Mitchell A. Winnik

Dr. Winnik is well known for his innovative studies of synthetic polymers at the molecular level and the application of fluorescence spectroscopy to polymer systems. His research, particularly on coatings, has embraced a broad spectrum of novel techniques. Dr. Winnik was the first to use atomic force microscopy in studies of film formation from latex dispersions, and the first to use laser confocal fluorescence microscopy in the study of polymer blends. In addition, through collaborations with scientists at other universities, he was an early innovator in both freeze fracture electron microscopy and matrix-assisted laser desorption ionization (MALDI) mass spectrometry in their application to polymers.

Mitch Winnik was born and raised in Milwaukee WI, and attended high school in the immediate post-Sputnik era, when a career in science seemed to be the most rewarding activity that a person might choose to pursue. After a year at the University of Wisconsin, he transferred to Yale, where he received a B.A. Degree in Chemistry in 1965. He carried out his doctoral research under the direction of Professor Ronald Breslow at Columbia University on the topic of "remote oxidation" and received the Ph.D. Degree in Organic Chemistry in 1969. Before joining the faculty at the University of Toronto in 1970, he spent a year as an NIH Postdoctoral Fellow at the California Institute of Technology, studying organic photochemistry with Prof. George S. Hammond. Dr. Winnik received tenure as an organic chemist in 1975, and following a sabbatical in France, began research on polymers in 1978. He was promoted to Professor in the Department of Chemistry in 1980, and in 1998 was named University Professor, the University of Toronto's highest award in recognition of scholarly excellence.

A principal focus of Dr. Winnik's research is the formation of films from latex dispersions, the basis of waterborne coatings technology. His major contribution to the coatings field has been the development of a technique based upon energy transfer measurements to study the rate of polymer diffusion across particle-particle interfaces in latex films. This is the process at the molecular level that leads to the development of mechanical strength in latex coatings. Dr. Winnik and his students have examined the influence of many additives and operational parameters used in industry on the rate of polymer diffusion in latex films. Examples include temperature and moisture effects, and the influence of coalescing aids and other plasticizers, as well as surfactants and pigments. These experiments have established a knowledge base that helps scientists in industry prepare more effective coatings formulations. More recently, Dr. Winnik and his students have been studying thermoset latex films, in which they compare the rates at which polymers diffuse across the interface with the rate of crosslinking in the film.

A parallel research focus, in many ways even more challenging, is an attempt to develop energy transfer techniques to characterize the interface between different types of polymers. The Winnik group has had its greatest success in the study of interfaces formed by block copolymers, either in the bulk state or in the form of block copolymer micelles in a selective solvent. To carry out these experiments, Dr. Winnik's students synthesize block copolymers with a single dye attached at the junction. When the block copolymers self-assemble to form periodic structures or form micelles in solution, the dyes are forced to congregate in the interface. Energy transfer measurements convey information about the distribution of distances between the dye molecules, from which the students in the Winnik group can calculate the thickness of the interface between the two polymers.

Dr. Winnik has also made seminal contributions to the study of water-soluble polymers bearing hydrophobic substituents. These polymers are used as associative thickeners in a variety of industrial products. They used fluorescence quenching experiments to determine the mean number of hydrophobic groups in the micelle-like structures that form through association. By combining fluorescence experiments with light scattering, pulsed-gradient nuclear magnetic resonance (NMR) and rheology measurements, they were able to develop a mechanistic picture of how flow affects the polymer structure in solution.

The author of more than 400 technical paper, Dr. Winnik holds 12 patents. He received three first place finishes in the FSCT's Roon Awards Competition in 1991, 1995, and 1998. Dr. Winnik was the recipient of the 1999 Roy W. Tess Award in Coatings from the Division of Polymeric Materials: Science and Engineering, of ACS. He has also served on the Editorial Review Boards of Macromolecules, the Journal of Polymer Science (Polymer Physics), the Canadian Journal of Chemistry, Langmuir, the JOURNAL OF COATINGS TECHNOLOGY, and Chemistry of Materials.

In addition, Dr. Winnik chaired the Polymers (West) Gordon Research Conference in 1992, and served on several NATO and IUPAC Commissions. He was the recipient of the 1995 Bell Forum Award for excellence in university-industry research. He has held visiting professorships in Bordeaux, France (1977-78), in Tokyo, Japan (1985-86), and in Mainz, Germany (1996), at the Max Planck Institute for Polymer Research, where he held an Alexander von Humboldt Senior Scientist Award. In 1983 he was a World Trade Scholar at the IBM San Jose Research Laboratories, and in the fall of 2000, as a visiting professor in France, he held the position of la Chaire de Paris Sciences.

** The 2001 Mattiello Memorial Lecture **

Interdiffusion and Crosslinking in Thermoset Latex Films

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INTRODUCTION

For more than a decade the coatings industry has been in the process of developing major changes to its technology. These changes are being driven by concern for the environment, particularly the presence in coatings formulations of volatile organic solvents, which are lost to the atmosphere as the coating dries. In response, new approaches have been developed to replace traditional solvent-based coatings with waterborne alternatives. The challenge within the industry has been to maintain or improve properties at a reasonable cost, while at the same time to meet the need for environmentally friendly coatings.

High performance coatings require crosslinking to obtain their optimal properties. Crosslinking improves film toughness, provides solvent resistance, and reduces soil pick-up. Solventborne coatings have a particular prominence in the area of industrial coatings, where performance is essential. In solventborne systems, the binder in these coatings consists of a solution of relatively low molecular weight polymer that builds up its properties, once dry on the substrate, through the formation of crosslinks. Waterborne polymer systems can be designed to provide the properties required of an industrial coating by introducing functional groups which are capable of forming crosslinks.[1,2] These thermoset systems include functional latex particles containing, for example, epoxy groups, N-methylolamide groups, N-isobutoxymethylamide, and acetoacetyl groups. Some functional groups like epoxy or alkoxymethylamine will self-react under suitable reaction conditions, whereas other functional groups require the addition of a multifunctional reactant (external crosslinker) to introduce crosslinking.

Thermoset coatings that depend on functional latex particles differ in a fundamental respect from solventborne coatings. For coatings applied from solution in an organic solvent, the polymers, oligomers, and other reactive species in the formulation are intimately (molecularly) mixed in the solvent. One assumes that these components remain mixed after the coating formulation is applied to the

PRINTER TO PLACE

Thermoset latex systems represent an attractive approach to obtaining the high performance needed in many different kinds of industrial coatings, while satisfying the growing requirement for environmental friendliness. In these coatings in the dispersed state, the reactive groups are packaged inside of polymer particles. These latex particles deform as the coating dries to form a transparent binder phase. The useful properties of mechanical strength, as well as scrub and solvent resistance, develop over time. This paper focuses on the idea that to achieve the desired properties in a thermoset latex coating, one has to pay proper attention to the relative rates of polymer diffusion and crosslinking in the coating. Strength in these films develops as a consequence of chains that connect crosslink points on opposite sides of interface formed between adjacent particles in the film. Thus polymer diffusion must precede extensive bond formation created by the crosslinking chemistry. This paper reviews fundamental concepts and then describes experiments in three separate systems. These experiments show that the formulator has three main strategies to vary the relative rates of these processes: 1. Catalyst strength and concentration will affect the reaction rate. 2. Polymer chain length will affect the polymer diffusion rate. 3. Temperature changes will normally have a larger affect on the polymer diffusion rate than on the crosslinking reaction rate.

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substrate and the solvent evaporates. The chemical reactions that occur build up the molar mass of the polymers in the coating until, under ideal circumstances, the entire binder is converted to a single molecule with the desired crosslink density. At the early stages of cure, only a limited extent of polymer diffusion is required to bring the reactive groups into proximity. Constraints to diffusion occur primarily at high conversion, well past the gel point, where crosslinks inhibit the local diffusion of polymer segments that span existing crosslink junctions. This type of diffusion is necessary to build up the crosslink density, i.e., to reduce the molar mass between crosslinks, an important factor in reducing the extent of swelling of the coating upon exposure to solvent.

Polymer Diffusion and Crosslinking

In latex-based coatings, the polymer molecules are packaged in small discrete particles. As water evaporates and the film dries, each of these "containers" is deformed into a space-filling polyhedral cell.[3] The interface between cells acts as a dividing surface separating the polymer molecules from one cell from those in the adjacent cells. While this binder phase of the newly formed film is transparent, it also has very poor mechanical properties. Adhesion at the intercellular boundaries is limited to van der Waals interactions between the polymers in the individual cells and hydrogen bonding and ion-pairing interactions between functional groups at the particle surface. Surfactant, salts, and other nonvolatile substances present in the aqueous phase tend to become trapped in these boundaries and contribute to the poor mechanical properties of the initially formed films. In latex films, mechanical strength develops through polymer diffusion across the intercellular boundaries. Polymer chains that span the boundary act to "sew-up" the interface.

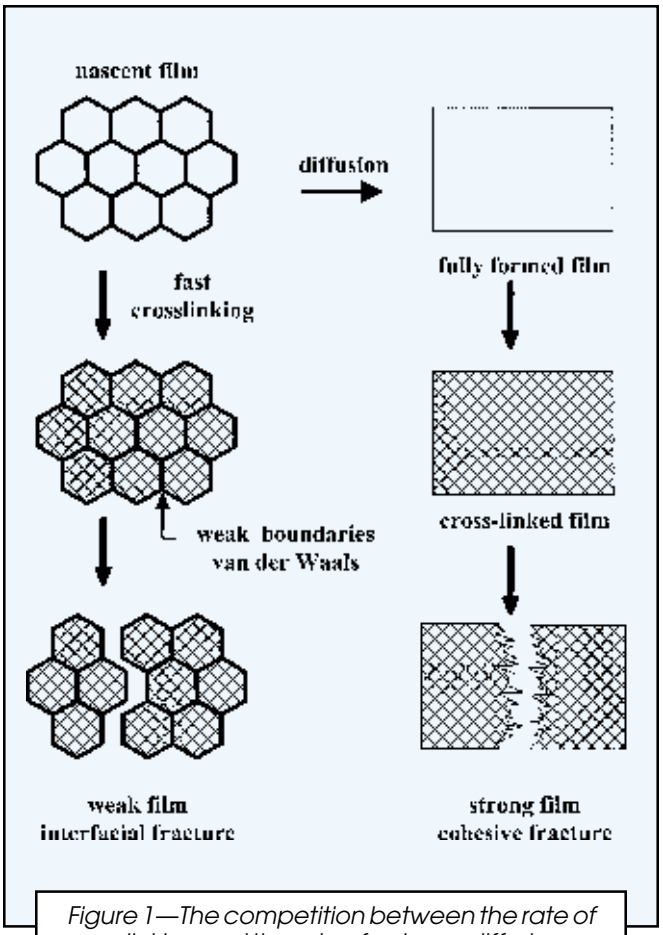


Figure 1—The competition between the rate of crosslinking and the rate of polymer diffusion on the development of mechanical strength in a latex film in which the reactive groups are distributed throughout the individual cells of the nascent film. If the crosslinking occurs very rapidly, the reaction occurs within individual cells, with few if any crosslinks involving chains that span the interface between cells. Adhesion is weak, and films fracture by interfacial failure. If polymer diffusion is rapid, the interfaces heal, and subsequent crosslinking generates a mechanically strong film. These films will fracture by cohesive failure.

In thermoset latex films, we imagine that the performance of the coating depends in a sensitive way on the relative timing of the polymer diffusion step and the chemical reaction step. A drawing indicating the nature of this problem is shown in *Figure* 1. In the upper left-hand part of the figure, the 10 hexagons represent cells formed from latex particles as they dried to form a film. The functional groups that participate in crosslinking are assumed to be uniformly distributed in the film. If the rate of the crosslinking reaction is much faster than the rate of diffusion, then crosslinking will take place exclusively within each cell. The film will have the properties of a film formed from precrosslinked latex particles.[4] There will be only weak adhesion at the intercellular boundaries. The right-hand side of the figure shows the consequences of polymer diffusion occurring much more rapidly than the chemical reaction. Extensive polymer diffusion leads to the disappearance of the boundaries between adjacent cells. Subsequent crosslinking produces a coherent reticulated film, which will undergo cohesive failure when subjected to fracture.

To understand the competition between polymer diffusion and the extent of chemical reaction in latex films, we need to examine the factors that affect both steps and how they both respond to temperature. We begin by considering the special features that affect the rate of polymer diffusion across interfaces.

Polymer Diffusion Across Interfaces

Polymer diffusion is driven by Brownian motion, and consists of random thermal jumps of segments of polymer chains between adjacent voids or "free volume elements." Two models, the Rouse model[5] and the reptation model,[6] are commonly employed to describe self-diffusion of polymer chains in the melt state. The Rouse model takes account of the effect of chain connectivity on the friction coefficient f of a diffusing chain. This model assumes that each polymer chain consists of N beads connected by (N-1) springs, and each bead feels the same friction from the surrounding media. This model provides a normal-mode description of the polymer dynamics, characterized by a distribution of relaxation times. Thus for center-of-mass diffusion, the diffusion coefficient $D=k_BT/Nf$. The k_BT term (k_B is the Boltzmann constant) describes the energy associated with thermal motion, and D is predicted to decrease as N^{-1}. The longest relaxation time τ_{ro} is often

referred to as the Rouse time. When the molecular weight of polymer is not too high, $M<2M_e$ (M_e is the critical entanglement molecular weight), the Rouse model can be used to describe the translational diffusion of polymer molecules.

The reptation model adds topological (entanglement) effects to the description of chain dynamics for high M polymers, where entanglements influence the polymer dynamics. In this model, neighboring chains are obstacles, restricting the lateral motion of a polymer chain, and confining the chain to a "tube" where curvilinear, one-dimensional, diffusion occurs along its contour. Random motion occurs in both directions along the tube. Memory of the initial chain conformation (tube conformation) is gradually lost because the motion of chain ends is random. Finally after a reptation time, T_{rep}, a chain disengages itself from the initial tube and takes a new conformation, for $M>>M_e$, $D \sim N^{-2}$, a much stronger dependence on chain length. At times much shorter than T_{rep}, the Rouse model is employed to describe the relaxation of the chain confined to its tube.

For polymer diffusion across an interface, one has to take into account the influence of the interface as a dividing plane on the initial chain conformation.[7-10] Prior to the onset of diffusion, the conformation of the polymer chains close to the interface is distorted from the normal Gaussian distribution of segments typifying polymer chains in the bulk state. This distortion is referred to as confinement entropy. The diffusion of polymer molecules across the interface leads to conformational randomization and recovery of Gaussian chain statistics. For short chains, in which translational diffusion can be described by the Rouse model, the chain relaxation time at the interface is very short, and polymer diffusion follows Fick's[7,11] laws. For entangled chains, the process is substantially more complex. According to the reptation model, the diffusion process is dominated by segmental motion for times shorter than T_{rep}, whereas center-of-mass diffusion prevails at longer times.

The theory of polymer diffusion across interfaces for entangled chains[4-7] predicts that the diffusion will follow Fick's law when the diffusion time is larger than the reptation time (T_{rep}). In this case, the mass transfer scales with time as $t^{1/2}$. The interesting predictions are those that pertain to reptation dynamics at $t < T_{rep}$. The properties examined include the number of chains crossing the interface n(t), the number of bridges crossing the interface p(t), the number of monomers crossing the interface N(t), and the average monomer penetration depth X(t). The most profound prediction is that the monomer concentration of chains crossing the interface is discontinuous for healing times shorter than the reptation time. The gap occurs because there are regions of the interface plane at $t < T_{rep}$ that have not yet been threaded by reptating chains. As the number of chains crossing the interface increases, the gap decreases, and the discontinuity becomes smaller. The gap is predicted to disappear at $t = T_{rep}$.

Almost all of the experiments that have been employed to test this theory have involved simple systems consisting of thin films of polymer like polystyrene with a very narrow molecular weight distribution. Latex films are more complex in several ways. First, the polymer has a broad molecular weight distribution. Second, many of the

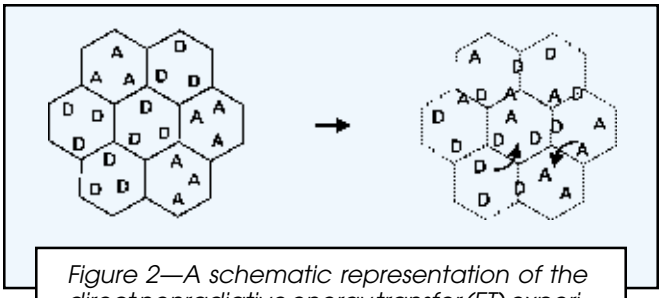


Figure 2—A schematic representation of the direct nonradiative energy transfer (ET) experiment. A film is prepared from a mixture of donor (D)- and acceptor (A)-labeled latex particles. For ET to take place, polymer molecules have to diffuse across the intercellular boundaries, leading to the mixing of D and A groups.

chains have polar end groups arising from the free radical initiator. Third, there may be polar groups at or near the surface of the latex particles as a consequence of comonomers like acrylic acid introduced into the particle synthesis. Finally there is often polar material like salts and surfactant that gets trapped in the spaces between the cells in the film, whose influence on polymer diffusion in the film is poorly understood. These factors complicate the theoretical description of diffusion of polymers in latex films.

Temperature Effects on Polymer Diffusion and Reaction Kinetics

The rate of a chemical reaction depends upon the product of its rate constant *k* with the concentration (activity) of

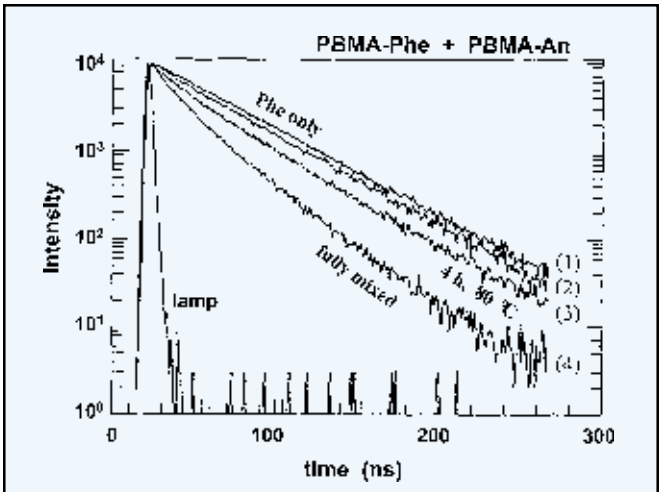


Figure 3—Phenanthrene (donor) fluorescence decay curves ($I_D(t)$) measured at 23°C for PBMA latex films. Curve (1) is from a film prepared from the pure Phe-labeled latex, and exhibits an exponential decay. Curve (2) is from a newly formed film prepared from a 1:1 mixture of Phe- and An-labeled particles with a diameter of 105 nm. Curve (3) is the $I_D(t)$ profile for the sample in curve (2) after four hours annealing at 80°C. Curve (4) is obtained from the same film after it was dissolved in ethyl acetate to obtain full mixing of the constituent polymers and then recast onto the quartz substrate.

the reactants and catalysts present in the system. Because these reactions are activated processes, the magnitude of k depends on the height of the activation barrier separating reactants from products. Activation energies E_a are determined experimentally by fitting the rate constant k, determined through kinetic studies at different temperatures, to the Arrhenius equation.

$$k = A'\exp\left(-\frac{E_a}{R'T}\right) \quad (1)$$

Here R' is the gas constant, and A' is the preexponential factor, related to the entropy of activation of the reaction. The plot of ln k vs 1/T is linear, with a slope equal to $-E_a/R'$.

In the free-volume model of polymer dynamics, an increase in temperature operates through the polymer thermal expansion coefficient α_T to increase the free volume in the system, and thereby reduce the magnitude of the friction coefficient f. The temperature dependence of polymer diffusion can be described in terms of the Williams-Landel-Ferry (WLF) equation,[12] with parameters close to those obtained from viscoelastic relaxation measurements.[13] Over a sufficiently broad range of temperatures, a plot of ln D versus 1/T is curved. The WLF expression for diffusion is written

$$\log\left(\frac{D\,T_o}{T\,D_o}\right) = \frac{C_1(T-T_o)}{C_2+T-T_o} \quad (2)$$

and requires two parameters (C_1, C_2) to describe the temperature dependence of D. In this expression T_o is a reference temperature, and C_1 and C_2 are parameters associated with a given polymer structure whose values vary with the choice of T_o. Other viscoelastic properties of polymers exhibit the same dependence on temperature, and give very similar values of C_1 and C_2. Over a more limited range of temperatures, a plot of ln D versus 1/T appears linear, and one can calculate an effective activation energy E_a^{diff} from the slope. This quantity, instead of being temperature independent as in the case of chemical reactions, increases rapidly with decreasing temperature

$$E_a^{diff} = R'\frac{C_1C_2T^2}{C_2-T-T_o} \quad (3)$$

and at T_g attains the value $R'C_{1g}C_{2g}T_g^2/C_{2g} = R'T_g2\alpha_f/f_g^2$. Thus E_a^{diff} is predicted to be independent of chemical structure except as reflected by T_g itself and in minor variations in the fractional free volume f_g and the thermal expansion coefficient α_f in the vicinity of T_g. The magnitude of E_a^{diff} is of the order of 60 kcal/mol if T_g = 200 K and 250 kcal/mol if T_g = 400 K.

Variation of temperature turns out to be one of the most powerful tools for one to control the relative rates of crosslinking and polymer diffusion in latex films. If the activation energy for the chemical reaction is less than the effective activation energy for polymer diffusion, raising the temperature will enhance the rate of polymer diffusion to a greater extent than that of the crosslinking reaction.

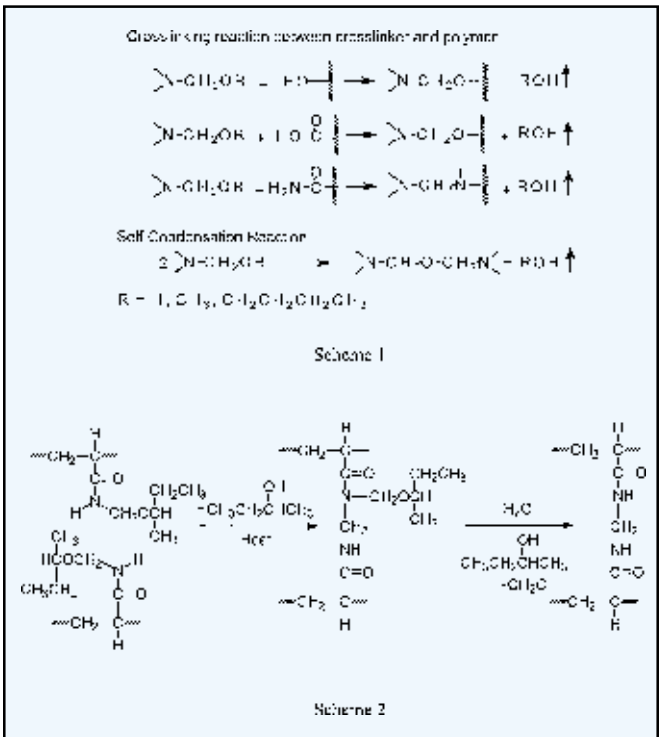


Figure 4—Schematic representation of the reactions of alkoxymethylamine groups. Scheme 1: the acid catalyzed reaction of these groups with alcohol, acid, and amide groups. Scheme 2: the acid or heat-catalyzed coupling of isobutoxymethylamine groups.

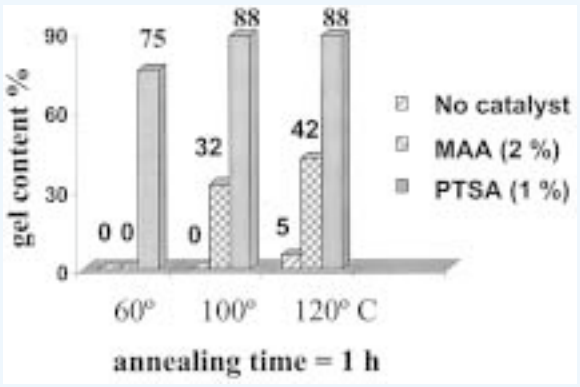


Figure 5—Gel content for samples of IBMA-containing P(MMA-co-BA) latex films annealed for one hour at different temperatures. The three types of films all contain 2 wt% IBMA with different levels of acid catalyst: no catalyst; 2 wt% MAA incorporated as a co-monomer with IBMA and ion exchanged prior to film formation to ensure protonation of the –COOH groups; and a MAA-free film to which 1 wt % PTSA was added.

Measuring Polymer Diffusion by Energy Transfer

To study polymer diffusion across interfaces in latex films, one needs a source of contrast. In small angle neutron scattering experiments, contrast comes from deuteration of some of the latex particles in the film. One prepares films from a blend of normal latex with a small fraction of latex particles synthesized from deuterated monomer. In the energy transfer (ET) technique, contrast comes from the presence in each latex particle of a small fraction of fluorescent dyes covalently bound to the polymer back-

bone. One synthesizes two sets of latex, one consisting of particles containing a donor dye D and the other containing an acceptor dye A. One prepares a mixture of the two dispersions and casts a film from the blend. In both experiments, if the two types of particles have a similar composition, particle size, and surface functionality, the two types of latex particles (deuterated and nondeuterated, or donor- and acceptor-labeled) will be randomly mixed in the film that is formed.

The term direct "nonradiative energy transfer" refers to the transfer of energy from an exited donor dye to an acceptor dye through resonant coupling of their transition dipoles. The rate of this process $w(r)$ decreases with the 6th power of the distance r between the donor and acceptor dyes[14]

$$w(r) = \frac{1}{\tau_D}\left(\frac{R_o}{r}\right)^6 \tag{4}$$

where τ_D is the unquenched donor fluorescence lifetime, and R_o is the characteristic (Förster) distance for ET. In the ET experiment, one uses fluorescence decay measurements to monitor the diffusion of polymer across the boundary between donor-labeled cells and acceptor-labeled cells. A film is excited with a pulse of light, and one monitors the decay of donor fluorescence intensity $I_D(t')$ as a function of time. While there are various ways to analyze these decay curves, the most straightforward and model-free approach is to calculate the quantum efficiency of ET (Φ_{ET}). This parameter is defined by the middle term in the expression

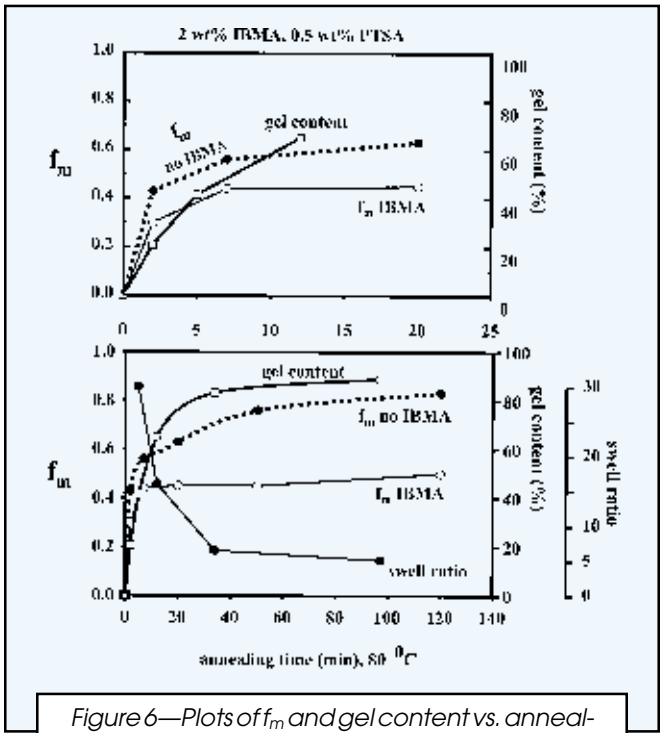


Figure 6—Plots of f_m and gel content vs. annealing time at 80°C for films cast from a P(BA-co-MMA-co-IBMA) latex (M_w = 200,000) plus 0.5 wt% PTSA. The corresponding f_m values for a film cast from the IBMA-free P(BA-co-MMA) latex (M_w = 200,000 without added acid) annealed simultaneously, are also plotted as filled circles (•). The upper graph shows the data on an expanded time scale.

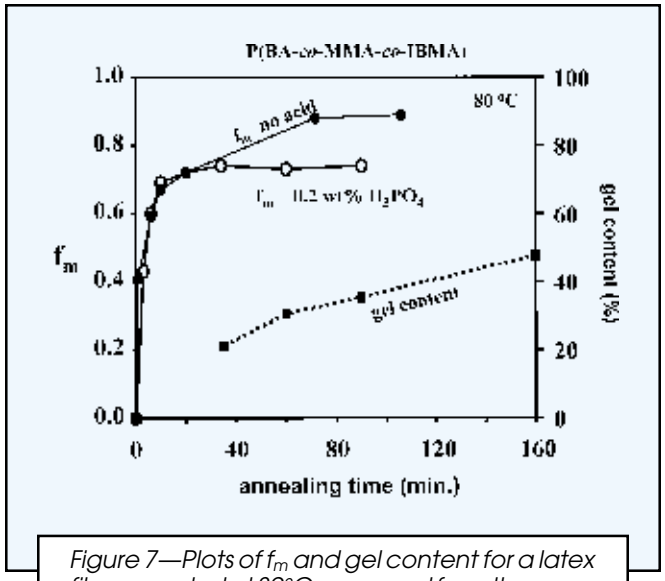


Figure 7—Plots of f_m and gel content for a latex film annealed at 80°C, prepared from the same P(BA-co-MMA-co-IBMA) latex as in Figure 6, but in the presence of 0.2 wt% H_3PO_4 as the acid catalyst. For comparison, we show the growth in f_m (•) for a film prepared from the same latex without added acid.

$$\Phi_{ET} = 1 - \frac{\int_0^\infty I_D(t')dt'}{\int_0^\infty I_D^o(t')dt'} = 1 - \frac{Area(t)}{Area([A]=0)} \tag{5}$$

where $I_D^o(t')$ is the donor decay profile in the absence of acceptor. The time integral of $I_D(t')$ is the area under the decay curve. This integral has units of time, and defines the mean decay time for the donor dye in the film. *Area(t)* represents the integrated area under the fluorescence decay profile of a latex film sample annealed for a time t, and *Area([A] = 0)* refers to the area under the decay profile of a film containing only donor. In our experiments, we normally use phenanthrene (Phe) as the donor dye and anthracene (An) as the acceptor dye. For latex films containing phenanthrene as the donor, $I_D^o(t')$ is always exponential, and its integral is equal to τ_D.

A drawing describing the essential features of this experiment is shown in *Figure* 2. The film consists of a mixture of cells formed from donor- and acceptor-labeled latex particles. In the initial film, the D and A groups are confined to their respective cells. The characteristic distance R_o for ET is on the order of tens of Ångstroms, much smaller than the cell diameter (typically 50 to 200 nm). In the newly formed film, one can measure a small amount of ET between D* groups in one cell and A groups in the adjacent cell. The extent of the interfacial ET is sensitive to the ratio of D- and A-labeled particles in the blend and the concentration of A-groups in the A-labeled cells. In principle, the magnitude of the quantum efficiency of ET (Φ_{ET}) at this point measures the amount of interfacial area between D- and A-labeled cells. As the film is annealed, polymer diffusion occurs. The polymers carry with them their covalently bound dyes. When polymer diffusion occurs across the boundary between a cell consisting of

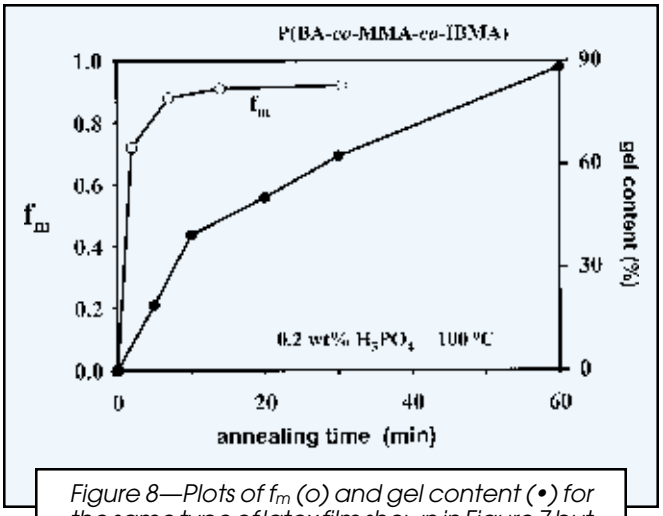


Figure 8—Plots of f_m (o) and gel content (•) for the same type of latex film shown in Figure 7 but annealed at 100°C.

donor-labeled polymer and that containing acceptor-labeled polymer, there is an increase in the number of D and A groups in proximity. As a consequence, the magnitude of Φ_{ET} evolves from its initial value $\Phi_{ET}(0)$ to that characteristic of a homogeneously mixed film $\Phi_{ET}(\infty)$.

The evolution of Φ_{ET} as a function of annealing time t can be used to calculate the extent of mixing of the two-labeled polymers.

$$f_m = \frac{\Phi_{ET}(t) - \Phi_{ET}(0)}{\Phi_{ET}(\infty) - \Phi_{ET}(0)} \quad (6)$$

where f_m is defined in terms of the evolution of the quantum efficiency of energy transfer. These values of f_m are only indirectly related to the fraction of mass f_s that has diffused across the interface.[15-17] We have employed simulations[18] based on Fickian diffusion to assess the relationship between f_m and the mass fraction f_s of polymer that diffuses across the intercellular boundary in latex films, using parameters (100 nm cells, 1 mol % chromophore, R_o = 2.3 nm) typical of our experiments. The simulations show, as expected, that f_s increases as $t^{1/2}$. They also show that for linear polymer chains for which entanglements are not important, that f_m also increases as $t^{1/2}$. The simulations show that f_m is proportional to f_s for values of $f_m \leq$ 0.7. In addition, the simulations show that f_m approaches 1.0 for a mean polymer diffusion distance on the order of a cell radius.

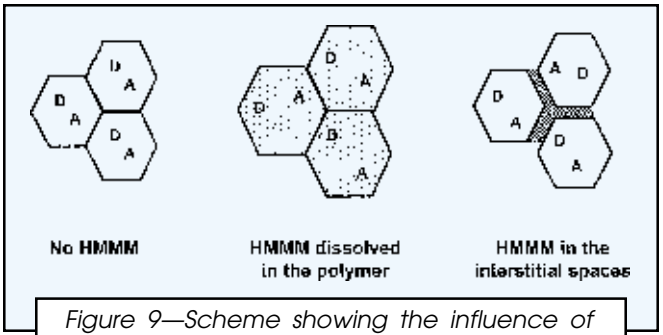


Figure 9—Scheme showing the influence of HMMM on the mean separation of D and A groups in a film prepared from doubly labeled latex particles. If the HMMM dissolves in the polymer, it acts as a swelling agent, increasing the distance between D and A groups. If HMMM is preferentially localized in the interstitial spaces, it will have little effect on the D – A distance.

For more than a decade, we have employed ET experiments to study polymer diffusion in latex films.[19] Most of the systems we examined involved linear PBMA and its copolymers. We have employed this technique to evaluate the influence of external variables such as temperature, plasticizers, surfactant, moisture, and filler particles on the rate of polymer diffusion. The use of ET to study polymer diffusion in latex films has also been reported by Boczar et al.[20] at Rohm and Haas and by the Lang group[21] in Strasbourg.

The results of a typical experiment are shown in *Figure* 3, where we choose for example a latex film of poly(butyl methacrylate) prepared from a 1:1 mixture of 100 nm diameter Phe- and An-labeled PBMA particles, both containing polymer with M_w = 34,000. In curve (1) one sees that the film containing only Phe-labeled polymer has an exponential decay profile. The curve (2) is taken shortly after the film dried. The slight curvature seen at early times is due to energy transfer across the interparticle boundaries plus a small extent of polymer diffusion during drying. The curve (3) shows the nature of the change that occurs when the film is heated for four hours at 80°C and then cooled to room temperature (23°C) for the fluorescence decay measurement. Curve (4) is a film prepared by dissolving the polymer in an organic solvent such as ethyl acetate to ensure full mixing and then casting a film. A similar curve is obtained if the film is annealed for a long time at 80°C or a shorter period of time at 120°C.

At this point we are interested in the competition between the polymer diffusion rate and the rate of crosslinking in latex films.[22] From the previous discussion, we recognize that the polymer diffusion rate for linear polymers is sensitive to two main factors, polymer chain length and temperature. Chain length affects the magnitude of the diffusion coefficient characterizing the diffusion rate of each polymer molecule, and the diffusion rate decreases strongly (as N^{-2} for entangled chains) with increasing chain length. Temperature effects operate on the microscopic friction coefficient through changes in free volume in the polymer. The key parameter is $T - T_g$, the extent to which the system is above its glass transition. Crosslinking introduces two additional complications. First, the chemical reactions that precede gel formation introduce branches into the polymer. Branching, particularly long branches in entangled polymers, causes a substantial decrease in the polymer diffusion rate. Once a polymer is part of a crosslinked network, its center-of-mass diffusion ceases, and its motion in the matrix is limited to local diffusion of its segments attached to crosslink points. The second effect is that of the crosslink density on T_g. While small extents of crosslinking, even well above the gel point, have little effect on T_g, extensive crosslinking as in epoxy resins, can lead to a substantial increase in T_g. This increase in T_g decreases the mobility of polymer segments in the film.

Studies of Diffusion and Crosslinking in Latex Films

In the following sections, we describe some of the research carried out in my laboratory to measure the

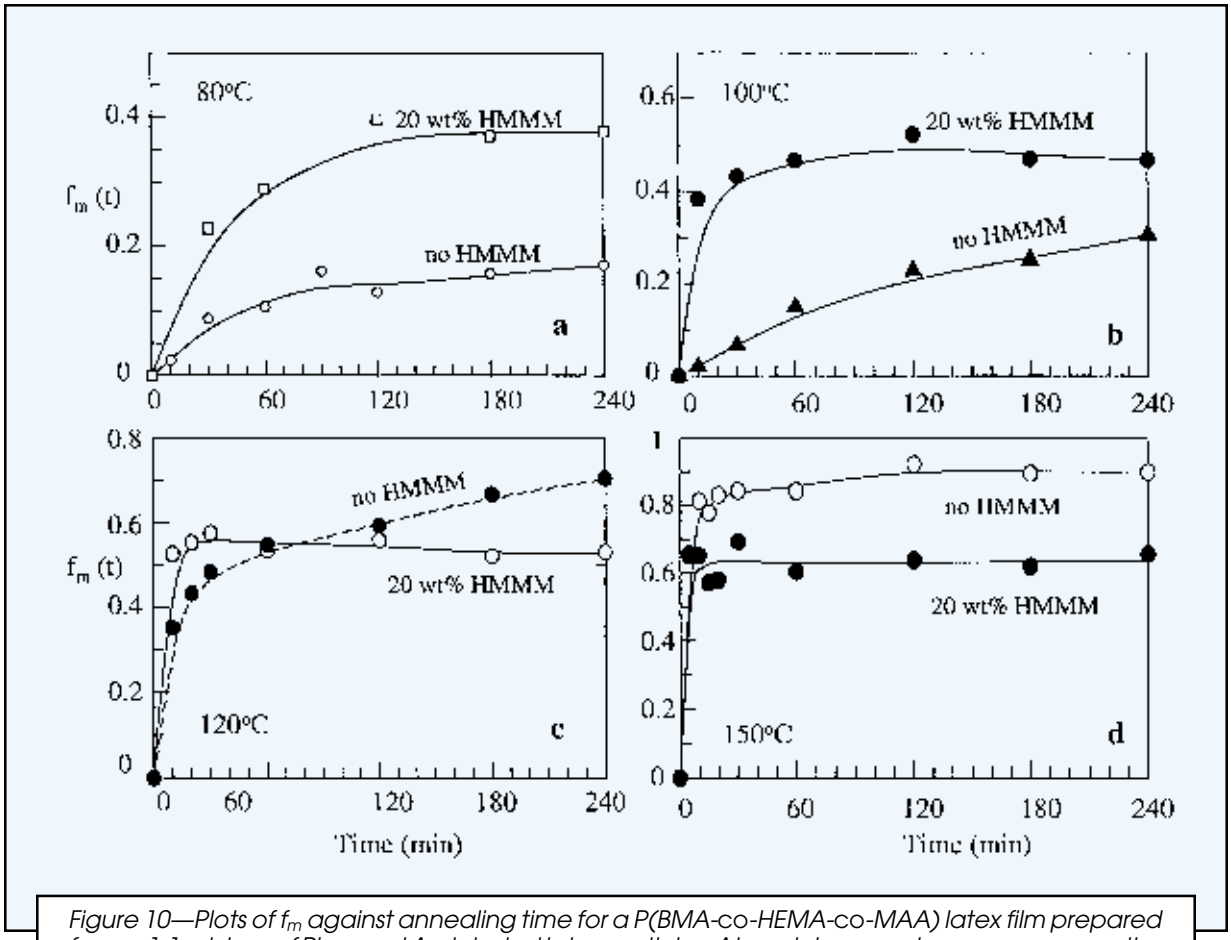
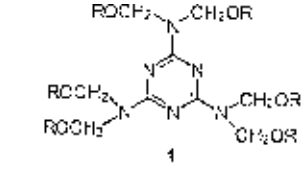
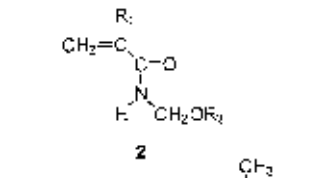


Figure 10—Plots of f_m against annealing time for a P(BMA-co-HEMA-co-MAA) latex film prepared from a 1:1 mixture of Phe- and An-labeled latex particles. At each temperature, we compare the growth in f_m for a film to which 20 wt% HMMM (Cymel 301, based on latex solids) was added to the dispersion prior to film formation to a film without any added HMMM.

relative rates of polymer diffusion and crosslinking in different thermoset latex systems. Energy transfer measurements were used to follow the extent of polymer diffusion. The extent of crosslinking was followed by measuring the gel content and the swell ratio of the polymer film as a function of time after the film was prepared. We have found that 1,4-dioxane is a convenient solvent for these measurements. The gel fraction is determined as the fraction of polymer that will not dissolve when a film is immersed in dioxane for 48 hr. The swell ratio is calculated from the ratio of the wet weight of the insoluble polymer divided by its dry weight after solvent evaporation.

We begin with a discussion of two reactions involving N-alkoxymethylene groups. The first involves acid-catalyzed crosslinking through self-condensation of isobutoxyacrylamide groups. The second involves reactions of a methoxymelamine derivative with a latex polymer containing both primary hydroxyl and free carboxylic acid groups.





Methylol groups ($CH_3O–CH_2–N$) readily condense under mildly acidic conditions with hydroxyl, carboxyl, or amide functionality. Methylol groups also combine with each other under acidic or basic conditions. Alkyloxymethyl groups self condense under more acidic conditions. For the case of isobutoxymethylacrylamide, the self-condensation reaction is shown as *Scheme* 2 in *Figure* 4. Methoxylmethyl groups of a methoxymelamine derivative, its reactions with hydroxyl groups, carboxyl groups, and with itself are shown as *Scheme* 1 in this figure.

Isobutoxymethylacrylamide (IBMA)

In our experiments,[23] we chose a methyl methacrylate-butyl acrylate copolymer latex P(BA-*co*-MMA) as the base polymer with a monomer weight ratio of 5:4 (mole ratio = 3:5, estimated T_g = 12°C). We prepared five pairs of An- and Phe-labeled poly(BA-*co*-MMA) latex samples by seeded emulsion polymerization. The seed consisted of a similar copolymer and represented 12 wt% of the final particles prepared by two-stage emulsion polymerization. Other monomers such as IBMA (2 wt%), fluorescent dye co-monomers (1 mol%), and methacrylic acid (MAA) were introduced in the second stage. Dodecyl mercaptan was used as a chain transfer agent to control the polymer molecular weight. In all of the syntheses, the final latex dispersion was obtained with a solids content of 24 wt%,

with particle diameters in the range of 140 nm, and with a narrow size distribution. The experiments described here involved latex polymers with M_w = 230,000 (as estimated by gel permeation chromatography) and M_w/M_n = 2.8.

We began by assessing the conditions necessary to induce gel formation in the latex films. An example is shown in *Figure* 5. All film samples contained 2 wt% IBMA. One sample contained no added acid catalyst. Another sample contained 1 wt% p-toluenesulfonic acid (PTSA) added to the dispersion just before the film was cast. The third film had no added acid catalyst, but contained 2 wt% MAA as a co-monomer. This latex was ion-exchanged to ensure that the MAA groups were in the protonated form. The films were heated for an hour. The measured gel contents for the films containing PTSA were 62% for the film heated at 60°C and 88% for the films heated at 100 and 120°C. Since 12 wt% of the latex is the polymer from the seed, which contains no IBMA and therefore remains gel free, 88% gel content is the value expected for full conversion of the IBMA-containing polymer to gel. Under the same conditions, the acid free latex undergoes almost no significant crosslinking, whereas the latex containing the MAA groups forms a substantial amount of gel when heated for one hour at 100 and 120°C.

Energy transfer experiments were carried out first on a sample of P(BA-*co*-MMA) latex without the IBMA group. Values of f_m were determined as a function of annealing time, for samples annealed at 51, 67, and 81°C. Analysis of these data, through calculation of apparent diffusion coefficients,[13] gave a value of E_a^{diff} = 43 kcal/mol. This value can be compared to the value of 38 kcal/mol determined for poly(butyl methacrylate) (PBMA) over the temperature range of 70 to 100°C,[24] and 49 kcal/mol determined for poly(methyl methacrylate) over the temperature range of 120 to 150°C.[25] In addition, we found that a sample of P(BA-*co*-MMA-*co*-IBMA) containing 2 wt% IBMA, without acid catalyst, exhibited a growth in f_m with annealing time very similar to that of the P(BA-*co*-MMA) latex film of similar molecular weight. We infer that a small fraction of IBMA in the polymer backbone has a negligible effect on the polymer diffusion rate.

In *Figure* 6 we compare the results for a P(BA-*co*-MMA-*co*-IBMA) latex film in the presence of 0.5 wt% PTSA to that obtained from a P(BA-*co*-MMA) latex film of similar molecular weight annealed simultaneously. We plot values of the extent of mixing (f_m), the gel content, and the swell ratio as a function of the annealing time at 80°C. The upper figure emphasizes changes that occurred over the first 25 min of the annealing process. Here we see for P(BA-*co*-MMA-*co*-IBMA) that the gel content increased quickly with annealing time. After t = 12 min, the gel content reached 65% with a swell ratio = 18. The lower figure provides data on a much longer time scale. Upon longer annealing (one hour), we found 88% gel formation (swell ratio = 4.5). Taking account of the linear polymer present in the seed, this represents 100% gelation of the IBMA-containing polymer. We also see that f_m increases with time, especially during the early stages of annealing. At early stages, as shown by the slopes of the f_m versus time plots, the interdiffusion rates of the IBMA-containing film and the IBMA-free film are very close. The similarity in diffusion rates reflects the similarity in the molecular weight and composition of the different polymers. After seven min, however, the f_m value of the IBMA-containing polymer ceased to increase, an indication that polymer interdiffusion has been suppressed or its rate has been substantially reduced. At this point, f_m = 0.4 and the gel content was 42%. For the film without IBMA, f_m continued to increase, and if the film were heated for a sufficient length of time f_m would approach 1.0.

In order to obtain films in which a greater extent of polymer interdiffusion precedes full gelation, we need either to increase the interdiffusion rate or to slow down the crosslinking rate. The two most straightforward variables to manipulate are temperature and the acid catalyst. In *Figure* 7, we show the results of an experiment which employs a much weaker acid catalyst, 0.2 wt% phosphoric acid, for a film annealed at 80°C. For comparison, we simultaneously examined a similar latex film in which no acid

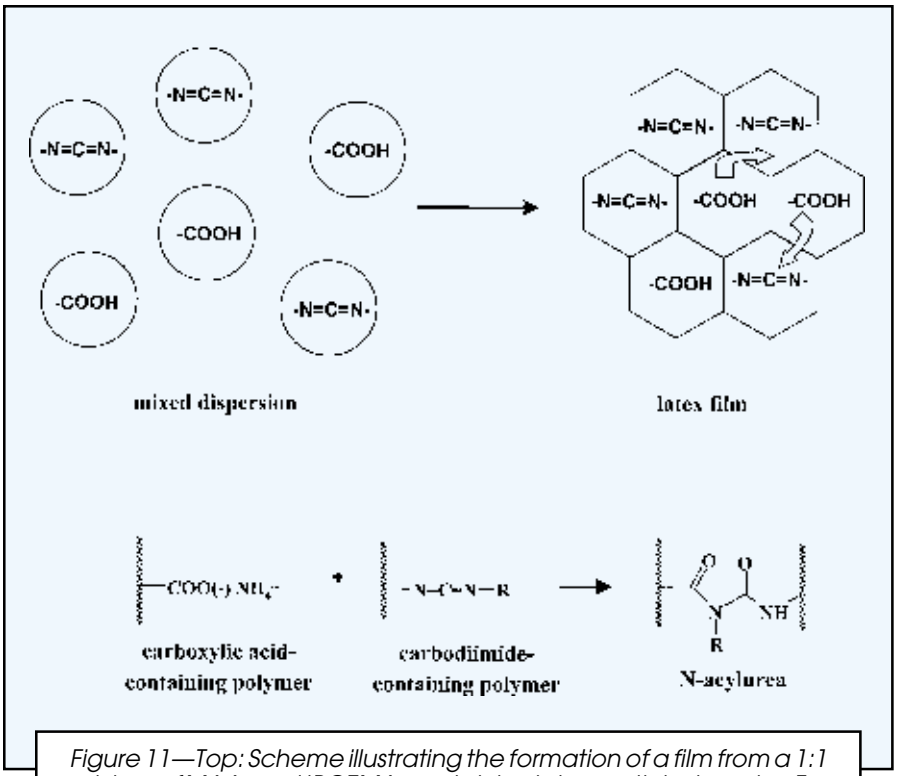


Figure 11—Top: Scheme illustrating the formation of a film from a 1:1 mixture of MAA- and tBCEMA-containing latex particles in water. For the reaction between the –COOH and –N=C=N– groups to occur, the groups must approach to within a reaction distance (a few Å). For this to occur, polymer molecules bearing these reactive groups have to diffuse across the intercellular boundaries in the film. Bottom: The chemical reaction between the –COOH and –N=C=N– groups to form an N-acyl urea.

Table 1—Typical Recipes to Prepare Labeled Latex Particles

Reactants	PEHMA-D	D-MAA-11	A-tBCEMA-5
Seed[a] (g)	60.0	120.0	60.0
EHMA (g)	35.0	66.5	33.1
MAA (g)	—	3.50	—
t-BCEMA (g)	—	—	1.92
PheMMA (g)	0.49	0.77	—
AnMA (g)	—	—	0.47
DM[b] (g)	0.32	0.61	0.32
KPS (g)	0.06	0.12	0.07
SDS[c] (g)	0.70	1.29	0.70
$NaHCO_3$ (g)	—	—	0.31
H_2O (g)	27.0	55.0	27.1
Temperature (°C)	80	80	80

(a) PEHMA dispersion, 5 wt% solids.
(b) 1-Dodecylmercaptan.
(c) Sodium dodecyl sulfate.

catalyst was added. For the acid-free film, there was no gel detected up to three hours at 80°C. For the film containing phosphoric acid, the rate of gel formation is much slower than that seen in *Figure* 6 for the reaction catalyzed by PTSA. At the early stage of annealing (t = 20 min, up to $f_m \approx 0.65$), the interdiffusion rates of the polymers in the two films are almost the same. No gel in the H_3PO_4-containing film could be detected until the annealing time reached 35 min. Shortly thereafter, polymer diffusion in the acid-containing film appeared to cease, reaching a limiting f_m value of 0.7 after 20 min at 80°C. In contrast, the f_m value for the acid-free film continued to increase. What is striking about the results in *Figure* 7 is how closely the polymer diffusion in the reactive film follows that of the catalyst-free film until a certain extent of reaction is reached. At this point the diffusion appears to come rapidly to a halt. To understand this result, one should recognize that even before any gel can be detected, reactions of the IBMA group lead to the formation of branched polymer of higher molecular weight. If the branches are relatively short, this new polymer will be able to diffuse, but at a much reduced rate. If the branches are long, one expects little or any diffusion of this polymer on the time scale of the experiment.

Temperature has a strong effect on both the rate of polymer diffusion and the rate of gel formation. As shown in *Figure* 8, polymer diffusion is very rapid at 100°C. For the same formulation, containing 0.2 wt% H_3PO_4, f_m reached a value of 0.75 in about five minutes, during which time very little gel formed. Gel formation increased steadily over the next 40 min, but it took over an hour for the system to gel completely. *Figures* 6-8 emphasize the importance of the two variables that one can manipulate in IBMA-containing latex films, acid content, as well as cure temperature. The presence of strong acid promotes the rate of the crosslinking reaction without having much effect on the rate of polymer diffusion. An increase in temperature augments both rates, but has a large influence on the rate of polymer diffusion.

Table 2—Characteristics of the Labeled Latex Polymers

	Particle Diameter (nm)	Solids Content (%)	Mw, Mw/Mn	pH	–N=C=N– Content (%)
PEHMA-D[a]	98	30.9	39 000, 2.44	5	—
PEHMA-A[b]	97	31.1	56 000, 2.07	5	—
D-MAA-11[c]	101	31.2	41 000, 1.95	5	—
D-MAA-20[d]	113	31.0	50 500, 2.35	5	—
A-tBCEMA-5[e]	106	31.9	63 000, 3.15	8	98
A-tBCEMA-11[f]	102	31.7	45 500, 2.39	8	98

(a) P(EHMA-co-PheMMA): 1 mol % PheMMA.
(b) P(EHMA-co-AnMA): 1 mol % AnMA.
(c) P(EHMA-co-PheMMA-co-MAA): 1 mol % PheMMA, 11 mol% MAA.
(d) P(EHMA-co-PheMMA-co-MAA): 1 mol % PheMMA, 20 mol% MAA.
(e) P(EHMA-co-AnMA-co-tBCEMA): 1 mol % AnMA, 5 mol% tBCEMA.
(f) P(EHMA-co-AnMA-co-tBCEMA): 1 mol % AnMA, 11 mol% tBCEMA.

Latex-OH Plus Hexamethoxymethylmelamine (HMMM)

Our experiments on methoxymethyl melamine crosslinking were carried out with a butyl methacrylate copolymer with hydroxyethyl methacrylate (HEMA) and methacrylic acid, containing 4 mol%-OH groups and 1 mol%-COOH groups.[26] The particles were prepared by seeded emulsion polymerization under monomer-starved conditions from a common unlabeled seed. In this way we prepared matched pairs of Phe- and An-labeled latex particles each containing 1 mol% dye, plus a third latex consisting of 0.5 mol% each of Phe and An groups. We used a 1:1 mixture of the donor- and acceptor-labeled particles to study polymer diffusion rates in latex films with and without Cymel 301, a melamine product rich in HMMM. We used the doubly labeled particles to assess the location of HMMM in the films once the water had evaporated.

Location of the Melamine: There have been many years of speculation about the location of melamine formaldehyde derivatives in latex films. It is commonly thought that the melamine reactant accumulates in the interstitial spaces between particles in a latex film and reacts selectively with functional groups near the particle surface. It is also possible that the melamine derivative could dissolve in the latex polymer and become uniformly distributed in the film. These two possibilities are shown in *Figure* 9. Until very recently, there has been no evidence to support or to cast doubt on these assertions. Hexamethoxymethyl melamine (HMMM) is soluble in water, whereas its higher oligomers tend to give turbid solutions. These differences complicate the problem of identifying the location of the melamine derivative in the system.

When we prepared films from a pure PBMA latex with 20 wt% HMMM added, the films were cloudy. The turbidity indicates that HMMM did not fully dissolve in the PBMA polymer, but formed separate domains large enough to scatter light. When HMMM was mixed with the P(BMA-*co*-HEMA-*co*-MAA) latex described above, the films obtained were completely transparent. To assess the location of the HMMM in the film, we repeated this experiment on films prepared from the doubly labeled latex, in which donor and acceptor groups are randomly distributed within each cell as shown. If HMMM dissolves in the latex polymer, it dilutes the dyes and increases their mean separation as shown in *Figure* 9. As a consequence, one expects the ET quantum efficiency Φ_{ET} to decrease. On the other hand, if HMMM is confined to the interstitial spaces between the particles, one expects Φ_{ET} to have a

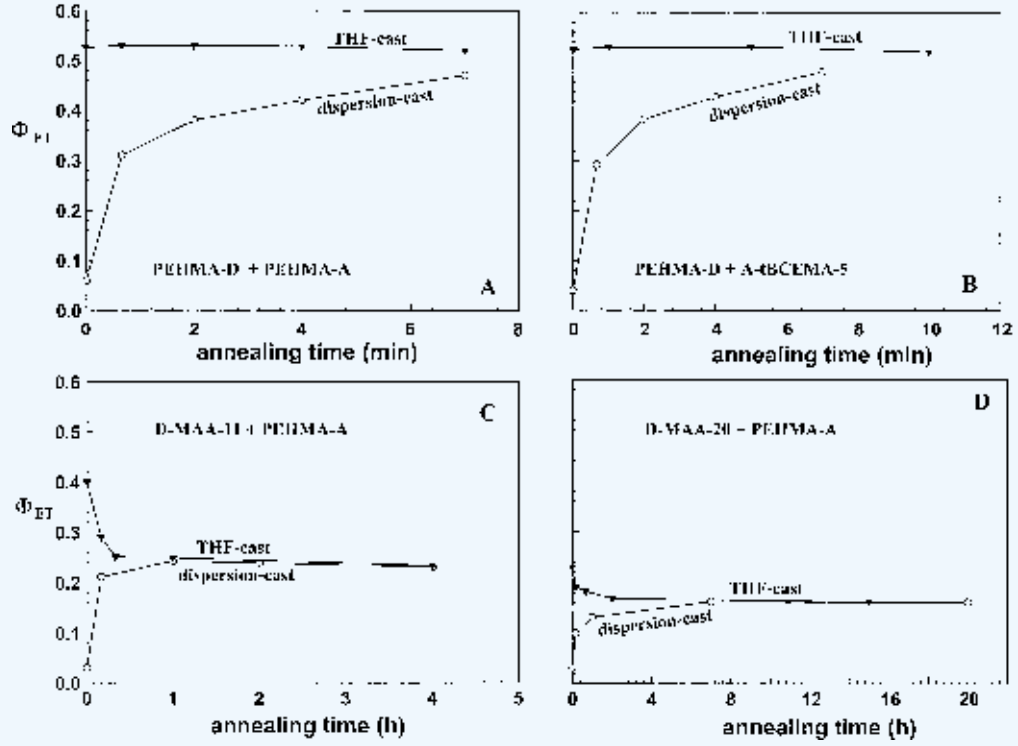


Figure 12—Plots of the F_{ET} vs. annealing time for four pairs of latex films. In each example, the upper curve refers to a film cast from a mixture of the two polymers dissolved in THF. The lower curve refers to a film prepared from a mixed dispersion of the two types of latex in water. All films were annealed at 60°C. All of the polymers have similar molecular weights.

value similar to that in the film without HMMM. The experiment is decisive. For 10 and 20 wt % HMMM, Φ_{ET} values decrease by the amount expected if the HMMM were uniformly dissolved in the latex polymer. The solubility of HMMM in the polymer is promoted by the 4 mol%-OH and 1 mol%–COOH groups present in the PBMA copolymer.

Diffusion and Crosslinking Rates: To study intercellular polymer diffusion rates, we examined films in which half of the P(BMA-HEMA-MAA) latex were labeled with Phe and half were labeled with An. In this system, no acid catalyst was added. Rather, the latex dispersion was treated with an ion-exchange resin to convert all the carboxyl groups to the –COOH form, conditions which Hahn[27] reported to be very effective for the acid-catalyzed cure of –OH containing latex films with glycoluril. In the P(BMA-HEMA-MAA) system, less than 10% gel was detected when films containing 20 wt% HMMM were heated for four hours at 80°C, but a similar treatment at 100°C led to a gel content of greater than 80% and a swell ratio (1,4-dioxane) of six. After four hours at 150°C, the system was fully crosslinked, with a swell ratio of three. In a subsequent set of experiments, films containing 20 wt % HMMM were annealed at 80°, 100°, 120°, and 150°C, and examined periodically by energy transfer measurements to assess the degree of polymer interdiffusion. These results are shown in *Figure* 10 for a polymer of M_w = 750,000 (M_w/M_n = 3).

In *Figure* 10A we see that at 80°C, in the absence of HMMM, polymer diffusion is slow, reaching an f_m value of 0.12 after four hours. When such films were heated for much longer times, f_m continued to increase, eventually reaching 1.0. In the presence of 20 wt% HMMM, the diffusion rate was strongly accelerated, reaching an f_m value of 0.3 at 80°C after two hours. The first important conclusion from these experiments is that HMMM acts as a plasticizer to promote the polymer diffusion rate in these films. Even though no gel formation occurs on this time scale, there is a suggestion in the data of diffusion coming to a halt after an hour. While this point requires further investigation, it is consistent with the formation of long chain branches in an already high molecular weight polymer.

At 100°C, the polymer diffusion rate is substantially faster than at 80°C. In the presence of HMMM, polymer diffusion is accelerated at early annealing times, but diffusion ceases after an hour. These effects are even more pronounced at 120°C (*Figure* 10C), and one observes that after 70 min, the extent of diffusion in the film without HMMM exceeds that in the HMMM-containing film. The data show, not surprisingly, that both the diffusion rate and the chemical reaction rate are accelerated by an increase in temperature. One expects the two processes to have different sensitivities to temperature. The data show that the system evolves to a higher extent of mixing when the polymer is cured for a short time at 150°C than when it is cured for a much longer time at lower temperatures. From this result, we conclude that the activation energy

for the crosslinking reaction is smaller than the effective activation energy for polymer diffusion.

Another more important lesson from these experiments is that the crosslinking agent acted as a plasticizer and a reactive diluent in the system. Prior to crosslinking it increased the free volume of the system and markedly enhanced the rate of polymer diffusion. Eventually it reacted to become part of the network. A crosslinking agent can only behave in this way if it is fully soluble in the polymer matrix at the cure temperature. If the crosslinking agent is confined to the interstitial spaces between cells in the film, or swells only the surface region of the cells as suggested in *Figure* 9, it can still react in a way as to enhance the mechanical properties of the film after cure, but it will not promote polymer diffusion in the film.

Carbodiimide-Latex Plus Carboxy-Latex

In this section we consider a prototype system for a "two-pack in one pot" formulation. In a two-pack formulation, one mixes components that have a high intrinsic reactivity toward one another. To create a formulation in which both components can be stored for long periods of time in the same container, one needs to separate the reactants into separate packages. This type of approach is possible with a blend of two different types of latex particles. Here we consider a system in which one type of particle contains carbodiimide (–N=C=N–) groups.[28] The other type of latex particle contains carboxylic acid groups. As shown in *Figure* 11, the reactive functional groups are localized in separate particles. When the dispersion dries to form a film, some of the –N=C=N– containing cells are adjacent to –COOH-containing cells. Crosslinking occurs when the –N=C=N– groups and –COOH groups react to form an N-acyl urea. The two arrows in the drawing of the latex film emphasize that the crosslinking reaction has to be described as a reaction-diffusion process. The chemical reaction cannot take place until the polymer chains containing the two different groups diffuse across the intercellular boundary to bring the groups into proximity. Each time a reaction occurs, a linear polymer is converted to a branched polymer, or becomes incorporated into a polymer network. Branching will cause a substantial decrease in the polymer diffusion rate, and polymers that are part of crosslinked networks are limited to local diffusion of the chains between branch points and somewhat larger amplitude diffusion of their dangling ends. If the reaction is significantly faster than the diffusion step, the polymers will create a tightly crosslinked membrane at the interface between the two types of cells, which will suppress further diffusion across that boundary.

Carbodiimide groups can be introduced into acrylate latex via emulsion copolymerization using t-butylcarbodiimidoethyl methacrylate (tBCEMA) or cyclohexylcarbodiimidoethyl methacrylate as the functional co-monomer. Pham in my group examined this system as part of his Ph.D. thesis research.[29] He prepared a series of latex particles containing these two methacrylates as co-monomers. He showed that the –N=C=N– group was much more stable to hydrolysis if the t-butyl derivative was employed and if 2-ethylhexyl methacrylate was used as the base monomer instead of butyl methacrylate.[30] Typical recipes used for the synthesis of these latex particles are shown in *Table* 1, and the characteristics of the samples are listed in *Table* 2. The –N=C=N– group is very sensitive to acid, as well as to strong base. This latex was prepared and stored at pH 8. The MAA-containing latex was prepared in the absence of buffer to maximize incorporation of MAA into the latex particles. The dispersions were then neutralized to pH 8 with ammonia for all of the experiments described here.

Our notation is also described in *Table* 2. We use D to refer to Phe-labeled particles, A to refer to An-labeled particles. For the methacrylic-acid-containing latex particles, MAA-11 and MAA-20 refer to the samples containing 11 mol% and 20 mol% MAA groups respectively; A-tBCEMA-5 refers to the An-labeled latex containing 5 mol% t-butyl-carbodiimidoethyl methacrylate. Since all of the particles were prepared under monomer-starved conditions (from a common seed latex), we assume that the functional groups are uniformly distributed throughout the particle. Titration of the acid groups in MAA-11 and MAA-20 shows that only a fraction of these groups are located at the particle surface. Pham found that essentially all of the –N=C=N– groups survived the emulsion polymerization reaction conditions, and 91% of the –N=C=N– groups in a t-butyl-carbodiimidoethyl containing PEHMA latex survived storage for one year in water at pH 8.

Polymer Miscibility: When we designed the experiments previously described, we imagined that the carbodiimide-containing latex polymer and the carboxylic acid-containing polymer would be fully miscible, and that the development of optimum film properties would be related only to the timing of polymer diffusion and crosslink formation. This assumption turned out to be incorrect. The presence of a significant fraction of –COOH groups in P(EHMA-*co*-MAA) seriously limits its miscibility with PEHMA itself and with P(EHMA-*co*-tBCEMA).[31] We summarize these results in *Figure* 12. These films were prepared at 4°C to minimize the extent of film formation occurring during sample preparation. The newly formed film exhibited initial values of $\Phi_{ET} \approx 0.06$, which we attribute to interfacial ET. The films were then heated at 60°C to promote polymer diffusion.

In *Figure* 12A we show the results for a film prepared from a mixture of PEHMA-D + PEHMA-A. Polymer diffusion is rapid at 60°C. The value of Φ_{ET} of 0.45 after 7.5 min annealing signifies that the mixing between the PEHMA-D and PEHMA-A polymers was nearly complete and would reach completion if the film were annealed for a sufficient time. To test the meaning of this value, we dissolved the film in an organic solvent (tetrahydrofuran, THF) and cast a film. We expect that the two labeled polymers are intimately mixed in this solution. In the freshly cast film we found $\Phi_{ET} = 0.52$, and this value remained stable as the film was annealed at 60°C. This value corresponds to a random mixture of the donor and acceptor chromophores in the film, and the magnitude of Φ_{ET} is determined only by the concentration of An groups in the film. This is the type of behavior one expects for polymers (here PEHMA-D and PEHMA-A) that are fully miscible.

In the latex film formed from D-MAA-11 and PEHMA-A, the evolution of Φ_{ET} was very different (*Figure* 12C).

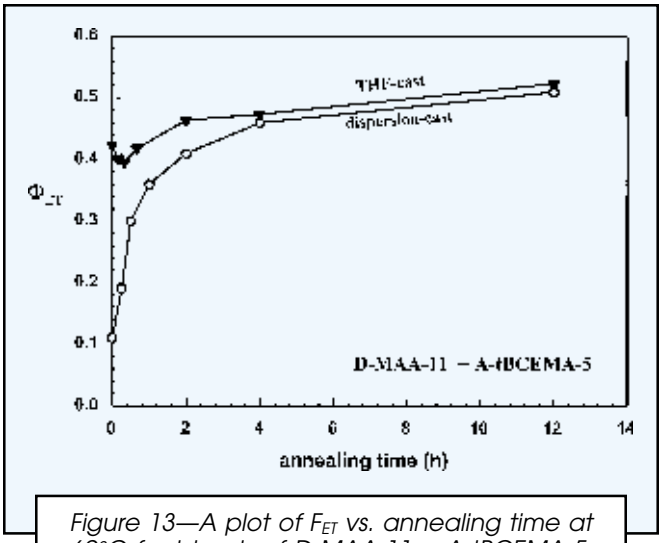


Figure 13—A plot of F_{ET} vs. annealing time at 60°C for blends of D-MAA-11 + A-tBCEMA-5. The upper curve refers to a film cast from THF solution; the lower curve to a latex film formed at 22°C.

When this film was heated at 60°C, Φ_{ET} increased in magnitude, but leveled off at $\Phi_{ET} = 0.25$. In the film formed from D-MAA-20 and PEHMA-A (*Figure* 12D), polymer diffusion occurred in the initial stages of annealing, but now, with 20 mol% MAA in the acid-containing copolymer, Φ_{ET} reached a limiting value of only 0.16. One can see in *Figure* 12 that the presence of the acid groups slows down the rate of diffusion. In the acid-free latex film, extensive polymer diffusion occurs on the time scale of minutes at 60°C. In the film prepared with MAA-11, it took an hour for the film to reach its limiting value of Φ_{ET}, and more than four hours for the film prepared with MAA-20. The clearest indication of limited miscibility is seen in the corresponding solvent-cast films. When equal amounts of D-MAA-11 and PEHMA-A were dissolved in THF and then cast onto a quartz substrate, the initial value of Φ_{ET} was 0.4, indicating that demixing occurred as the solvent evaporated. When this film was heated, Φ_{ET} values decreased. A similar result was found for the solvent cast mixture of D-MAA-20 and PEHMA-A, where the initial value of Φ_{ET} was 0.25. For both solvent-cast films, annealing promoted further demixing, and the systems leveled off at the same Φ_{ET} value as the annealed latex film. In contrast, the films prepared from a mixture of PEHMA-A + A-tBCEMA-5 have a limiting Φ_{ET} value of 0.52 (*Figure* 12B). The presence of 5 mol% (or even 10 mol %) –N=C=N– groups does not interfere with polymer miscibility.

Competition Between the Reaction and Polymer Diffusion: The blend of D-MAA-11 + A-tBCEMA-5 constitutes a reactive system in which the two polymers contain functional groups that can react initially to produce a graft copolymer, and eventually a crosslinked network. The reaction is that of the carbodiimide group of the A-tBCEMA-5 with the carboxylic acid group of the D-MAA-11 to form an N-acyl urea. The films we examined contained an equal number of the two particles but a 2:1 ratio of –COOH to –N=C=N– groups. An example is shown in *Figure* 13.[32] The film from this latex blend, freshly prepared at room temperature, has $\Phi_{ET} = 0.11$. It is likely that

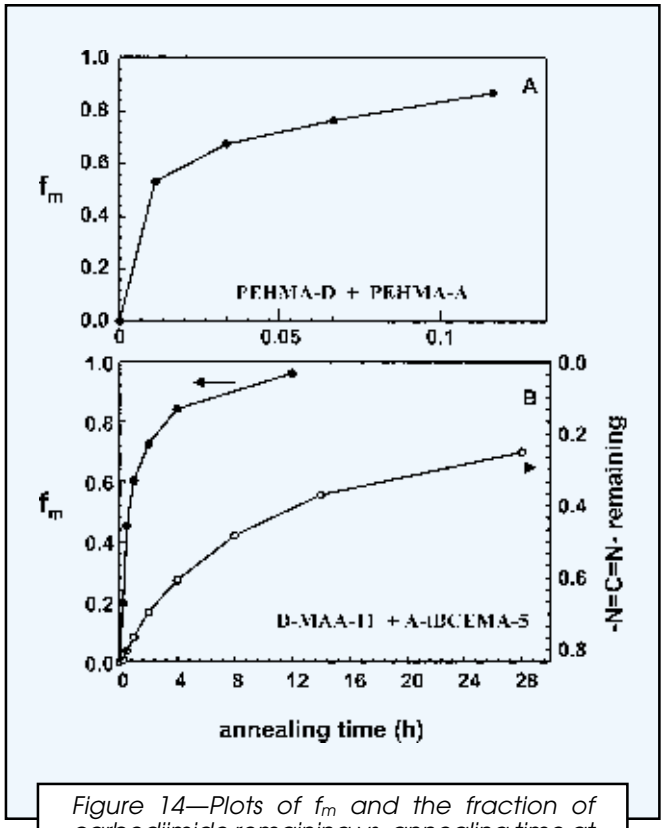


Figure 14—Plots of f_m and the fraction of carbodiimide remaining vs. annealing time at 60°C for two latex films. A refers to a PEHMA film with no reactive functionality; B refers to a film prepared from a 1:1 mixture of D-MAA-11 + A-tBCEMA-5.

local polymer interdiffusion contributes to this value, since this film was formed at 22°C, not 4°C. When the film was annealed at 60°C, Φ_{ET} increased to 0.36 over one hour, and then to 0.52 over 12 hr. This is a fascinating result, because it indicates that a fully mixed film was obtained. In this film, polymer diffusion is faster than crosslinking, and thus the film achieves full mixing. The chemical reaction plays an important part in the process because it provides a means of making the two components miscible. One can also see its influence in terms of the rate of the interdiffusion process since the growth in Φ_{ET} is significantly slower than in the case of D-MAA-11 + PEHMA-A.

In order to point out some of the important features of the competition between polymer diffusion and the crosslinking reaction in the D-MAA-11 + A-tBCEMA-5 latex films, we replot the data in *Figure* 14 to show how the growth of f_m compares with the consumption of –N=C=N– groups. We note that about 18% of the –N=C=N– groups reacted as the film formed at 22°C. It is likely that the graft copolymer that formed was responsible for the relatively rapid interdiffusion that occurred during the early stages of annealing. As a benchmark, we also show the corresponding plot of f_m versus time for the PEHMA-D/PEHMA-A blend. Here full mixing occurred on the time scale of minutes. In the reactive film, the rate of polymer diffusion is much slower. It took about two hours for f_m to reach 0.6. At this point, the gel content was small (10%) but growing rapidly, and 75% of the –N=C=N– groups

remained unreacted. When f_m = 0.75, the gel content reached 50%, and the swell ratio of the gel was about six. At f_m = 0.80, the gel content reached 75%. As f_m approached one, the gel content reached 100% with a swell ratio below five. We note that f_m = 1 corresponds to polymer diffusion over a distance comparable to a cell radius. Thus by the time the polymers diffused an average distance of 50 nm, the gel content in the latex reached unity, the swell ratio was small, and 40% of the –N=C=N– groups remained unreacted. As *Figure* 14 shows, the reaction of –COOH and –N=C=N– continued long after the gel content reached 100%, coupled to local motion of the chain segments between crosslinks.

To emphasize the role that the chemical reaction plays in promoting miscibility of the two polymers, we show the results of a solvent cast film as the upper curve in *Figure* 13. We prepared separate freeze-dried samples of the two latex polymers D-MAA-11 and A-tBCEMA-5, and dissolved them individually in THF. These solutions were mixed and then rapidly cast onto a quartz substrate and allowed to dry. As one can see in *Figure* 13, the two polymers undergo partial demixing upon drying (Φ_{ET} = 0.40), and then further demixing when heated to 60°C. Φ_{ET} drops to 0.38 during the first half hour of annealing before it begins to grow. As the reaction proceeds, Φ_{ET} reaches its limiting value of 0.52.

Tensile Measurements and Ambient Cure: The experiments described earlier indicate that polymer diffusion and crosslinking take place readily at 60°C. These experiments were carried out on films with a thickness (50 to 60 µm) typical of latex coatings. In order to test the consequences of ambient cure on film properties, we carried out a series of experiments on thicker films to be used for tensile testing. These experiments allowed us to examine the evolution of the mechanical properties of the films.

To obtain the defect-free 0.5 mm films required for tensile testing, the dispersions were dried slowly at ambient temperature over a period of three days. This procedure led to tough elastomeric films, with an extension to break of nearly a factor of seven! This is a surprising result. The entanglement length of PEHMA is in the range of 30,000 to 40,000. The latex polymers in this sample are too short to give this kind of elastic behavior. While these unannealed films had only a small gel content, a fraction of the –N=C=N– groups reacted during preparation and drying of the films. This reaction led to a build up of the polymer chain length, creating the entanglements from which the mechanical properties derive. Upon heating of these films at 60°C, both the chemical reaction rate and the polymer diffusion rates were enhanced. The net effect of annealing was that the tensile strength increased and the extension-to-break decreased.

CONCLUSIONS

We have examined the competition between the rate of crosslinking and the rate of polymer diffusion in three different types of latex films. Experiments with IBMA-containing latex are a prototype of a system in which the reactive groups are uniformly distributed throughout the latex polymer, but remain unreactive except in the presence of sufficient heat, or heat plus an acid catalyst. We showed that in the presence of strong acid (0.5 wt% PTSA at 80°C), a small but significant extent of polymer diffusion took place, but rapidly slowed as the reaction between IBMA groups created long-chain branches and crosslinks in the film. Gel formation limited the extent of mixing to $f_m \approx 0.4$. When a much weaker acid catalyst was employed (0.2 wt% H_3PO_4 at 80°C) the rate of polymer diffusion was almost identical to that in a film lacking an acid catalyst until $f_m \approx 0.8$. At this point, the growing gel content and branch formation cause a marked slowing down in the rate of further polymer diffusion. When similar films were heated at 100°C, both the diffusion rate and the crosslinking rate were accelerated. The value of f_m increased rapidly to 0.9 and then ceased to increase. In this type of film, the variables that can be manipulated to control the relative rates of cure and polymer diffusion are the choice of acid catalyst and the reaction temperature.

Experiments with HMMM in a latex film containing hydroxyl and carboxylic acid groups are a prototype of a system in which one adds a multifunctional crosslinking agent to a film containing appropriate functional groups. We showed that in this system in the dispersed state, HMMM remains primarily in the aqueous phase, but as the film dries, it dissolves in the polymer film. In the film, it acts as a plasticizer to promote the rate of polymer diffusion, and as a reactive diluent, which becomes completely incorporated into the final cured latex film. With a weak acid catalyst (ion exchanged –COOH groups), cure occurred very slowly at 80°C (over much more than four hours), but relatively rapidly at 100° and 120°C. We found that the rates of polymer diffusion and the rates of the cure reactions were both accelerated with increasing temperature. The system appears to reach higher levels of mixing (larger limiting values of f_m) at elevated temperatures.

We also carried out extensive studies on latex blends in which one of the components contained the carbodiimide group as the reactive functionality. This system is a prototype of a "two-pack in one pot" system, in which the two reactive functional groups are packaged in separate latex particles, and thus cannot react while the latex remains in the dispersed state. We used a carboxylated latex (a methacrylic acid copolymer) as the reaction partner for the –N=C=N– containing latex, with 2-ethylhexyl methacrylate as the main monomer. The film formed from this blend of latex particles is expected to have a random distribution of –COOH and –N=C=N– containing cells. A special feature of this system is that the presence of the –COOH groups in the EHMA copolymer limits the miscibility of this polymer with PEHMA itself and with the carbodiimide-containing EHMA copolymer. As these films are annealed, polymer diffusion across the intercellular boundaries brings the –COOH and –N=C=N– groups into proximity for them to react (to form an N-acyl urea). This reaction generates graft copolymer, which acts as a compatiblizing agent for the two polymers and drives their miscibility. When this reaction is carried out at 60°C, the diffusion step is significantly faster than the formation of gel. The system evolves to reach f_m = 1.0 while a significant fraction of the –N=C=N– groups remain unreacted.

A recent theoretical paper from the de Gennes group[33] examined the competition between polymer interdiffusion and crosslinking in a system conceptually similar to

that of the IBMA-containing latex films. To simplify the problem, they considered polymer chains of identical length, separated initially by a dividing plane. Each chain contained a small fraction of reactive groups, and they assumed that a single reaction between two such groups would create a branched polymer incapable of further diffusion. They examined the factors that promote the growth in adhesive strength between adjacent cells in the film. Among the most important conclusions are that the major contributions to the strength of the interface are crosslinks involving chains that span the interface. For this to occur, polymer diffusion has to be faster than the crosslinking reaction, but the extent of mixing does not have to involve all the polymer in each cell. Rather, the chains initially adjacent to the interface have to diffuse a distance comparable to their radius of gyration. A thermoset latex film can achieve full strength for f_m values less than 1.0. In terms of the ET experiment, the magnitude of f_m required depends upon the length of the polymer and the size of the latex particles. Long chains bearing relatively few functional groups are required to undergo more extensive diffusion than a system consisting of lower molar mass polymer rich in reactive functionality.

For many applications, other properties of the cured film are important other than mechanical strength. For example, to achieve good solvent resistance, a film must reach a sufficient crosslink density that the swell ratio is less than two.

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