5. (a) Plots of f_m (●) and the percentage of −NCN− groups remaining in the sample (□) vs annealing times of latex films annealed at 60 °C for latex films prepared from a 1:1 mixture of the D-MAA-20/A-tBCEMA-11 samples. (b) Plots of the growth in gel content (◆) and decrease of the swell ratio (△) vs annealing times at 60 °C.

11 + A-tBCEMA-5.2) film (82%). The much smaller extent of polymer diffusion in the latex film formed from (D-MAA-20 + A-tBCEMA-11) can be attributed in part to the higher T_g of the D-MAA-20 component. According to the Fox equation, an increase in the amount of MAA comonomer from 11 to 20 mol % in a PEHMA polymer should result in an increase in polymer T_g value from −4 °C to +3 °C.[19]

The time evolution of f_m and the −NCN− signal in the FTIR spectra for (D-MAA-20/A-tBCEMA-11) at 60 °C (Figure 5a) at early times resembles the corresponding behavior of these values for the (D-MAA-11 + A-tBCEMA-5.2) film annealed at 40 °C (Figure 3b). The initial rate of polymer diffusion was rapid compared to the rate of carbodiimide group consumption, but after a few hours at 60 °C, the diffusion rate became significantly slower. When the film was annealed for longer times, f_m values increased and the −NCN− continued to react, but the growth in f_m was reduced to a greater extent than the rate of −NCN− consumption.

To examine the consequences of increasing the reactant concentration on the diffusion−reaction system, we compare the data in Figure 5a to those in Figure 3a. In Figure 5a, we see that f_m values obtained from the film prepared from the D-MAA-20/A-tBCEMA-11 dispersion reached 0.22 over 0.5 h, a value much lower than that obtained (0.45) from the film prepared from the D-MAA-11/A-tBCEMA-5.2 dispersion. This result indicates that the increase in the concentration of reactive comonomers led to a decrease in the initial rate of polymer diffusion. We find that a similar fraction of −NCN− groups are lost from both films during the evaporation of water (16% for the D-MAA-20/A-tBCEMA-11 film and 18% for the D-MAA-11/A-tBCEMA-5.2 film). This result implies that twice the number of reactive groups was consumed in the D-MAA-20/A-tBCEMA-11 film. As a result, more polymer coupling occurred and more branches formed in the D-MAA-20/A-tBCEMA-11 film, which in turn decreased the rate of polymer diffusion.

We follow the extent of cross-linking in the D-MAA-20/A-tBCEMA-11 blend at 60 °C by measuring gel content and swell ratio and plot these values in Figure 5b. There was no gel formation in the freshly formed film and in the film annealed for 0.5 h. When the film was annealed for 1 h, we detected a 20% gel fraction. The gel fraction increased rapidly to 65% over 4.5 h. During this time, f_m reached 0.51 and the amount of −NCN− remaining decreased from 84% to 65% of that present in the original latex, i.e., 19% of −NCN− groups reacted. When the same film was annealed for longer times, the gel content continued to build, to 79% over 19 h. As the annealing time was increased to 38 h, the gel content remained unchanged at 80%. During this time (19−36 h), f_m increased slightly, from 0.62 to 0.70, and the amount of −NCN− remaining decreased from 48% to 40%. Here the gel content did not reach 100%.

D-MAA-11/A-CCEMA-4.6 Latex Blend. In this section we examine what happens to the polymer diffusion and cross-linking reaction processes when we replace tBCEMA with CCEMA as the reactive comonomer. One should note that the CCEMA and tBCEMA comonomer differ only in the substituent attached to the "other end" of the −NCN− group, the cyclohexyl group vs the *tert*-butyl group. One should also note that the CCEMA group undergoes partial hydrolysis during emulsion polymerization, resulting in the loss of ca. 20% of the −NCN− groups introduced in the particle synthesis reaction.

Like the other blends, we prepared films at 22 °C from a 1:1 mixture of neutralized D-MAA-11 and A-CCEMA-4.6 latex and carried out ET and FTIR measurements on films annealed at 60 °C. In Figure 6a, we plot f_m vs time for this film as well as the percentage of −NCN− remaining. During the transformation of the latex dispersion into a solid film, we found that 32% of the −NCN− groups were lost, a value much higher than that (18%) for the film prepared from the D-MAA-11/A-tBCEMA-5.2 latex dispersion. In the newly formed dispersion-cast film, we obtained $f_m = 0.04$, a smaller value compared to that (0.11) obtained for the film prepared from the D-MAA-11/A-tBCEMA-5.2 sample. The increase in the loss of −NCN− group during drying, in conjunction with the low $f_m(t_0)$ value, suggests that some high molar mass molecules are formed due to the cross-linking reaction at the particle−particle boundary. When this film was then annealed at 60 °C, f_m increased to 0.46 over 0.5 h and then to 0.64 over 2 h. During this time, the percentage of −NCN− remaining decreased from 68% to 44%. Upon longer annealing, f_m continued to increase, reaching 0.75 over 15 h, and the amount of −NCN− remaining slowly decreased.

There are several interesting features that become apparent when we compare the data in Figure 6a to those in Figure 3a. The cross-linking reaction occurs faster in the D-MAA-11/A-

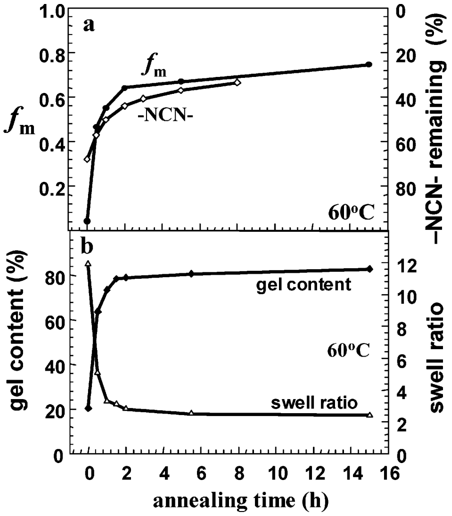


Figure 6. (a) Plots of f_m (●) and the percentage of −NCN− groups remaining in the sample (□) vs annealing times of latex films annealed at 60 °C for latex films prepared from a 1:1 mixture of the D-MAA-11/A-CCEMA-4.6 samples. (b) Plots of the growth in gel content (◆) and decrease of the swell ratio (△) vs annealing times at 60 °C.

CCEMA-4.6 film than in the D-MAA-11/A-tBCEMA-5.2 film, implying that the −NCN− group of the CCEMA is more reactive than the −NCN− group of the tBCEMA toward the −COOH group of the MAA. During the first half hour of annealing, 11% of the −NCN− groups in the D-MAA-11/A-CCEMA-4.6 film reacted (only 57% of the original carbodiimide groups remained at this point), whereas only 4% of the −NCN− groups reacted in the D-MAA-11/A-tBCEMA-5.2 film (Figure 3a), and 78% of these groups initially present in the latex remained intact. This result is consistent with our earlier finding that the −NCN− groups of tBCEMA-containing latex particles are more stable to hydrolysis on storage than those containing CCEMA groups.[7]

To compare interdiffusion rates in the two systems, we begin by noting that the polymer molecular weight of A-CCEMA-4.6 ($M_w = 86\,000$) is somewhat larger than that of A-tBCEMA-5.2 ($M_w = 63\,000$). The same D-MAA-11 latex polymer was used in both systems. At early stages of film annealing at 60 °C, polymer diffusion was faster in the D-MAA-11/A-tBCEMA-5.2 film than in the D-MAA-11/A-CCEMA-4.6 sample. For example, f_m of the D-MAA-11/A-tBCEMA-5.2 sample (Figure 3a) reached 0.65 over only 1 h, whereas f_m of the D-MAA-11/A-CCEMA-4.6 sample (Figure 6a) required 2 h to increase to a similar value. Upon longer annealing, f_m of the D-MAA-11/A-tBCEMA-5.2 sample reached 0.98 over 12 h, whereas over this time f_m of the D-MAA-11/A-CCEMA-4.6 film increased only to 0.7. Part of this difference, particularly at early times, is due to the higher average molecular weight of the A-CCEMA latex sample. At later times, the reduction of interdiffusion rate of the D-MAA-11/A-CCEMA-4.6 sample is caused by the more rapid reaction between the −NCN− group of the CCEMA and the −COOH of the D-labeled latex polymer.

We follow the extent of cross-linking in the D-MAA-11/A-CCEMA-4.6 blend at 60 °C by measuring gel content and swell ratio and plot these values in Figure 6b. In the newly formed film, we obtain 20% of insoluble polymers. We note that 32% of −NCN− groups of the original latex are lost during the evaporation of water leading to film formation. We believe that most of this loss is due to the cross-linking reaction, and that this reaction occurs primarily at the particle−particle boundary. When these films were annealed over 2 h, the gel content increased rapidly to 79%, corresponding to a rapid increase in f_m to 0.65. Upon longer annealing, the gel content increased only slightly to 83% over 15 h. During this time, f_m increased to 0.75.

D-MAA-5/A-CCEMA-3.2 Blend. We next examine what happens to the system when we decreased the amount of the reactive comonomers, from 11 to 5 mol % for MAA and from 4.6 to 3.2 mol % for CCEMA. For the −NCN-containing latex, 3.2 mol % CCEMA was used in the original recipe, but the fraction of total monomer that survived the particle synthesis was 2.5 mol %, and only 1.7 mol % remained after film formation in the presence of D-MAA-5. In Figure 7a, we plot f_m and the percentage of −NCN− remaining, monitored in latex films prepared from a 1:1 mixture of D-MAA-5 and A-CCEMA-3.2 particles. In the freshly formed film cast from a mixture of latex dispersions at 22 °C, we found $f_m = 0$. When this film was annealed at 60 °C, f_m rapidly increased to 0.68 over 0.25 h and then to 0.78 over 0.5 h. Over this time, the percent of −NCN− groups present in the original latex decreased from 68% to 48%. Upon annealing for 6 h, f_m increased to 0.96; i.e., essentially full diffusive mixing took place. During this time, the amount of −NCN− remaining decreased from 48% to 12%. From these results we deduce that one method to increase the rate of polymer diffusion in a system in which the functional groups are very reactive is to reduce the reactant concentration in the polymer. For example, in the latex blend of D-MAA-11/A-CCEMA-4.6, it took 15 h for the system to reach $f_m = 0.75$. By reducing the amount of both MAA and CCEMA in the polymer, we found that it took less than 0.5 h for the D-MAA-5/A-CCEMA-3.2 film to reach a similar f_m value.

In Figure 7c, we plot the results of gel content and swell ratio measurements on films prepared from the D-MAA-5/A-CCEMA-3.2 blend. There was no measurable gel at t_0. When the films were annealed at 60 °C, the gel content rapidly increased to 56% over 0.5 h and then to 77% over 2 h. Upon longer annealing (7 h), we obtained 92% gel. This corresponds to complete gel formation if we take into account the amount of linear polymer present in the seed latex. Over this time, f_m grew to 0.96, and the amount of −NCN− remaining decreased to about 9%.

To examine the effect of temperature on these processes, we repeated ET and FTIR measurements on films formed from the same mixture of latex dispersions annealed at 40 °C. In the freshly formed film cast from the mixed dispersions at 22 °C, we found $f_m = 0.15$. We plot f_m values and the percentage of −NCN− remaining in Figure 7b. When the annealing temperature was decreased from 60 °C to 40 °C, both the polymer diffusion rate and the carbodiimide group reaction rate were reduced, but the rate of polymer diffusion appears to be retarded more than the rate of cross-linking. Upon longer annealing (>5 h), little further polymer diffusion took place, but the chemical reaction continued to proceed.

Some further insights into the behavior of the system are possible through a temperature-jump experiment. In Figure 7b, we show what happens for a film annealed for a substantial time at 40 °C and then suddenly heated to 60 °C. The extent of polymer interdiffusion, which had appeared to level off, again increased, and there was an increase in the rate of −NCN− group consumption. Following the temperature jump, the initial rate of polymer diffusion at 60 °C appeared to be faster than the rate of cross-linking. At longer times, the rates were reversed, such that the rate of the reaction was faster than that of polymer diffusion. We also observe that a large increase in f_m (from 0.50 to 0.80) occurred when the temperature was raised to 60 °C.

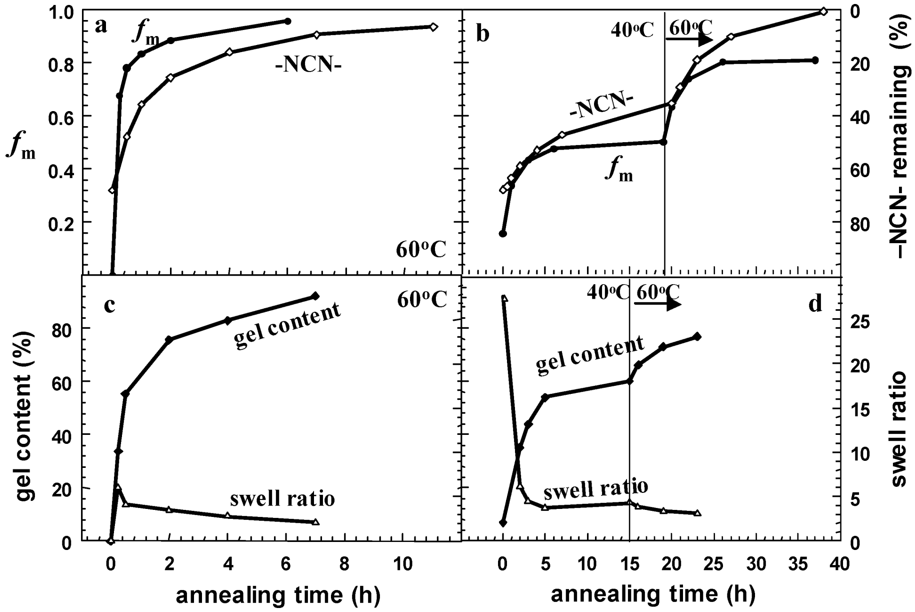


Figure 7. Plots of f_m (●) and the percentage of −NCN− groups remaining in the sample (□) vs annealing times of latex films annealed at (a) 60 °C and (b) 40 °C for latex films prepared from a 1:1 mixture of the D-MAA-5/A-CCEMA-3.2 samples. Plots of the growth in gel content (◆) and decrease of the swell ratio (△) vs annealing times at (c) 60 °C and (d) 40 °C. The samples annealed at 40 °C were, after 15 h, subjected to a sudden increase in annealing temperature, as indicated by the vertical line in (b) and (d).

Polymer diffusion of mobile polymers and the local diffusion of branches contribute to this increase in f_m values.

The results of gel content and swell ratio measurements, on films annealed at 40 °C and on films then heated at 60 °C, are plotted in Figure 7d. In the newly formed film, we obtained a small fraction (7%) of insoluble polymers. When the films were annealed at 40 °C, the gel fraction increased to 54% over 5 h and then to 60% over 15 h. During this time, f_m reached about 0.48, and the amount of −NCN− remaining decreased from 68% to 40%. When the temperature was suddenly increased to 60 °C, the gel fraction also increased to 77% over the next 8 h (15 h to 23 h).

Discussion

The competition between polymer diffusion and the cross-linking reaction in the latex blend films examined here is a complex process. The two processes are coupled. Polymer diffusion is necessary to bring the functional groups into close enough proximity for them to react, but the formation of branches and the increase in polymer molecular weight reduce the rate of further polymer diffusion. In addition, there is another complication. As we reported previously,[10] the PEHMA−MAA copolymers have only limited miscibility with the PEHMA−NCN copolymers, and there is less miscibility for the PEHMA−MAA polymer with the higher −COOH group content. As the reaction between the carboxylic acid and carbodiimide groups proceeds, the polymers are rendered miscible.

We can demonstrate this effect here for the mixture of D-MAA-11/A-tBCEMA-5.2 latex by comparing in Figure 8 values of the quantum efficiency of ET (Φ_{ET}) measured as a function of annealing times at 60 °C for a dispersion-cast latex film and for a solvent-cast film. The solvent-cast film is the more interesting. One imagines that the mixture of polymers present in a THF solution is intimate and uniform. The fact that the value of Φ_{ET} for the solvent-cast film is less than 0.52 indicates that polymer demixing has occurred as the solvent evaporated, and the *decrease* in this value upon annealing indicates that heating initially enhances demixing. Eventually the reaction between the −COOH and −NCN− groups takes over, and the system evolves to full mixing. Miscibility is likely driven by two effects: formation of graft copolymer and the reduction of the number of free −COOH groups through their conversion to *N*-acylurea groups.

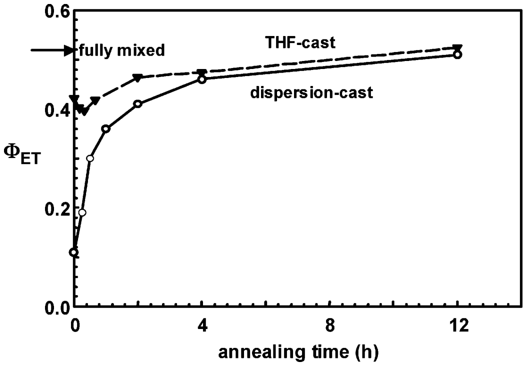


Figure 8. Plots of Φ_{ET} vs time for a latex film and a THF-cast film prepared from the D-MAA-11/A-tBCEMA-5.2 blend. Both films were then annealed at 60 °C. The arrow at $\Phi_{ET} = 0.52$ corresponds to the ET efficiency expected for uniform mixing of the donor- and acceptor-labeled polymer.

In the latex film, the consequences of limited miscibility are not immediately obvious in the f_m vs annealing time curve in Figure 3a. Nevertheless, this effect must play an important role in determining the polymer interdiffusion rate. In the dispersion-cast film, where reactive polymers are initially confined within their own cells, the limited miscibility hinders polymer diffusion across the particle interfaces at early stages of the healing process. However, when the reaction between the −COOH and the −NCN− groups occurs, generating *N*-acylurea bonds, the branched polymers formed become compatibilizers. Bonner and Hope have reviewed the topic of compatibilizers produced in situ by chemical reactions in polymer blends.[21] In a simple picture of this process in our system, the domains containing the branched polymers (and even cross-linked polymers) provide regions for the mobile MAA-containing polymers and tBCEMA-containing polymers to mix.

The next level of complication is that as the reaction proceeds, the polymer molecular weight increases; branched polymers are formed, and the system begins to gel. It is well-known that the rate of polymer diffusion varies with chain length and is sensitive to the presence of branching. For linear polymers shorter than the entanglement molecular weight, the diffusion coefficient D_i, characterizing the diffusion of a given chain of length N_i, decrease approximately as N_i^{-1}, and for chains longer than the entanglement length, D_i is predicted to decrease as N_i^{-2}.[22] In all blends examined here, the polymer chains before reaction are linear, with an average chain length ($M_w = 60\,000$) on the order of twice the entanglement molar mass. When the reaction between the −COOH groups and −NCN− groups occurs, the linear polymers couple to form branches. As a result, the rate of polymer diffusion decreases substantially. When the rate of polymer diffusion decreases, the rate of cross-linking also decreases because both polymer diffusion and polymer segment diffusion are necessary to bring the reactive groups close enough to react.

One of the interesting discoveries made in the course of these experiments is the relationship between the extent of polymer diffusion and the extent of gel formation. In all samples examined here, for all for the reactive polymer to be converted to gel, complete mixing of the reactive polymers was necessary. We measure the extent of mixing through the f_m parameter. For this value to approach unity, the polymers must diffuse over a length comparable to radius of a latex particle (i.e., half the cell cross section). We found only two systems in which films evolve to this extent. In the D-MAA-11/A-tBCEMA-5.2 film examined at 60 °C, we see that f_m for this film reached 0.98 over 12 h (Figure 3a), and gel formation reaches 92% 3 h later. Recall that when the gel content plot reached 92%, the system was at full gelation because the seed latex in the particle synthesis consisted of linear polymer. Similarly, for the D-MAA-5/A-CCEMA-3.2 films, f_m reached 0.96 over 6 h (Figure 7a), whereas it required 7 h for the system to undergo full gelation (Figure 7c). From these results we learn that polymer diffusion must be complete prior to the system reaching its maximum possible gel content.

Three factors reduce the rate of polymer diffusion at the early stages of film annealing: a decrease in the annealing temperature, an increase in the reactant concentration, and an increase in the reactivity of the cross-linking reactant. The D-MAA-5/A-CCEMA-3.2 films provide an example showing that a reduction in the annealing temperature causes a decrease in the initial rate of interdiffusion and its consequence on the extent of gel formation. When this film was annealed at 60 °C, f_m increased rapidly to 0.68 over only 15 min (Figure 7a). At longer annealing times, f_m reached close to unity over 6 h. At an annealing temperature of 40 °C (Figure 7b), f_m for this film reached only 0.34 over 1 h and then 0.50 over 19 h. Over this time, the gel content reached only about 60%. The gel that formed over this time limited the amount of mixing that could take place in this film. For example, when this film after 19 h at 40 °C was suddenly heated to 60 °C, the gel content increased to 79% over the next 8 h. This amount of time is similar to that needed for the same type of film, not preannealed at 40 °C, to develop to a fully cross-linked network (92% gel).

We find two examples which show that an increase in the reactant concentrations leads to a cross-linked network with less than full gel formation. In the D-MAA-11/A-tBCEMA-5.2 samples annealed at 60 °C, f_m rapidly reached 0.65 over 1 h (Figure 3a) and full gel content over 15 h (Figure 3c). In contrast, for the D-MAA-20/A-tBCEMA-11 film, which contains a higher concentration of the reactive comonomers, f_m reached only 0.3 over 1 h (Figure 5a), and it took 39 h annealing for the gel content to reach 80% (Figure 5b). Comparing the data obtained from the D-MAA-5/A-CCEMA-3.2 samples (Figure 7) to those obtained at the same annealing temperature from the D-MAA-11/A-CCEMA-4.6 samples (Figure 6), we see a similar result. In the film containing the lower amount of the reactive comonomers, polymer diffusion was rapid in the early stages, and the films reached full gelation, whereas in the film containing the higher the reactant concentrations, interdiffusion was slow, and only 80% gel was obtained. From the results of the two examples, we learn that as the concentration of the reactant groups is increased, the extent of polymer diffusion in the initial stage of sample annealing decreases, and the annealed films have a lower gel content. It is possible that the films at less than full gel content may eventually reach 92% gel content because polymer segment diffusion can still occurs, but at a slow rate.

Table 4. Summary of the Time It Took for Individual Films To Reach $f_m = 0.6$ When Annealed at 60 °C

	time to 0.60 f_m (min)
PEHMA-D/PEHMA-A (Figure 4)	1.3
D-MAA-11/A-tBCEMA-5.2 (Figure 3a)	60
D-MAA-11/A-CCEMA-4.6 (Figure 6a)	120
D-MAA-5/A-CCEMA-3.2 (Figure 7a)	15
D-MAA-20/A-tBCEMA-11 (Figure 5a)	960

To see the effect of the increase in the reactivity of the reaction on the initial rate of polymer diffusion and its consequences on the cross-linked network, we compare the D-MAA-11/A-tBCEMA-5.2 system to the D-MAA-11/A-CCEMA-4.6 system. The reaction is faster in the film containing CCEMA than in the film containing tBCEMA. In the D-MAA-11/A-tBCEMA-5.2 sample annealed at 60 °C, f_m increases to 0.65 over 1 h (Figure 3a). In the D-MAA-11/A-CCEMA-4.6 sample annealed at the same temperature, the film requires 2 h for f_m to reach to an identical value (Figure 6a). The gel content of this film increased to 80% over 15 h (Figure 6b), the same amount of time needed for the gel content of the D-MAA-11/A-tBCEMA-5.2 system to reach 92%. From these results, we see that as the functional group reactivity is increased, the overall rate of polymer interdiffusion decreases substantially, such that the system does not develop a fully cross-linked network.

To facilitate comparison of the polymer diffusion rates for the various samples described in this paper, we created Table 4, which summarizes the amount of time required for each system to reach $f_m = 0.6$ when annealed at 60 °C. For the PEHMA-D/PEHMA-A film, without reactive functionality, the polymer diffusion is so fast that this extent of polymer diffusion takes place while the film prepared at 4 °C is heated to 60 °C. We estimate a time of only 1−2 min by interpolation of the data in Figure 4. In contrast, it took 1 h for films containing 11 mol % MAA and 5.2 mol % tBCEMA to reach $f_m = 0.6$. The film containing latex polymer with the cyclohexyl moiety on the −NCN− functionality required twice as long (120 min) to reach $f_m = 0.6$ as that with the *tert*-butyl-NCN−. A decrease in MAA from 11 to 5 mol % and CCEMA from 4.6 to 3.2 mol % led to a decrease in the annealing time needed to 15 min. An increase in the reactive group concentration of MAA from 11 to 20 mol % and of tBCEMA from 5.2 to 11 mol % increased significantly the annealing time needed to 960 min (16 h). This is the film in which it took the longest time to reach $f_m = 0.6$.

Summary

In thermoset latex films formed from a blend of carbodiimide-containing PEHMA latex and carboxylic acid-containing PEHMA latex, the reaction between the −NCN− and −COOH groups to form an *N*-acylurea is coupled to the intercellular diffusion of the two polymers. High gel content in the final film was promoted by factors that maximize the rate of polymer diffusion relative to the rate of the cross-linking reaction: high annealing temperature, low functional group content, and less reactive carbodiimide groups.

Acknowledgment. The authors thank NSERC Canada for their financial support.

References and Notes

(1) Wicks, Z. W., Jr. *Film Formation*; Federation Series on Coatings Technology; FSCT: Blue Bell, PA, 1986.

(2) (a) Bufkin, B. G.; Grawe, J. R. *J. Coat. Technol.* **1978**, *50* (641), 41−55. (b) Grawe, J. R.; Bufkin, B. G. *J. Coat. Technol.* **1978**, *50* (643), 67−83. (c) Bufkin, B. G.; Grawe, J. R. *J. Coat. Technol.* **1978**, *50* (644), 83−109. (d) Grawe, J. R.; Bufkin, B. G. *J. Coat. Technol.* **1978**, *50* (645), 70−100. (e) Bufkin, B. G.; Grawe, J. R. *J. Coat. Technol.* **1978**, *50* (647), 65−96.

(3) Taylor, J. W.; Winnik, M. A. *JCT Res.* **2004**, *1*, 163−190.

(4) Taylor, J. W.; Collins, M. J.; Bassett, D. R. *Prog. Org. Coat.* **1999**, *35*, 215−221.

(5) Pham, H. H.; Winnik, M. A. *Macromolecules* **1999**, *32*, 7692−7695.

(6) Pham, H. H. Ph.D. Thesis, University of Toronto, 2000.

(7) Pham, H. H.; Winnik, M. A. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 855−869.

(8) Zhao, C.-L.; Wang, Y.; Hruska, Z.; Winnik, M. A. *Macromolecules* **1990**, *23*, 4082−4087.

(9) Feng, J. Ph.D. Thesis, University of Toronto, 1996.

(10) Pham, H. H.; Farinha, J. P. S.; Winnik, M. A. *Macromolecules* **2000**, *33*, 5850−5862.

(11) O'Connor, D.; Phillips, D. *Time-Correlated Single-Photon Counting*; Academic Press: New York, 1984.

(12) (a) Liu, R.; Winnik, M. A.; Di Stefano, F.; Venkatesan, J. *Macromolecules* **2001**, *34*, 7306−7314. (b) Ye, X.; Farinha, J. P. S.; Oh, J. K.; Winnik, M. A.; Wu, C. *Macromolecules* **2003**, *36*, 8749−8760.

(13) Wang, Y.; Zhao, C.-L.; Winnik, M. A. *J. Phys. Chem.* **1991**, *95*, 2143−2145.

(14) Feng, J.; Winnik, M. A.; Siemiarczuk, A. *J. Polym. Sci., Part A: Polym. Phys.* **1998**, *36*, 115.

(15) Xu, Z.; Lu, G.; Cheng, S.; Li, L. *J. Appl. Polym. Sci.* **1995**, *56*, 575.

(16) Verstegen, J. M. G. Ph.D. Thesis, University of Eindhoven, 1998.

(17) We titrated the serum for acid content for the syntheses employing 5 and 11 wt % MAA but not for the reaction employing 20 wt % MAA. For this sample, we cannot draw a firm conclusion about the amount of acid remaining in the serum.

(18) Sosnowski, S.; Feng, J.; Winnik, M. A. *J. Polym. Sci., Polym. Chem.* **1994**, *32*, 1497.

(19) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

(20) Feng, J. R.; Pham, H. H.; Stoeva, V.; Winnik, M. A. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1129.

(21) Bonner, J. G.; Hope, P. S. In *Polymer Blends and Alloys: Compatibilisation and Reactive Blending*; Folkes, M. J., Hope, P. S., Eds.; Chapman & Hall: London, 1993; p 46.

(22) (a) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: New York, 1986. (b) Kausch, H. H.; Tirrell, M. *Annu. Rev. Mater. Sci.* **1989**, *19*, 341.

MA051685W