Crosslinking vs. Interdiffusion Rates in Melamine-Formaldehyde Cured Latex Coatings: A Model for Waterborne Automotive Basecoat

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INTRODUCTION

There is a trend within the general coatings industry to change from solvent-based formulations to more environmentally friendly options, which contain water as the main solvent. These waterborne coatings represent a major direction, where the challenge is to obtain comparable or improved performance, with little or no solvent emission, and at reasonable cost. In architectural coatings for example, thermoplastic latex coatings currently dominate the market. Here the efforts are directed toward higher gloss, better wet edge, and with less reliance on organic solvents added to promote coalescence. Industrial coatings normally have higher performance requirements where one relies on crosslinking in the coating to improve its performance. Crosslinking can provide the toughness, hardness, and resistance to solvent, acid, and base lacking in uncrosslinked thermoplastic coatings. However, excessive crosslinking can cause brittleness and drastically reduce mechanical properties such that care must be taken when incorporating the type and amount of crosslinker.[1]

A classic example involves automotive paints, where both the basecoat and the clearcoat have to meet stringent structural, mechanical, decorative, and durability requirements. Commercial waterborne systems have already made an incursion into the market for automotive basecoat, both in North America and Europe.[2] Some of these systems are water-reducible, i.e., formed from water-soluble and water-dispersible polymers bearing crosslinking functionality. Water reducible coatings not only have desirable mechanical properties, but have excellent homogeneity and can provide coated surfaces with very good appearance. These formulations, unfortunately, often have substantial levels of organic sol-

Designing optimal formulations for automotive waterborne basecoats can be fairly complex, often requiring knowledge of events that occur at the molecular level. The ultimate performance of the coating can depend upon the success with which this knowledge is applied. We examine a system in which an aqueous dispersion of an acrylic latex with –OH functionality reacts with a melamine derivative when heated. We use fluorescence-labeling and energy transfer measurements to obtain information on the relative rates of crosslinking and interparticle polymer diffusion in these films. We show that temperature and particle morphology play an important role in the development of film properties. Finally, these energy transfer experiments provide information on the location of the melamine-formaldehyde resin in the dry film before the onset of crosslinking. This system can serve as a model for waterborne basecoat development in many automotive applications.
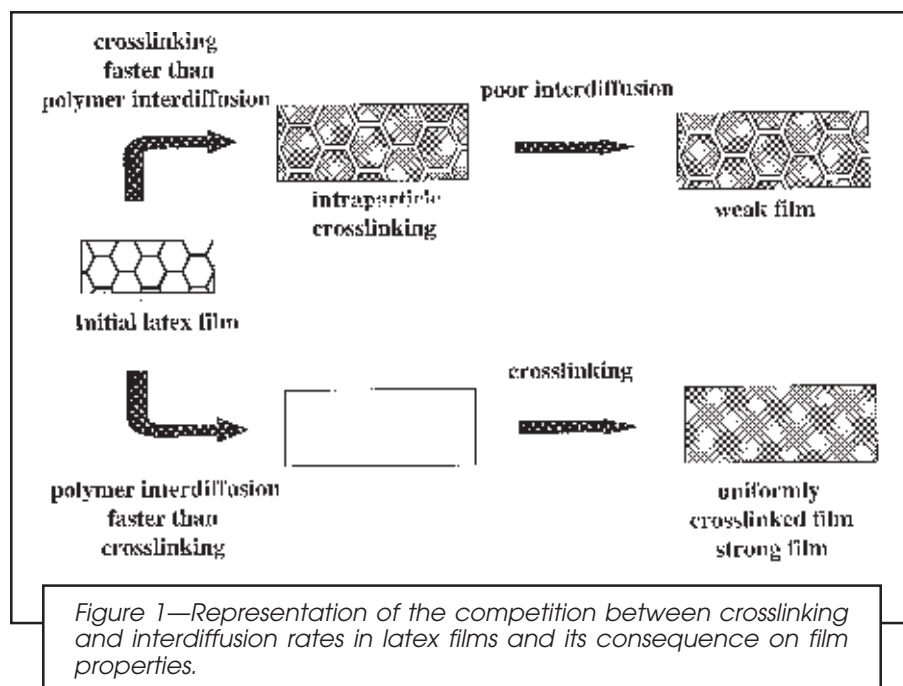
vents which contribute to VOC emissions. As a consequence, greater attention is being paid to waterborne latex dispersions, which contain crosslinkable functionality and offer the potential for lower VOC emission.[3]

Latex-based waterborne basecoats used in automotive coatings usually consist of an acrylic latex, a melamine crosslinker resin, coalescing solvents and may

Figure 1—Representation of the competition between crosslinking and interdiffusion rates in latex films and its consequence on film properties.

weak adhesion between adjacent cells. A similar effect should operate in a latex film system designed to undergo crosslinking after dry down. If crosslinking occurs within the individual latex particles faster than the polymers diffuse across the particle-particle boundary, films with less than optimum strength will be obtained. If, however, interdiffusion precedes crosslinking, the entanglements needed for good adhesion will be formed. A drawing conceptualizing this problem is shown in *Figure* 1.

This competition between interdiffusion and crosslinking is, in principle, rather complex and involves subtle features of the competition between reaction and diffusion. It is well understood, for example, that the rate of polymer diffusion varies sensitively with chain length, and is sensitive to the presence of branching. For polymers longer than the entanglement molecular weight, the diffusion coefficient D_i characterizing the diffusion of a given chain of length N_i, decreases as N_i^{-2}, and is even further retarded by the presence of long branches. When reaction and diffusion are coupled, the polymer chain length and the extent of branching increase as the reaction proceeds, and once the gel content reaches unity, diffusion and mixing are limited to the dangling ends of chains anchored into the network. The dilemma in terms of formulating thermoset latex coatings is to understand the balance required between interdiffusion and crosslinking rates to obtain optimal film properties. Should one for example choose a latex consisting of low molecular weight polymer, which will undergo rapid diffusion in the film, using a high level of reactive polymer functionality to obtain high crosslink density? Or is it preferable to employ polymer with a mean molecular weight above the entanglement limit with a smaller fraction of reactive functionality to generate tougher films through formation of physical entanglements in addition to chemical crosslinks?

Thermoset resins have been studied for years. The most common strategies for following the cure reaction is through the use of spectroscopy to follow the chemical changes, and dynamic mechanical measurements to follow the changes in modulus and in T_g of the film. Fourier-transform infrared spectroscopy is particularly useful for following conversion of isocyanate to urethane, ring-opening of epoxides, but not widely applied to follow ether exchange in melamine formaldehyde resins. Swelling experiments with organic solvents are useful for measuring the build-up of gel content, and the swell ratio provides information about the build-up of crosslink density. What is missing are measurements of polymer interdiffusion rates in thermoset latex films, in which one monitors simultaneously the rates of interdiffusion and crosslinking in order to assess the relative effects of temperature, catalyst, and other formulation

contain an aqueous polyurethane dispersion. The latter is added to reduce the minimum film forming temperature and increase film hardness provided by the polyurethane monomers.[4] Most of today's automotive waterborne basecoats are applied in conjunction with a two-component urethane clearcoat for optimum appearance and durability.[5] As automotive performance specifications (including humidity) are becoming more demanding, one needs to be able to maximize waterborne basecoat integrity and overall product attributes. Incorporation of a melamine crosslinker to the system is a major contributor to maximizing performance in waterbased systems.

One particular type of system that has been in relatively widespread use over the past 30 years, and recently has seen application in waterborne basecoat formulations, involves latex dispersions crosslinked after drying through reaction with etherified melamine formaldehyde derivatives such as hexamethoxymethyl melamine (HMMM). The latex particles are prepared by emulsion polymerization. During the latex synthesis, co-monomers are introduced to provide hydroxyl groups (–OH) and carboxylic acid groups (–COOH) that can react upon heating with the alkoxymethyl groups of the melamine-formaldehyde derivative. Although this is an active field of research, there are not many publications in the scientific literature describing recent developments in this field. A recent paper by Huang and Jones[6] provides a useful review of the field and addresses several issues related to catalyst and cure conditions for obtaining films with good properties.

Our concern in this paper is with a very special aspect of thermoset resins prepared from latex dispersions. This aspect was first described in the literature in a paper by Zosel and Ley,[7] and merits careful reading. These authors showed that if one prepares a film from previously crosslinked particles, the individual particles will be deformed into space-filling cells, but there will be only

Table 1—Recipes for the Preparation of Poly(butyl methacrylate-co-hydroxyethyl methacrylate-co-methacrylic acid) (P(BMA-co-HEMA-co-MAA) Latex Particles

Materials (g)	Latex, low M			Latex, high M			
	Seed 1	J36 (Phe) Stage 2	J31 (An) Stage 2	Seed 2	J23(Phe) Stage 2	J24 (An) Stage 2	J48 (Phe/An) Stage 2
BMA	28.8	11.4	11.4	14	30	30	11.4
HEMA		0.439	0.439		1.16	1.16	0.44
MAA		0.073	0.073		0.2	0.2	0.073
An-MA			0.221			0.541	0.112
V-Phe		0.17			0.45		0.085
1-dodecanethiol		0.058	0.058				
Water	720	30		240	30	30	30
KPS	0.864	0.045		0.245	0.06	0.06	0.045
SDS	4.32	0.056		0.504	0.6	0.6	0.56
NaHCO$_3$	0.864	-		0.244			
Seed dispersion		7.7[a]	7.7[a]		64[b]	64[b]	7.7[a]

(a) Seed 1.
(b) Seed 2.

and processing conditions on the development of film properties.

Over the past 10 years, we have been developing techniques based upon fluorescence measurements of energy transfer to follow the rate of polymer diffusion in latex films. More recently we have been encouraged to extend these studies to the case of reaction-diffusion, where crosslinking competes with polymer diffusion, to help provide the information described in the previous paragraph.[8,9] A useful place to begin is with hexamethoxymethyl melamine (HMMM) crosslinked latex films. We have designed several model latex systems, chosen to be models for a waterborne automotive basecoat component. It is our hope that these initial studies will have broader implications for other types of melamine crosslinked latex coatings, as for example in hardboard coatings and various industrial coatings for metal surfaces.

Our model system includes a series of acrylate latexes, typically copolymers of butyl methacrylate (BMA), hydroxyethyl methacrylate (HEMA), and methacrylic acid (MAA). We prepared matched pairs of samples, one labeled with ca. 1 mol% of phenanthrene, a dye which serves as a donor in an energy transfer (ET) experiment; and the other, labeled with anthracene, which acts as the acceptor. Dispersions containing a 1:1 mixture of these labeled latexes were mixed with different amounts of HMMM, drawn down to form films, and then annealed for various amounts of time. We examined the rate of polymer diffusion in the presence and absence of HMMM as a crosslinking reagent. We take advantage of the observation that polymer diffusion occurs with virtually no crosslinking at 80°C, whereas HMMM undergoes significant reaction at higher temperatures. These experiments allow us to determine the location of HMMM in the latex films and to assess the competition between polymer diffusion and crosslinking, as a function of temperature, in these model latex films.

EXPERIMENTAL

Materials

9-Anthryl methacrylate (AnMA) and 9-vinyl phenanthrene (V-Phe) were synthesized as described previously.[9] BMA, MAA, and HEMA (all Aldrich) were distilled under vacuum prior to use. Potassium persulfate (KPS), sodium bicarbonate (NaHCO$_3$), and sodium dodecyl sulfate (SDS, Aldrich) were used as received. Distilled water was further purified through a Millipore Milli-Q^{TM} system. A melamine sample (Cymel 303) was used as the crosslinker in these experiments. By ^{1}H-NMR (200 MHz) it appeared to be primarily HMMM.

Table 2—Recipes for the Three-Stage Synthesis of PBMA Latex Particles with a Shell Rich in –OH and –COOH Groups

Materials (g)	CS-Phe (Donor Labeled)			CS-An (Acceptor Labeled)			CS-u (Unlabeled)		
	Seed	Stage 2	Stage 3	Seed	Stage 2	Stage 3	Seed	Stage 2	Stage 3
BMA	3	24.5	8.3	3	24.5	8.3	3.5	28.48	9.7
HEMA			0.42			0.42			0.49
MAA			0.28			0.28			0.33
An-MA					0.53				
V-Phe		0.41							
Water	50	25	7	50	25	7	60	26	10
KPS	0.052	0.051	0.017	0.052	0.051	0.017	0.06	0.06	0.02
SDS	0.86	0.51		0.86	0.51		0.1	0.6	
NaHCO$_3$	0.052			0.052	2		0.06		

LATEX PREPARATION: All latex samples were prepared by seeded semi-continuous emulsion polymerization under monomer-starved conditions. An unlabeled seed was prepared by batch emulsion polymerization and used for the preparation of a series of labeled latex samples. The seed commonly represents about 8 wt% of the final latex. A typical example is given in the following; a summary of the recipes used is presented in *Tables* 1 and 2.

A 500 mL flask equipped with a condenser and mechanical stirring was filled with water (240 mL), BMA (14.0 g), sodium dodecyl sulfate (SDS, 0.504 g), sodium bicarbonate (0.245 g), and potassium persulfate (KPS, 0.245 g). The solution was purged with nitrogen gas for two hours, then heated to 80°C for an additional two hours. This produced a solution (6.06 wt% by gravimetric analysis) of particles with a diameter (dynamic light scattering) of 59 nm and a narrow size distribution. In the second stage polymerization, a portion of the seed dispersion (64 g) was introduced into the reaction flask and purged with nitrogen for 15 min. The flask was heated to 80°C under N_2, and two solutions were then fed into the flask at a constant rate over six hours. One contained the monomers BMA (30 g), MAA (0.2 g), HEMA (1.16 g), and a fluorescent co-monomer (1 mol%); the other, surfactant SDS (0.6 g) and initiator KPS (0.06 g) in water (30 g). Stirring at 80°C was continued for an additional 10 hr before cooling to room temperature. This reaction produced a dispersion at 28 wt% solids content and a particle diameter of 120 nm and a narrow size distribution. Dodecyl mercaptan was added to some reactions as a chain transfer agent to lower the average molecular weight.

Table 3—Particle Size and Polymer Molecular Weight Characteristics of the Latex Particles Examined

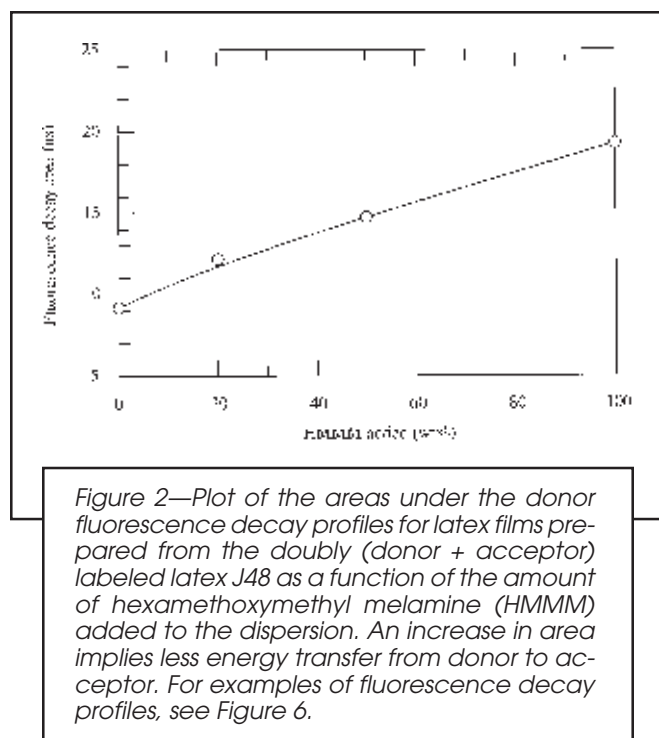| Latex sample	Diameter (nm)	$10^5 M_w$ (g mol^{-1})	M_w/M_n
CS-Phe			
seed	69		
stage 2	138	1.45	4.2
stage 3	149	5.3	3.7
CS-An			
seed	69		
stage 2	129	8.13	4.2
stage 3	139	5.17	3.4
CS-u			
seed	70		
stage 2	150	5.95	3.7
stage 3	165	5.2	4
J36			
seed	39		
Stage 2	120	1.2	
J31			
stage 2	120	1.2	
J23			
seed	59		
stage 2	126	7.2	
J24			
stage 2	126	7.2	
J48			
stage 2	118	7.5	

Core-shell surface-functionalized latexes were prepared by a three-stage emulsion polymerization at 80°C under a N_2 atmosphere, using KPS as radical initiator and SDS as surfactant. The labeled PBMA core particles were prepared in a two-stage emulsion polymerization under conditions like those described previously. In these materials, the HEMA and MAA co-monomers were introduced in the third stage of the polymerization, which represents 25 wt% of the total monomer employed. The recipes of all these synthesis are described in *Table* 2.

CLEANING OF THE LATEX PARTICLES: The dispersions were cleaned by ion-exchange to remove surfactant and other water-soluble ionic materials. The ion-exchange resin (Bio-Rad AG® 501-X8) was washed with hot deionized water (> 80ºC), methanol, and deionized water before use. Twice the weight of the resin, based upon the weight of solid present in the dispersion to be cleaned, was added to the diluted latex dispersion (solids content about 8 wt%), and then the mixture was stirred at room temperature for about 24 hr. Over this time, the viscosity of the dispersion increased and the dispersion became opalescent, indicating formation of colloidal crystalline domains. The ion-exchange resin was removed by gravity filtration.

Latex Characterization

Particle size and the size distribution were measured by dynamic light scattering employing a Brookhaven BI-90 Particle Sizer. Molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC), using two Ultrastyragel columns (500 + 10^4 Å) with THF as the eluent with a flow rate of 0.8 mL/min. These molecular weights are "nominal," based upon poly(methyl methacrylate) (PMMA) standards. Dual detectors (refractive index and fluorescence detectors) were used to detect the presence of the donor and acceptor dyes and to ensure random labeling of the polymer chains.[10] Unstructured latex samples were prepared in both high ($M_w = 720,000$) and low ($M_w = 120,000$) molecular weight versions.

Conductometric and potentiometric titrations were carried out to characterize the surface of the particles. These titrations were conducted under N_2 bubbling on both unlabeled cleaned latex dispersions and on an aliquot of the aqueous supernatant phase of a raw latex dispersion after sedimenting the particles by centrifugation. Both forward and back titrations were performed. Each titration lasted 45 min. Once the forward titration (with a standard N/100 NaOH solution) was completed, an excess of base was added to the solution. After stirring the solution under N_2 bubbling for two hours at room temperature, the backward titration was conducted using a standard N/100 HCl solution. In some cases potentiometric titrations were also conducted in presence of NaCl ([NaCl] = 0.05 M) in order to improve the accuracy of some of the equivalence-point determinations that were not always reliable at low ionic strength. The charge density (D_c) of the latex was calculated as the ratio of the moles of acid groups detected in the titration to the total dry weight of latex in the titration. Latex characteristics are summarized in *Table* 3.

Figure 2—Plot of the areas under the donor fluorescence decay profiles for latex films prepared from the doubly (donor + acceptor) labeled latex J48 as a function of the amount of hexamethoxymethyl melamine (HMMM) added to the dispersion. An increase in area implies less energy transfer from donor to acceptor. For examples of fluorescence decay profiles, see Figure 6.

Transmission electron microscopy (TEM) experiments were also conducted to examine the core-shell morphology. First, a sample of the unlabeled latex was freeze dried. Then a small amount of it was embedded in an Epon epoxy resin that was later cured at 40°C overnight. The samples were rough-trimmed, and then microtomed with a glass knife, and finally microtomed with a diamond knife to a slice thickness of 70 nm using an RMC MT 7000 microtome. The sections were then placed on a 300 mesh Gilder copper grid and stained with a 0.5% aqueous solution of ruthenium tetroxide (RuO_4) for eight minutes. A Hitachi model 600 electron microscope was used to observe the sample.

Film Formation, Annealing, and Fluorescence Measurements

All experiments employed latex dispersions cleaned by ion exchange. Labeled latexes were used for the fluorescence measurements. In some experiments, crosslinking experiments were carried out in parallel with unlabeled latex of similar size, molecular weight, and composition. For polymer diffusion analysis by direct non-radiative energy transfer, a few drops of a dispersion containing equal amounts of Phe-labeled and An-labeled latex were put on a small quartz plate (20 × 10 mm) and placed in a covered petri dish in order to slow the drying process and to allow drying to proceed at 100% relative humidity. Drying occurred in an air-flushed oven pre-warmed to 38°C. Under these conditions transparent films were formed over a period of six to 10 hours. Films on their substrates to be annealed for short periods of time were placed directly on a high mass aluminum plate in an oven preheated to the annealing temperature. Films heated for more than two hours were heated under nitrogen in a quartz tube sealed with a septum. For fluorescence decay measurements, the labeled films were placed in a similar quartz tube and degassed with N_2.
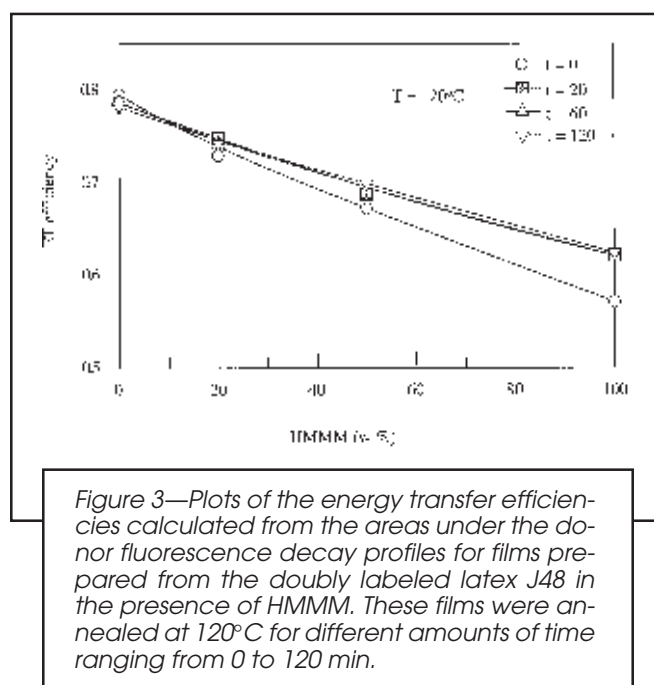
To induce crosslinking of the latex films , an aliquot of the dispersion was mixed with a known amount of HMMM. In many experiments we employed 20 wt% HMMM based upon latex solids, which for the core-shell latex represents a molar ratio of HMMM/HEMA = 6. Crosslinking experiments were carried out in a vacuum oven at temperatures ranging from 80° to 150°C. Film samples were placed in petri dishes, which were then introduced into the oven. During the annealing process the oven was flushed with N_2. The extent of crosslinking was characterized by a solvent extraction and swelling protocol. Film specimens (weight: W_0, dimension: $15 \times 15 \times 0.1$ mm) were immersed in p-dioxane for 24 hr at room temperature to attain swelling and dissolution equilibrium. The films were then carefully removed from the dioxane, and the solvent attached to the surface was removed by touching the film surface with a filter paper. The weight of film (W_1) was measured. This procedure was completed as quickly as possible (within five seconds) to assure accurate and consistent measurements. The film was then dried again to a constant weight (W_2) under vacuum in a vacuum oven. The gel content (%) and swelling ratio are calculated from the expressions
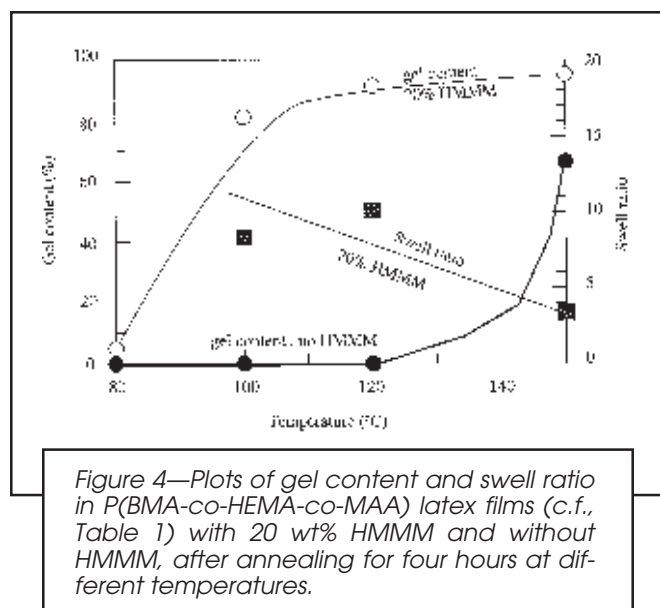
$$\text{Gel content (\%)} = (W_2/W_0) \times 100\% \qquad (1)$$

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

We recognize that this approach may overestimate the gel content because some of the soluble polymer may not have sufficient time to diffuse out of the gel phase. Nevertheless, the convenience of the method and reproducibility of the results make this a reliable protocol, particularly for handling small samples.

Fluorescence measurements were carried out with an SPEX Fluorolog 2 fluorescence spectrometer in the front-

Figure 3—Plots of the energy transfer efficiencies calculated from the areas under the donor fluorescence decay profiles for films prepared from the doubly labeled latex J48 in the presence of HMMM. These films were annealed at 120°C for different amounts of time ranging from 0 to 120 min.

Figure 4—Plots of gel content and swell ratio in P(BMA-co-HEMA-co-MAA) latex films (c.f., Table 1) with 20 wt% HMMM and without HMMM, after annealing for four hours at different temperatures.

face geometry. Fluorescence decay measurements employed the single photon timing technique,[11] as described previously,[12] using a pulsed deuterium lamp as the excitation source. In the absence of An as an energy transfer acceptor, Phe decay profiles were always exponential, with τ_0 values ranging from 44.8 ns in PBMA to 46.5 ns in P(BMA-co-HEMA-co-MAA). The influence of HMMM on the fluorescence decay of phenanthrene was examined by preparing a series of acceptor-free film samples, prepared from Phe-labeled P(BMA-co-HEMA-co-MAA) latex, which contained 20 wt% HMMM. If HMMM acts as a quencher of Phe fluorescence, the measured Phe lifetime would decrease. Some film samples were heated for various times at 120°C, cooled to room temperature, and remeasured. In each experiment, the decay of Phe fluorescence remained exponential with a fluorescence lifetime of 46.5 ± 0.2 ns, virtually identical to the lifetime in the absence of HMMM.

FLUORESCENCE DATA AND DATA ANALYSIS

Many of the experiments described are based upon Förster non-radiative ET between a donor dye D, which is selectively excited, and a second dye, the acceptor A. The attractive feature of this process is that the rate of energy transfer w(r) depends sensitively on the distance r between the donor and acceptor chromophores, $w(r) = (1/\tau_0)(R_o/r)^6$, in which τ_0 is the donor fluorescence lifetime in the absence of acceptors, and R_o is the characteristic distance (the Förster distance) over which ET takes place. Typical values of R_o are 2 to 5 nm. Thus ET measurements represent a powerful method to measure distances, or the distribution of distances, in complex samples. In our experiments, the D and A groups are attached to the backbone of individual polymer molecules. ET experiments measure the rate or extent of processes that bring D and A groups together, or cause them to move apart. For the phenanthrene-anthracene pair employed here, $R_o = 2.3$ nm.

In a system with uniformly distributed donors and acceptors in three dimensions, the donor fluorescence intensity decay $I_D(t)$, following a δ-pulse excitation, is described by equation (3), where P is proportional to the acceptor (quencher) concentration [Q]:[13,14]

$$I_D(t) = A \exp\left[-\frac{t}{\tau_0} - P\left(\frac{t}{\tau_0}\right)^{0.5}\right] \quad (3)$$

$$P = \gamma \bullet \frac{4\pi^{3/2} N_A R_0^3 [Q]}{3000} \quad (4)$$

In equation (4), γ is an orientation factor, and N_A is Avogadro's number. The quantum efficiency of energy transfer Φ_{ET} is defined as[15]

$$\Phi_{ET} = 1 - \frac{\int_0^\infty I_D(t)\,dt}{\int_0^\infty I_D^0(t)\,dt} \quad (5)$$

where $I_D(t)$ and $I_D^o(t)$ are the decay functions of donor fluorescence in the presence and absence of acceptor, respectively. The integrals of the donor emission in equation (5) can be evaluated from the areas obtained experimentally under the donor decay curves (normalizing the decay curves at decay time zero),[16,17] giving

$$\Phi_{ET} = 1 - Area_D / Area_D^o \quad (6)$$

where $Area_D$, $Area_D^o$ are the areas under the normalized decay curves of donor fluorescence in the presence and absence of acceptor, respectively. It is important to note that the integrated area under the fluorescence decay profile has units of time (ns). The decay profile of the phenanthrene donor employed here is exponential in the absence of acceptors, and the denominator in equation (5) is equal to τ_0. In film samples where interdiffusion is followed by energy transfer measurements, the extent of mixing is determined from the integrated area under the normalized decay curves as explained in a later section of this paper.

RESULTS AND DISCUSSION

Latex Preparation and Characterization

By seeded emulsion polymerization, we prepared a series of acrylate copolymer latex samples in which the fundamental composition was 90+ wt% poly(butyl methacrylate) plus the functional monomers HEMA and MAA. For polymer interdiffusion experiments, we need matched pairs of latex samples, identical in size, morphology, molecular weight, and molecular weight distribution. This can be achieved by preparing both latex samples from a common (unlabeled) seed, which typically represents eight percent of the final particle volume. In our first set of experiments, we prepared unstructured latex, in which the HEMA, MAA, and fluorescent co-monomer(s) were added under monomer-starved conditions in the second stage of the polymerization. Here we prepared samples of high molecular weight ($M_w = 720,000$), and by use of a chain transfer agent, samples of much lower molecular weight ($M_w = $

120,000). These samples allow us to investigate the effect of molecular weight on the relative rates of polymer interdiffusion and crosslinking. Characteristics of all the latex samples we prepared are given in *Table* 3.

The acid content of the particles was examined by a combination of potentiometric and conductometric titration. The forward titration showed that about one third of the –COOH groups were at the particle surface. When the latex dispersion was stirred under nitrogen for three days in the presence of a three-fold excess of NaOH and back titrated with HCl, essentially all of the –COOH groups could be titrated.

In the second set of experiments, we prepared a pair of core-shell latexes in which the second stage was PBMA copolymerized with 1 mol% of the dye co-monomer, and the shell containing the functional monomers plus BMA was introduced via a third stage polymerization, also under monomer-starved conditions. The core-shell structure was confirmed by transmission electron microscopy (TEM). A TEM image is presented in a subsequent section of this paper. These latex samples were also characterized by potentiometric and conductometric titrations, at both the second stage and third stage polymerization. For the third-stage polymer, we find that 58% of the COOH groups are neutralized during the forward titration and, after neutralization of the latex with excess base, 94% are detected in the back titration. In this case, the particles were incubated with excess base for two hours before back titrating. From these data, we have also calculated both the charge density and the surface area per acid group.[18] We find, for example, 61 $Å^2$/(COOH group) from the back titration, close to the value of 88 $Å^2$ reported by Kawaguchi et al. for a similar latex sample.

Where Is the Melamine Located?

IN THE DISPERSION: HMMM is soluble in water. When HMMM is added to an aqueous dispersion of latex, it will partition between the aqueous and latex polymer environments. If a significant amount of the HMMM enters the latex phase, the particles will swell. These changes in particle dimensions can be observed by dynamic light scattering (DLS). Here we examine latex J-36, a copolymer of BMA (95 mol%), HEMA (4 mol%) and MAA (1 mol%) with a diameter of 128 nm and a narrow size distribution. Aliquots of HMMM were added to samples of the latex to produce dispersions in media containing 10, 20, 30 and 50 wt% HMMM in water. These samples were allowed to stand at room temperature for one week, after which DLS experiments were repeated. Each of these samples gave particle diameters of 125 ± 1 nm, suggesting that there was negligible swelling of the latex by the HMMM. We conclude that when the latex is dispersed in water, the HMMM remains in the water phase.

IN THE DRY FILM: One can imagine two limiting scenarios for the locus of the HMMM in the latex film. At one extreme, the additive could be trapped in the interstitial spaces between the cells formed by the latex particles. In this situation, the crosslinking agent would diffuse into the latex polymer only upon heating. At the

other extreme, the HMMM would penetrate rapidly into the film, where it swells the polymer and might also act as a plasticizer. The drawing conceptualizes the different morphologies that would be produced in the two limiting situations.

melamine dissolved in the polymer   melamine in the interstitial spaces
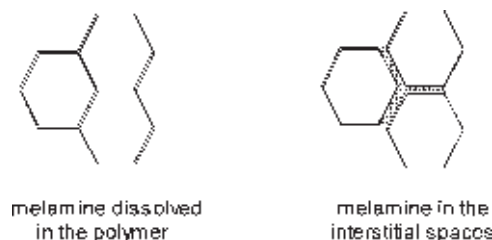
There are two approaches to distinguishing these morphologies. Turbidity experiments monitor phase separation that leads to domains with a spatial scale comparable to the wavelength of light. For example, films prepared from a dispersion of pure PBMA latex (Mw = 350,000) in the presence of 20 wt% HMMM were turbid. This result suggests that the melamine derivative does not dissolve significantly into the latex polymer. Other results suggest that even at 120°C there is only limited miscibility between HMMM and PBMA. On the other hand, the copolymer latex samples containing 4 mol% HEMA and 1 mol% MAA appear to be miscible with HMMM. These films were transparent at room temperature and remained transparent upon heating.

Energy transfer experiments provide a means of monitoring miscibility on a molecular scale. A polymer film labeled randomly by donor and acceptor groups is characterized by a random distribution of A groups around each donor. The $I_D(t)$ profile for this film should be described by equation (3), with a P parameter (equation (4)) consistent with the bulk concentration of the A-groups in the film. If a solvent swells the film to a significant extent, the mean separation between D and A groups will increase. The area under the $I_D(t)$ profile will increase, and the efficiency of energy transfer will drop.
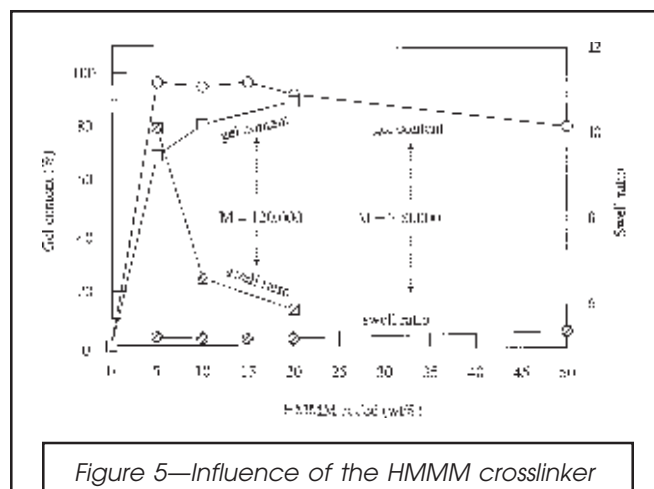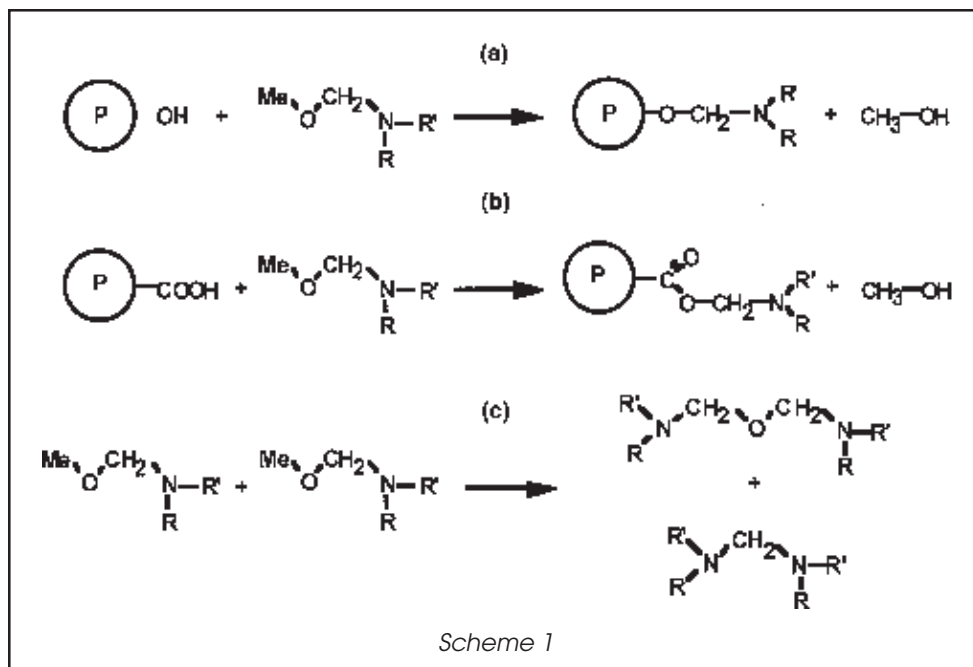

Figure 5—Influence of the HMMM crosslinker concentration on the gel content and swell ratio of latex films formed from the high molecular weight and the low molecular weight P(BMA-co-HEMA-co-MAA) latex samples. All films were annealed at 120°C for four hours.

Scheme 1

We carried out experiments to examine the extent to which HMMM penetrates into the polymer phase of the latex film. Films were prepared at room temperature from latex dispersions containing various amounts of HMMM. We examined films containing 20 wt% and 50 wt% HMMM, based upon the weight of latex, and compared these samples to a latex film containing no additive, and to a liquid film containing a trace of latex polymer in excess HMMM (i.e., nearly 100 wt% HMMM). These experiments employed latex J 48, which contains both donor (phenanthrene, Phe) and acceptor (anthracene, An) groups attached to its backbone. The area under the donor decay profile in the additive-free film is 9.2 ns. In the presence of a vast excess of HMMM, the area increases to 19.3 ns, indicating substantial swelling of the film. The full set of data are presented in *Figure* 2, and replotted as ET efficiency versus wt% HMMM in the bottom line in *Figure* 3. When the samples are heated, crosslinking occurs. The three sets of data points in the upper curve in *Figure* 3 show the consequences of heating the sample for various times at 120°C. Crosslinking leads to shrinkage of the resin, accompanied by an increase in the quantum efficiency of ET.

These results raise an interesting question in the case of core-shell latex particles which contain a polar copolymer shell surrounding a PBMA core: where in the core-shell structure does the HMMM reside? These samples always give clear films when prepared at ordinary temperatures, and the films remained transparent upon heating. It is possible, however, that the HMMM in such films mixes with and swells only the shell phase of the latex in the dry film. While this view is at this point speculative, evidence in favor of this idea emerges from energy transfer studies of polymer diffusion to be described later.

Crosslinking, Gel Content, and Swell Ratio

Most commercial coatings containing fully alkylated melamine derivatives are cured with the aid of a strong acid catalyst such as p-toluenesulfonic acid. Our experiments take advantage of a strategy developed by Hahn[19,20] for relatively low temperature cure of melamine and other crosslinked coatings. In this approach one uses an ion exchange resin both to clean the latex and to convert carboxyl groups to the –COOH form. These groups serve as the acid catalyst for the reaction of HMMM. Alkoxymethylene melamine derivatives react with –OH groups in the polymer via acid-catalyzed alkoxy exchange. They can react with the carboxylic acid groups of the MAA co-monomer. Self-condensation of the alkoxymethyleneamino groups can also occur. These reactions, for the specific example of HMMM, are shown in *Scheme* 1.

In addition, we noted that at a high enough temperature, the polymer backbone itself can crosslink via ester exchange through reaction of the ester groups of the BMA with –OH groups from HEMA, in a reaction that does not require melamine. This reaction is shown in *Scheme* 2.

A typical curing temperature for thermoset coatings containing HMMM is 150°C, where the HMMM-polyol reaction reaches completion in ca. 15 min.[21] We are interested in examining the effect of temperature both on the crosslinking reaction and on the rate of polymer diffusion. An example for a set of our films containing 20 wt% HMMM, prepared from the unstructured latex of $M_w = 120,000$, is shown in *Figure* 4. A series of films was prepared and heated for four hours at the temperatures indicated, ranging from 80° to 150°C. We determine the extent of reaction in terms of two parameters, the gel content of the film and the degree of swelling of the gel phase. Very little gel (<10%) is formed at 80°C. At 100°C, the gel content is substantial, and four hours at 120°C suffices to convert essentially all the polymer to gel. *Figure* 4 also indicates that heating the films at a higher temperature
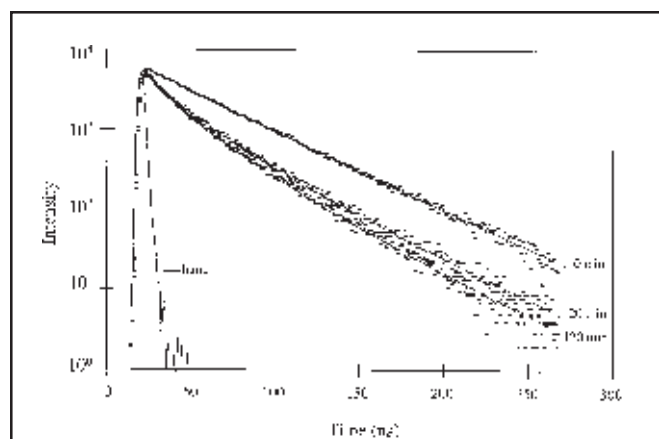

Scheme 2
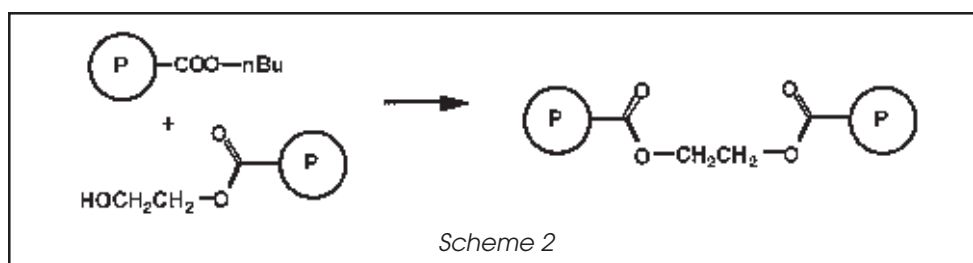
Figure 6—Donor fluorescence decay profiles of a latex film sample annealed for the time indicated at 150°C. The film was prepared from a dispersion containing a 1/1 particle ratio of the CS-Phe and CS-An latex samples mixed with 20 wt% solids HMMM. The lines through the data points represent the fitted curves used for the area calculations.

for four hours also leads to a decrease in swell ratio. This result tells us that increasing the extent of crosslinking leads to a decrease in the effective PBMA chain length between crosslinks. This figure also shows that in a control experiment, a latex film of the same polymer without melamine, crosslinking can still occur if the film is heated to 150°C for four hours. We presume that the reaction that occurs is that described in *Scheme* 2.

We compared the cure requirements of the low and high molecular weight PBMA latex in *Figure* 5. This figure plots the gel content and the swelling ratio as a function of the amount of HMMM in the film for films heated for four hours at 120°C. For the sample of M_w = 720,000, 5 wt% HMMM suffices to produce 100% gel content under these conditions, and the swell ratio is relatively low. Addition of significantly larger amounts (> 15 wt%) of HMMM actually causes the gel content to drop, and at 50 wt% HMMM, the swell ratio increases. This effect is likely caused by the limited extent of self-reaction of HMMM as shown in *Scheme* 1c. For the sample of M_w = 120,000, 5 wt% HMMM leads to about 75% gel content, and 20 wt% HMMM is needed to achieve 90% gelation in four hours at 120°C. As the amount of HMMM is raised from 5 to 20 wt%, the swell ratio decreases from 10 to 6. Under these conditions, the extent of reaction is probably limited by the number of
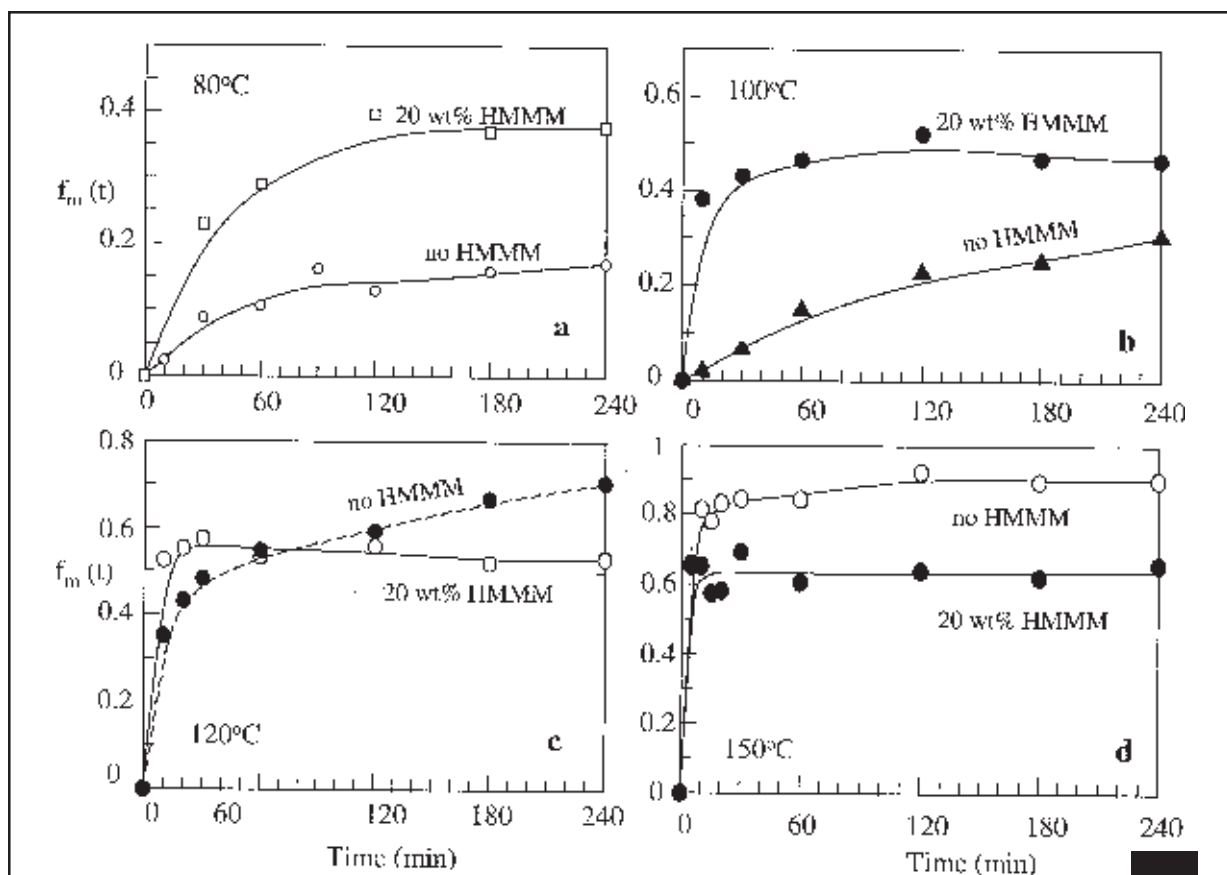

Figure 7—Plots of the extent of mixing $f_m(t)$ vs. time for latex films, with and without 20 wt% HMMM, prepared from a 1:1 mixture of the Phe- and An-labeled high molecular weight P(BMA-co-HEMA-co-MAA) latex. The film samples were annealed for various times at different temperatures: (a) 80°C; (b) 100°C; (c) 120°C; (d) 150°C.
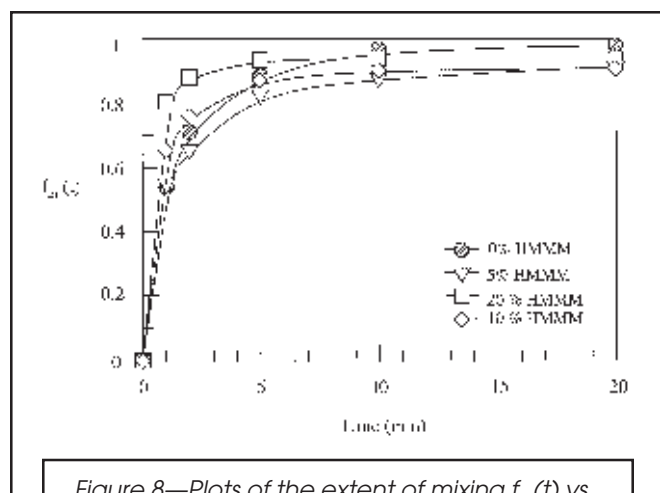
Figure 8—Plots of the extent of mixing $f_m(t)$ vs. time for latex films prepared from a 1:1 mixture of the Phe- and An-labeled low molecular weight latex containing different concentrations of HMMM. The annealing temperature was 120°C.

functional groups and the low molar mass polymer content of this latex.

The third comparison we make with respect to the unstructured latex concerns the effect of different ways of treating the dispersion before casting the film. We examined the higher molecular weight sample and compared films formed from the latex dispersion "as prepared," with a sample of the latex cleaned by ion exchange, and with a latex sample neutralized through addition of one equivalent of NaOH (based on latex –COOH groups). In the neutralized sample, the ion-exchanged dispersion was stirred in the presence of base for 48 hr before films were prepared. Each film contained 20 wt% HMMM. The ion-exchanged latex reacted relatively quickly at 120°C, reaching 80% gel content in 20 min. Rather surprisingly, the as-prepared latex reacted even faster, reaching 90% gel content in 40 min. The latex dispersion is synthesized in unbuffered water. Thus the carboxyl groups of this latex are in the –COOH form. The major difference between the raw latex and the ion-exchanged material is the presence of the SDS surfactant in the as-prepared sample. In contrast, for the neutralized sample, significant gel formation required several hours at 120°C.

Polymer Interdiffusion

We monitored the polymer diffusion process by measuring changes in the extent of energy transfer between donors and acceptors attached to the polymers originally separated in individual particles. Fluorescence decay measurements were carried out on our film samples as a means of assessing the extent of energy transfer and polymer diffusion as a function of thermal history. *Figure* 6 shows an example of a series of donor decay profiles for a film sample aged for different times at 150°C. These films were prepared from 1:1 mixture of Phe- and An- labeled latex samples in the presence of HMMM. As seen in *Figure* 6, when the film is annealed, the curvature

of the decay profile becomes more pronounced. This indicates that molecular mixing has occurred between donor- and acceptor-labeled polymers and the extent of energy transfer has increased, leading to a faster decay of donor fluorescence. It is our good fortune that the presence of HMMM has no quenching effect on the donor fluorescence and does not interfere with analysis of the energy transfer data.

To characterize the diffusion process, we calculate the extent of mixing due to diffusion by comparison of the fluorescence decay curves. In simple systems where one examines small molecule diffusion in polymers or the diffusion of polymers in a sample with a very narrow molecular weight distribution, this can be done in a rigorous manner, so that one can calculate the center of mass diffusion coefficients of the diffusing species.[22,23] Here, the situation is much more complex. The polymers themselves have a relatively broad distribution of chain
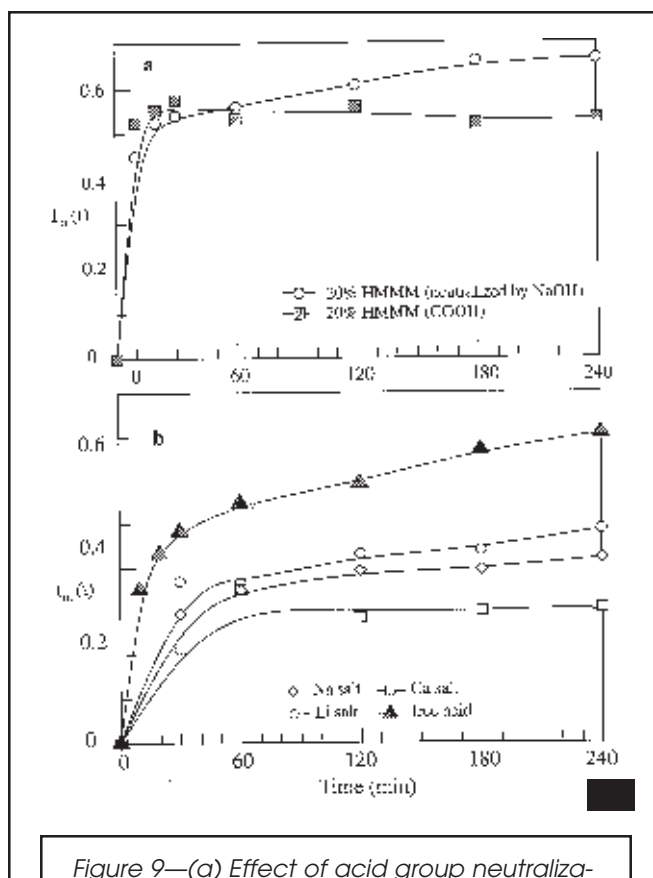

Figure 9—(a) Effect of acid group neutralization on plots of $f_m(t)$ vs. time at 120°C for the high molecular weight P(BMA-co-HEMA-co-MAA) latex films containing 20 wt% of HMMM. Filled squares: carboxylic acid groups are protonated. Open circles, carboxylic acid groups were neutralized with one equivalent of NaOH; (b) Effect of the counterion in acid group neutralization on polymer interdiffusion rates for the high molecular weight P(BMA-co-HEMA-co-MAA) latex films without HMMM. Here we plot $f_m(t)$ vs. time for films in which the acid groups were neutralized with one equivalent of base to the lithium (O), sodium (◊) and calcium (❑) salts.

lengths and the molecular weight of the sample increases (to infinity) as the crosslinking reaction proceeds. A simple measure of the fraction of mixing, $f_m(t)$, is the normalized growth in energy transfer efficiency [17]

$$f_m = \frac{\Phi_{ET}(t) - \Phi_{ET}(0)}{\Phi_{ET}(\infty) - \Phi_{ET}(0)} = \frac{\text{area}(0) - \text{area}(t)}{\text{area}(0) - \text{area}(\infty)} \qquad (7)$$

where $[\Phi_{ET}(t) - \Phi_{ET}(0)]$ represents the change in energy transfer efficiency between the initially prepared film and that aged for time t. In our experience the most reliable way to obtain Φ_{ET} is from the area under the normalized fluorescence decay curve. To obtain an accurate area for each decay profile, we fit the profile to a not entirely arbitrary mathematical function:

$$I_D(t_d) = A_1 \exp[-t_d/\tau_0 - P(t_d/\tau_0)^{1/2}] + A_2 \exp(-t_d/\tau_0) \qquad (8)$$

The physical meaning of the fitting parameters (A_1, A_2, P) in equation (8) is not important here, but one can use these parameters to calculate the area under the normalized decay profile by integrating $I_D(t_d)$ from time zero to infinity. The $f_m(t)$ values are obtained by comparing areas under the measured decay profiles for films without aging [area(0)], aged for certain times [area(t)], and aged for a sufficiently long time to approach a minimum value of area [area(∞)]. Here we obtained the area(∞) using a solvent-cast film, where we assume that no crosslinking takes place.

As a first example, we consider a film annealed at 80°C, prepared from the unstructured latex samples of $M_w = 720,000$. These conditions are interesting because, as we saw in *Figure* 4, almost no crosslinking occurs at this temperature when melamine is present. The data are presented in *Figure* 7a. Here we see that in the latex film without HMMM, $f_m(t)$ increases slowly, reaching a value of ca. 0.15 after 240 min. If annealed for a sufficiently long time, $f_m(t)$ will reach unity. With 20 wt% HMMM present, interdiffusion is accelerated substantially. HMMM acts as a plasticizer for the latex polymer and accelerates the rate of polymer diffusion. We certainly did not anticipate this result.

Figures 7b -7d show the results obtained when these experiments were repeated at 100°, 120°, and 150°C. Here crosslinking competes with polymer diffusion. At 100°C, the rate of polymer diffusion increases. We have previously shown that polymer diffusion rates in PBMA latex films have a temperature dependence that can be described quantitatively with Williams-Landel-Ferry (WLF) parameters determined independently for PBMA through creep-compliance measurements reported by Ferry's group.[24] In this range of temperatures, the diffusion rate has an apparent Arrhenius activation energy of 38 kcal/mol. In the presence of HMMM at 100°C, we observed an interesting result. The HMMM accelerates early diffusion, but after about 50 min, at which $f_m(t) \approx$ 0.5, polymer interdiffusion ceases. This is a much higher molecular weight polymer than that described in *Figure* 4, and the increase in molecular weight and in gel content has brought to a halt significant further diffusion in the system. We anticipate that at longer times the $f_m(t)$ value for the film without HMMM will cross that of the film containing 20 wt% HMMM. We see this crossover
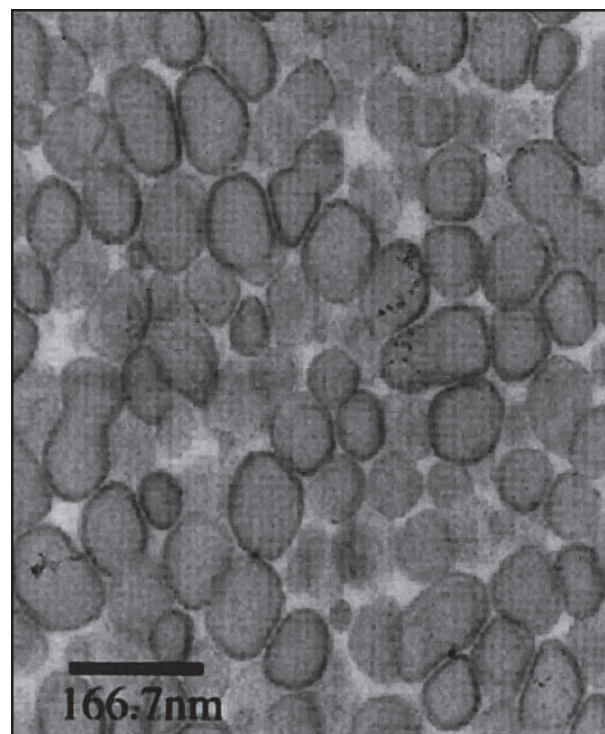

Figure 10—Transmission electron micrograph of the core-shell latex with a shell rich in -OH and -COOH groups. (CS-u latex sample). The particles have been stained with RuO_4.

in *Figure* 7c, for experiments carried out at 120°C. Here in the presence of HMMM, there is rapid interdiffusion to an $f_m(t)$ value of 0.5 to 0.6, after which the diffusion ceases because of crosslinking. Similar results appear in *Figure* 7d, where extensive mixing occurs in both samples over a very short time scale.

Results with the lower molecular weight sample at 120°C are shown in *Figure* 8. Here we compared the
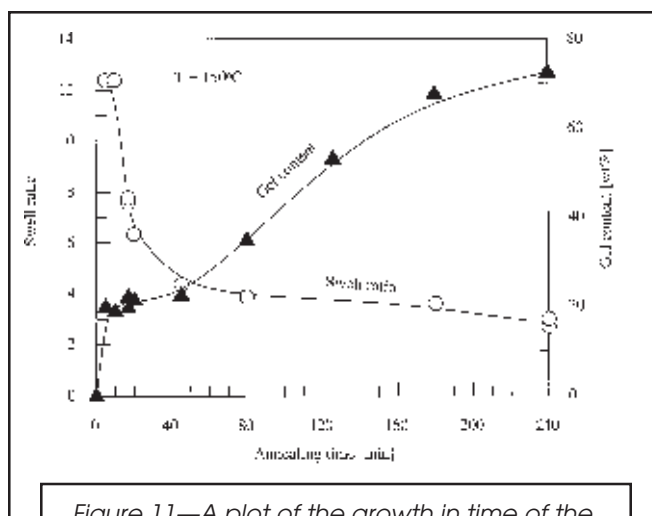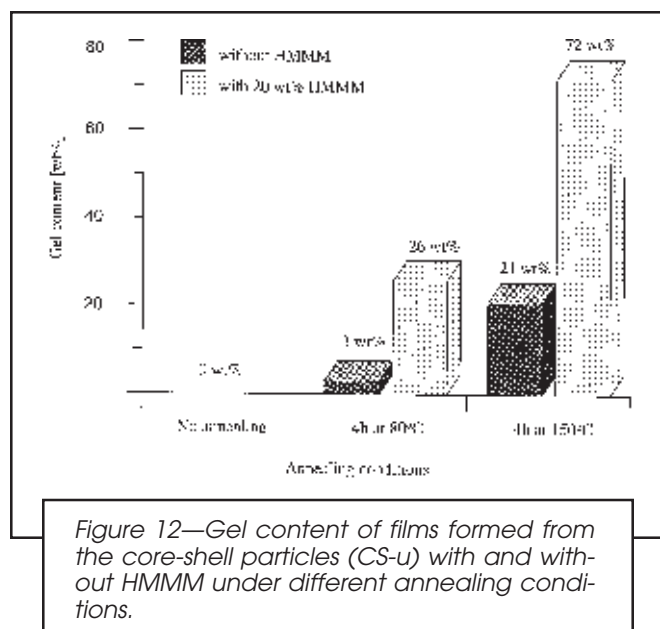

Figure 11—A plot of the growth in time of the gel content and swell ratio for the latex film (containing 20 wt% of HMMM) prepared from the 1:1 mixture of the donor- and acceptor-labeled core-shell latex. The annealing temperature is 150° C.

Figure 12—Gel content of films formed from the core-shell particles (CS-u) with and without HMMM under different annealing conditions.

influence of the amount of HMMM added on the rate of mixing as described by $f_m(t)$. For this relatively low molecular weight polymer, diffusion is rapid, and the plasticizing effect of HMMM is more difficult to detect. Neutralization of the acid groups has an interesting effect on the rate of polymer diffusion. In the presence of 20 wt% HMMM, polymer neutralization with NaOH has relatively little effect, as seen in *Figure* 9a for the sample of $M_w = 720,000$ annealed at 120°C. At early times, diffusion of the neutralized and ion-exchanged polymers proceed at comparable rates. Acid-group neutralization retards the crosslinking reaction, so that polymer diffusion continues in this sample well after the ion-exchanged polymer has completely gelled. In the absence of HMMM, ionomer effects dominate. The effect is shown in *Figure* 9b, where we compared the relative interdiffusion rates of polymers neutralized to form the Li^+, Na^+, and Ca^{2+} salts are compared with that bearing protonated -COOH groups. These results are similar to those reported previously by Kim et al.[25] for P(BMA-co-MAA) latex films. In the case of the calcium salt, the ionomer interaction is so strong that diffusion ceases, presumably through formation of a stable ionomerically crosslinked network.
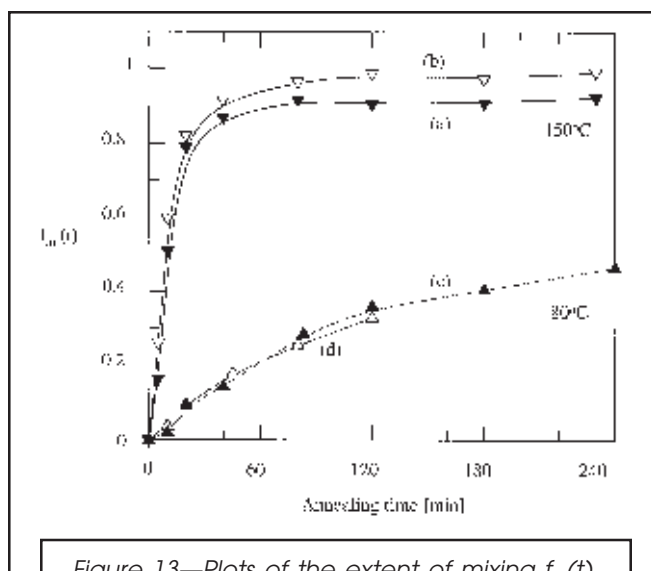
Core-Shell Latex Films

Among the many strategies for improving the effectiveness of a melamine-cured acrylic latex, one attractive approach involves the preparation of a core-shell structure in which the polar functionality is confined to the shell phase. To maximize desirable mechanical properties and to obtain resistance to solvents, the core itself should be crosslinked. One can imagine several variations on this theme, with a low T_g crosslinked core to impart impact resistance, or with a high T_g core to act as a rigidifying organic filler. Since ours is a model study, we wished to step back from these performance issues and focus on the effect of crosslinking reactions in the shell on the mobility of labeled polymer in the core. This situation is conceptualized in the following drawing.

We anticipated that to the extent that crosslinking precedes diffusion of the core polymer, the crosslinked network would serve as a barrier for interdiffusion of the core polymer. Thus we synthesized a pair of core-shell polymer dispersions in which the PBMA core was labeled with donor or acceptor groups, and the polar shell, added in a subsequent stage, contained the MAA and HEMA co-monomers to react with melamine derivative. In this set of samples, the third-stage polymer represents only 25 wt% of the entire latex. Note that in this material, the local concentration of polar groups in the shell (5 mol% HEMA, 5 mol% MAA) is significantly higher than the global concentration of these two monomers in the unstructured latex samples described. A transmission electron micrograph confirming the core-shell structure of this materials is shown in *Figure* 10.

Can crosslinking in the polar shell polymer suppress interdiffusion of the PBMA core polymer? Here only the core polymer is labeled with donor and acceptor dyes.

Films of the core-shell latex with 20 wt% HMMM were prepared and annealed at 150°C for various times. A typical example of the results of this kind of experiment is presented in *Figure* 11, where we plot the growth in gel content and the decrease in swell ratio as a function of annealing time. The reaction occurs in two steps. The first part of the reaction requires 10 to 20 min, and

Figure 13—Plots of the extent of mixing $f_m(t)$ vs. time for latex films prepared from a 1:1 mixture of the Phe- and An-labeled core-shell particles, with and without HMMM, annealed at different temperatures: (a) 150°C—20 wt% HMMM; (b) 150°C—no HMMM; (c) 80°C—20 wt% HMMM; (d) 80°C, no HMMM.

leads to a leveling off of the gel content at about 20 wt%. Subsequently, a slower reaction proceeds that leads over a period of hours to the gelling of the entire sample. During the first part of the reaction, the swell ratio (measured only for the gel component) falls to a value of about 4, and decreases only slowly after that. The easiest interpretation of these results is that the initial stage involves acid-catalyzed reaction of the HMMM with the local high concentration of –OH and –COOH groups in the interconnected shell phase of the film. The gel content at the end of the first stage is similar to the shell content (25 wt%) of the original latex. The slower reaction must involve ester exchange in the PBMA core.

At 80°C, crosslinking can also occur, although at a slower rate, as can be seen in the histogram of *Figure* 12. The reaction involving HMMM is more significant here than in the case of the unstructured latex. This enhanced reactivity must be due to the much higher local concentration of –COOH groups in the polar polymer phase. Even in the absence of HMMM, there is some gel content (ca. 3 %) after four hours heating at 80°C. Since the gel content is small, we imagine that this gel is formed through local ester formation between –OH groups from HEMA and –COOH groups from MAA in the polar copolymer phase. It may not be accidental that the gel content of the system after four hours at 80°C in the presence of HMMM and after four hours at 150°C in the absence of HMMM both correspond approximately to the amount of copolymer in the system containing –OH and –COOH groups.

In *Figure* 13 we plotted $f_m(t)$ versus annealing time for the core-shell latex films to examine the rates of polymer interdiffusion at 80° and 150°C. The first important observation is that polymer diffusion occurs as easily in these films as in the unstructured latex films. The polar latex shell may form an interconnected membrane in the film, but this membrane is not a very effective barrier to diffusion of the PBMA core polymer. Remember that only the PBMA core polymer is labeled, and the observation of energy transfer means that the core polymer of adjacent latex particles must interdiffuse and mix. This does not happen if the core polymer is fully crosslinked. We observed a strong temperature effect on the interdiffusion rate. This is expected. The film in the absence of HMMM at 150°C undergoes complete intermixing in about an hour. What is most interesting is the lack of influence of HMMM on the polymer diffusion rate at 80°C and the very small influence at 150°C, where the presence of HMMM appears only to suppress further mixing at $f_m > 0.8$.

In *Figure* 14 we compared the rates of interdiffusion and crosslinking for this sample at 150°C, focusing on the short-time behavior of the sample. We see that f_m reaches a value of 0.8 in about 20 min. In this experiment, the early-time rise in the gel content is complete after 10 min, whereas the major drop in the swell ratio occurs between 10 and 20 min after annealing. From *Figure* 11 we anticipate that the secondary reaction in this system of ester exchange to crosslink the PBMA becomes significant only after 40 min at 150°C, so that most of the chemistry competing with core-polymer diffusion is the HMMM reaction with the polar copolymer.
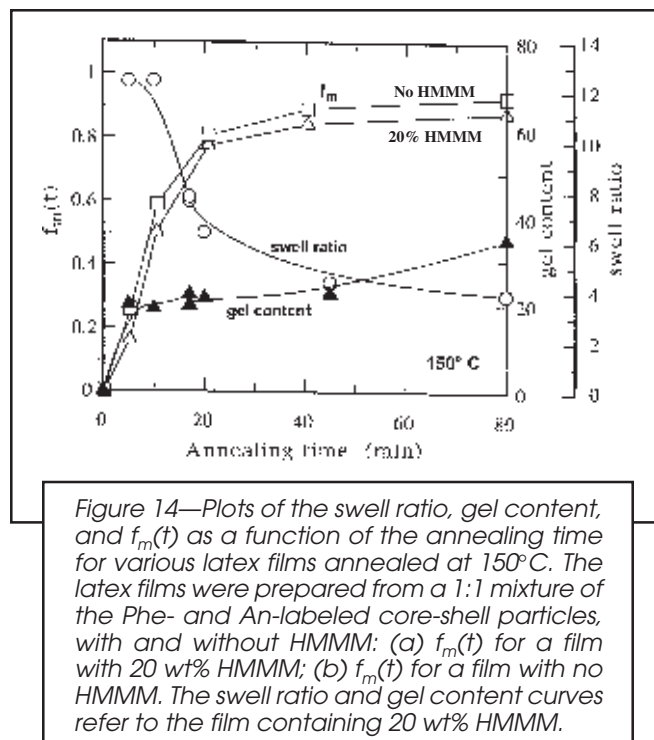

Figure 14—Plots of the swell ratio, gel content, and $f_m(t)$ as a function of the annealing time for various latex films annealed at 150°C. The latex films were prepared from a 1:1 mixture of the Phe- and An-labeled core-shell particles, with and without HMMM: (a) $f_m(t)$ for a film with 20 wt% HMMM; (b) $f_m(t)$ for a film with no HMMM. The swell ratio and gel content curves refer to the film containing 20 wt% HMMM.

We see that this reaction has relatively little effect on the extent of polymer diffusion. The data in *Figure* 14 indicate some retardation of the interdiffusion rate by the combination of the presence of the HMMM and its crosslinking reactions. What we do not observe is any influence of the HMMM as a plasticizing diffusion promoter as we found for the unstructured latex system.

CONCLUSIONS

While poly(butyl methacrylate) itself is not miscible with HMMM, its copolymers with hydroxyethyl methacrylate and methacrylic acid are miscible. In films prepared from the copolymer latex, the HMMM acts as a plasticizer promoting diffusion of the copolymer. In latex films prepared from core-shell particles in which the core is PBMA and the shell is a copolymer containing HEMA and MAA, the HMMM is confined to the polar-polymer membrane phase. Both systems react quickly with the HMMM, catalyzed by the –COOH groups present, even at temperatures as low as 80°C for the core-shell system and 100°C for the unstructured latex. No externally added acid catalyst is needed. For all temperatures examined here, polymer diffusion is faster than the crosslinking reaction, which means that entanglements form before the polymer network is locked in place. In this temperature range, polymer diffusion increases with temperature with an effective activation energy of 38 kcal/mol,[16] whereas the activation energy for the HMMM reaction is lower.

In preparing a coating with a melamine derivative and a waterborne dispersion, the formulator has a broad latitude of variables to manipulate. The polymer diffusion rate is affected primarily by the length of the chain and by temperature. The polymer diffusion rate decreases

as M_w^{-2} for entangled chains. Temperature operates on the microscopic friction coefficient for polymer diffusion for which $(T - T_g)$ is the key parameter. Here T is the annealing or cure temperature, and T_g is the glass transition temperature of the polymer. Increasing the number of polar substituents on the polymer can increase its T_g. The melamine reaction rate depends on temperature, the amount of acid (catalyst or –COOH groups) present, and the local concentration of crosslinkable functionality on the latex polymer. A low swell ratio (high solvent resistance) is promoted by a high concentration of groups such as –OH that can react with the melamine. If one uses a low molecular weight polymer to enhance its diffusion rate, one needs to have a high content of reactive functionality. Otherwise, during the crosslinking reaction, the low molar mass component of this polymer will not be fully incorporated into the thermoset resin.

ACKNOWLEDGMENTS

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