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Interdiffusion vs Cross-Linking Rates in Isobutoxyacrylamide-Containing Latex Coatings

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ABSTRACT: We describe the relative rates of polymer diffusion and cross-linking in a latex film containing 2 wt % (1.3 mol %) of *N*-isobutoxymethylacrylamide (IBMA) as a cross-linking agent. The latex base monomer is a 4:5 weight ratio copolymer of butyl acrylate and methyl methacrylate (BA−MMA) with a glass transition temperature of 12 °C. Polymer diffusion was monitored by direct energy transfer (ET) in films prepared from latex particles labeled with phenanthrene as the donor and anthracene as the acceptor. In a model film without IBMA, the quantum yield for ET (Φ_{ET}) increased to its maximum value of 0.62 in a few minutes at 120 °C, whereas at 80 °C the films required hours of annealing to achieve full mixing. The temperature dependence of the diffusion rate indicated an effective activation energy of 43 kcal/mol. In contrast, a film prepared from latex of similar molecular weight containing 2 wt % IBMA formed gel rapidly at 80 °C in the presence of 0.5 wt % toluenesulfonic acid. The system reached its maximum gel content over 40 min. Diffusion was retarded over all annealing times, but after 20 min at 80 °C, when the gel content was 60%, polymer diffusion ceased. If one uses a weaker acid, e.g., phosphoric acid instead of PTSA, the cross-linking rate is slower, whereas the polymer diffusion rate, prior to extensive gel formation, is not very much affected.

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 loss of volatile organic solvents to the atmosphere. In response, new approaches have been developed to replace traditional solvent-based coatings with waterborne alternatives. Solvent-borne coatings have had particular prominence in the area of industrial coatings, where performance is essential. 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, though the formation of cross-links. The challenge within the industry has been to maintain or improve properties at a reasonable cost, while at the same time meeting the need for environmentally friendly coatings.

Waterborne polymer systems can be designed to provide the properties required of industrial coatings by introducing functional groups that are capable of forming cross-links.[1,2] These systems include functional latex particles containing, for example, epoxy groups, *N*-methylolacrylamide groups, *N*-(isobutoxymethyl)-acrylamide (IBMA), and acetoacetate groups. Some functional groups like epoxy or IBMA will self-react under suitable reaction conditions, whereas other functional groups require the addition of a multifunctional reactant (external cross-linker) to introduce cross-linking.

Many of the replacement waterborne formulations themselves contain substantial amounts of organic solvents, for example as fugitive plasticizers, to promote the coalescence of latex films. As a consequence, the industry remains under pressure to further reduce or even eliminate all volatile organics from the next generations of waterborne coatings. Progress in that direction requires enhanced knowledge about the mechanism of film formation and the subsequent buildup of film properties in these systems. In latex coatings, the polymer that will serve as the binder is present as an aqueous dispersion of particles of colloidal dimensions. As the dispersion dries, the particles come into contact. If the temperature is above the minimum film-forming temperature (MFT) of the system, the particles are compressed into a void-free film consisting of close-packed polyhedral cells.[3] In the newly formed film, adhesion between these cells is weak. As polymers diffuse across these interfaces, the strength of the film increases.

One strategy for achieving enhanced performance in latex films without the need for volatile coalescing aids relies on building cross-linking chemistry into latex particles that have a glass transition temperature (T_g) below the application or processing temperature. Here an understanding of the relative rates of polymer diffusion and cross-link formation is essential. Recent studies[4] show that in thermoset latex films polymer diffusion across the intercellular boundary must precede cross-linking or the films will remain weak. If cross-linking is confined to individual cells, each cell remains an individual microgel with little adhesion to its neighboring cells.[5] The presence of cross-links provides thermoset coatings with enhanced tensile strength and with abrasion and mar resistance as well as acid, alkali,

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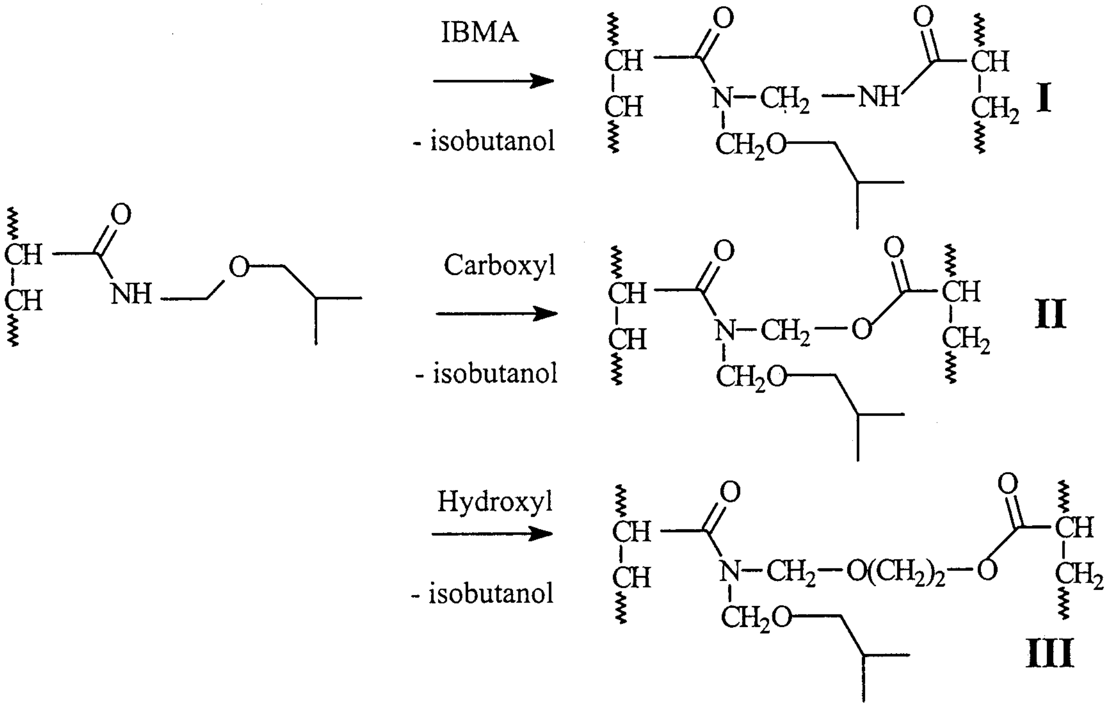
Scheme 1



and solvent resistance lacking in thermoplastic latex coatings. These performance criteria are essential for most industrial coatings.

In this paper we are concerned with the relative rates of polymer diffusion and cross-linking in latex films containing small amounts of *N*-(isobutoxymethyl)acrylamide (IBMA) as a cross-linking agent. Scheme 1 shows several reactions typical of IBMA cross-linking. The reaction between two IBMA groups forms a methylene–bis(acrylamide) linkage **I**. Structure **II** is the result of an exchange reaction with a polymer-bound –COOH group, and structure **III** is formed by a similar exchange reaction with a polymer-bound hydroxyl group.[6] Bassett et al.[7] monitored the heat evolution associated with these reactions and showed that these reactions of IBMA in latex films are strongly promoted by the presence of acid, either copolymerized carboxyl groups or an added strong acid like toluenesulfonic acid. The reaction rate is relatively unaffected by the presence of hydroxyl groups.

In this paper we examine butyl acrylate–methyl methacrylate (BA–MMA) copolymer latex films that contain small amounts of IBMA as a comonomer. We describe factors that affect the rates of polymer diffusion and cross-linking in these films as a function of temperature and the choice of acid catalyst. We monitor the interdiffusion rate by the direct energy transfer (ET) technique, which provides a convenient tool for monitoring intercellular polymer interdiffusion in the films,[8] and we measure the cross-linking rate by measuring the increase in gel content with annealing time.

Experimental Section

THF was distilled over metallic sodium and benzophenone. Other solvents and reagents were used as received. Methacrylic acid (MAA), butyl acrylate (BA), and methyl methacrylate (MMA) were distilled under vacuum prior to use. Potassium persulfate (KPS), sodium bicarbonate ($NaHCO_3$), dodecyl mercaptan (DM), and sodium dodecyl sulfate (SDS, Aldrich) were used as received. Distilled water was further purified through a Millipore Milli-Q system. Particle size and size distributions were measured by dynamic light scattering employing a Brookhaven BI-90 particle sizer. Molecular weight and molecular weight distributions were measured by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as the eluent and poly(methyl methacrylate) calibration standards. GPC measurements employed a Waters pump, two columns (HR3 and HR4, effective molecular weight range 500–500 000), and tandem fluorescence (Kratos FS 970) and refractive index (Waters R-400) detectors.

Latex Preparation. All latex dispersions were prepared by seeded semicontinuous emulsion polymerization under monomer-starved conditions. An unlabeled dispersion of seed particles was prepared on a large scale by batch emulsion polymerization with only base copolymer, and the same seed was used for the preparation of the all latex particles. The seed particles represent 12 wt % of the final latex. In the second stage, the aqueous solution containing the surfactant SDS and initiator (potassium persulfate) and the organic solution containing the base monomers, the fluorescent monomer (1 mol %), and other comonomers (IBMA, MAA) were fed continuously into the reactor which contained the preheated dispersion of seed particles. An example of the preparation of 9-phenanthylmethyl methacrylate (PheMMA)-labeled latex P(BA-*co*-MMA-*co*-IBMA-*co*-MAA) is given below. Typical recipes are given in Table 1.

A 2 L three-neck flask equipped with a condenser and a mechanical stirrer was filled with water (900 mL), BA (31.05 g), MMA (36.45 g), sodium bicarbonate (1.35 g), and sodium dodecyl sulfate (SDS, 0.90 g). The mixture was purged with N_2 for 30 min and then heated to 80 °C with an oil bath. A solution of potassium persulfate (KPS, 1.30 g) in water (25 mL) was added to the above mixture by a syringe to initiate the polymerization. After the reaction mixture was heated for another 2 h, the dispersion of seed particles ($d = 72$ nm, 7 wt % solids content) was obtained.

In the second-stage polymerization, an aliquot of the seed dispersion (60.0 g) described above was introduced into a 250 mL three-neck flask equipped with a condenser and a mechanical stirrer. The dispersion was purged with N_2 for 30 min and then heated to 84 °C under N_2. Two solutions were then fed into the flask at the same time and at constant feed rate (0.05 mL/min) over 12 h. One solution contained SDS (0.82 g), KPS (0.08 g), and water (30 mL). The other contained BA

Table 1. Recipes for the Synthesis of Anthracene-Labeled Poly(butyl acrylate-*co*-methyl methacrylate) Latex Particles

	first stage[a]	second stage
seeds (g)		60.00
BA (g)		12.00
MMA	31.05	15.18
IBMA	36.45	0.57[b]
MAA		0.53[b]
dodecyl mercaptan (mL)	0.0	0.07
water (mL)	900.0	30.0
KPS (g)	1.30	0.0736
SDS (g)	0.90	0.8144
$NaHCO_3$	1.35	
An(**2**) or An(**3**)		1 mol %
reaction time (h)	2	17
temp (°C)	80	84

[a] This seed latex was used for all emulsion polymerizations reported here. [b] The wt % MAA and IBMA reported in the text is calculated on the basis of total monomer in the second stage: 2 wt % MAA corresponds to 2.4 mol % MAA; 2 wt % IBMA corresponds to 1.5 mol % IBMA.

(12.0 g), MMA (15.0 g), dodecyl mercaptan (DM) (72 μL), IBMA (0.57 g, 2 wt % of the total monomers), a fluorescent comonomer (Phe-MMA, 0.66 g, 1 mol % of the total monomer), and MAA (0.53 g, 2 wt % of the total monomer). After the addition was complete, the reaction mixture was stirred and heated for another 6 h. This reaction produced a dispersion with 24.0 wt % solids content with a particle diameter about 140 nm and with a narrow size distribution.

By adding different amounts of DM as a chain transfer agent, the molecular weight of the latex polymers could be varied. For example, the low molecular weight latex polymer samples were obtained by adding 0.9 wt % DM based on total monomers, and the high molecular weight latex polymers were obtained by adding 0.2 wt % DM based on total monomers. The characteristics of the latex particles obtained are summarized in Table 2.

Film Formation. The films used for energy transfer experiments were prepared as follows: A few drops of a latex dispersion (containing 1:1 ratio of mixed Phe- and An-labeled particles, 10 wt % solids) were spread on a small quartz plate (20 × 10 mm). The film was allowed to dry at 23 °C in the open air in order to reduce the extent of interdiffusion before annealing. Films were dry and transparent within 2 h.

The preparation of films to be used for the gel content determination was slightly different. Dispersions of both the Phe- and An-labeled particles (20 wt % solids) were mixed in a 1:1 ratio. In some cases, 0.5 or 1 wt % of PTSA or 0.2 wt % H_3PO_4 as external catalyst was added to the dispersion. Then the mixed dispersions were poured into an all-Teflon mold, 7.0 cm × 7.0 cm, and 1.0 mm deep. The uncovered films were allowed to dry in the dark at 23 °C for a period of 48 h and then peeled out of the Teflon mold. The average thickness of the free-standing film was 0.2 mm.

Fluorescence Measurements and Data Analysis. The films on quartz plates were placed directly on a high mass aluminum plate in an oven preheated to the annealing temperature and then annealed for various periods of time. For fluorescence decay measurements, each labeled film, before and after annealing, was placed in a quartz tube and degassed with N_2 for 2 min before the measurement. Fluorescence decay profiles were measured by the time-correlated single photon counting technique.[9] The excitation wavelength was 300 nm, and emission from the sample was detected at 350 nm through an interference filter at 350 ± 5 nm. In the absence of anthracene as an energy transfer acceptor, Phe decay profiles were exponential, with $\tau_0 = 45.6$ ns for PheMMA-labeled P(BA-*co*-MMA) latex film and with $\tau_0 = 46.2$ ns for V-Phe-labeled P(BA-*co*-MMA) latex film. Each measurement was continued until there were 5000 counts in the maximum channel. This requires 10 min for the newly formed films and 12−15 min for films annealed for longer times.

$$\phi_{\mathrm{ET}}(t_{\mathrm{n}}) = 1 - \frac{\int_0^\infty I_{\mathrm{DA}}(t)\,\mathrm{d}t}{\int_0^\infty I_{\mathrm{D}}(t)\,\mathrm{d}t} \tag{1}$$

$$\phi_{\mathrm{ET}}(t_{\mathrm{n}}) = 1 - \frac{\mathrm{area}(t_{\mathrm{n}})}{\mathrm{area}(D)} = 1 - \frac{\langle\tau_{\mathrm{d}}\rangle}{\tau_0} \tag{2}$$

The quantum efficiency of energy transfer $\phi_{ET}(t_n)$, defined in eq 1, can be evaluated with eq 2, where $\int I_D(t)\,dt$ is the area under the donor decay profile of a film containing only donor. Since the unquenched donor decay profiles for the phenanthrene derivatives employed here are exponential, the value of the integral (area(D)) equals the unquenched donor lifetime τ_0. The term $\int I_{DA}(t)\,dt$ describes the area under the donor decay profile of a film containing both donor and acceptor. These areas have the dimension of time. Each defines an average decay times (area(t_n) = $\langle\tau_d\rangle$), where t_n refers to the time that a given sample was annealed prior to the fluorescence decay measurement. To obtain an accurate area for each decay profile, we fit each decay curve to the empirical eq 3 (with $A_1 + A_2 = 1$) and then evaluate the integral analytically from the magnitude of the fitting parameters.

$$I_{\mathrm{D}}(t) = A_1 \exp[-t/\tau_0 - P(t/\tau_0)^{1/2}] + A_2 \exp(-t/t_0) \tag{3}$$

To calculate the extent of mixing that occurs upon annealing time, we define another parameter f_m in eq 4. This parameter represents the fractional growth of ET in the system and is defined in such a way that it corrects for the energy transfer in the nascent films. In eq 4, $[\phi_{ET}(t_n) - \phi_{ET}(t_0)]$ represents the change in energy transfer efficiency between the freshly prepared film and that annealed for time t_n. $[\phi_{ET}(t_\infty) - \phi_{ET}(t_0)]$ is the difference in energy transfer efficiency between the fully mixed film and the newly formed film. To obtain values of $\phi_{ET}(t_\infty)$, representing full mixing, we took a latex film sample, dissolved it in THF, and then recast a film onto a quartz substrate.

$$f_{\mathrm{m}} = \frac{\Phi_{\mathrm{ET}}(t_{\mathrm{n}}) - \Phi_{\mathrm{ET}}(t_0)}{\Phi_{\mathrm{ET}}(t_\infty) - \Phi_{\mathrm{ET}}(t_0)} = \frac{\mathrm{area}(t_0) - \mathrm{area}(t_{\mathrm{n}})}{\mathrm{area}(t_0) - \mathrm{area}(t_\infty)} \tag{4}$$

Under some circumstances, it is useful to calculate the apparent mean diffusion coefficients, D_{app}, characterizing the rate of polymer diffusion that leads to mixing.[10,11] These D_{app} values were calculated by fitting the f_m values obtained from

Table 2. Characteristics of the Labeled Latex Particles

	latex composition	solids (%)	$10^{-3}M_w$	M_w/M_n	d (nm)	IBMA (wt %)	MAA (wt %)
1-Phe	PheMMA-labeled P(BA-*co*-MMA)	23.5	230	3.0	146		
1-An(**2**)	An(**2**)-labeled P(BA-*co*-MMA)	22.8	240	3.2	145		
2-Phe	PheMMA-labeled P(BA-*co*-MMA-*co*-IBMA)	24.6	48	2.3	140	6	
2-An(**2**)	An(**2**)-labeled P(BA-*co*-MMA-*co*-IBMA)	24.6	48	2.6	142	6	
3-Phe	PheMMA-labeled P(BA-*co*-MMA-*co*-IBMA-*co*-MAA)	24.3	37	2.9	143	2.1	1.95
3-An(**2**)	An(**2**)-labeled P(BA-*co*-MMA-*co*-IBMA-*co*-MAA	24.4	52	2.4	128	2.1	1.95
4-Phe	PheMMA-labeled P(BA-*co*-MMA-*co*-IBMA)	25.2	230	2.8	146	2.1	
4-An(**2**)	An(**2**)-labeled P(BA-*co*-MMA-*co*-IBMA)	23.2	220	2.8	142	2.1	
5-VPhe	V-Phe-labeled P(BA-*co*-MMA-*co*-IBMA)	24.5	210	3.3	135	2.1	
5-An(**3**)	An(**3**)-labeled P(BA-*co*-MMA-*co*-IBMA)	24.4	230	3.5	138	2.1	

energy transfer to a spherical diffusion model that satisfies Fick's laws of diffusion.[12] The details of the analysis and a discussion of the strengths and shortcomings of this calculation are presented in ref 11. In this analysis, a parameter f_s is needed that describes the fraction of substance (i.e., donor-labeled polymer) which has diffused across the initial boundaries after a certain time t_n. The key step is to find a relation between f_s and the growth in energy transfer efficiency (i.e., f_m) which characterizes the extent of mixing. Our analysis takes advantage of the fact that simulations of energy transfer in systems of linear polymers undergoing Fickian diffusion show that f_m is proportional to f_s up to f_m values of ca. 0.7.[13] Whether this analogy remains valid for the branched polymers present here is a topic for future investigation.

Gel Content Determination. To measure the cross-linking rate, free-standing film specimens (weight: W_0, dimension: $1.0 \times 2.0 \times 0.020$ cm^3) were immersed in 1,4-dioxane (20 mL) for 72 h. Under these conditions, almost 100% of the un-cross-linked polymer dissolves, and the gel swells. The swollen films were then carefully removed from dioxane, and the solvent on the film surface was removed by touching the polymer with a Kimwipe. The weight of the swollen film was measured (W_1). Each film was then dried again to a constant weight (W_2) in a vacuum oven. The gel content (%) is calculated from eq 5, and the swell ratio is calculated from eq 6.

$$\text{gel content (\%)} = (W_2/W_0) \times 100 \qquad (5)$$

$$\text{swell ratio} = W_1/W_2 \qquad (6)$$

Results and Discussion

Preparation and Characterization of the Latex Samples. The copolymer P(BA-*co*-MMA) with a monomer weight ratio 4:5 (mole ratio = 3:5) was chosen as the base polymer for these studies. This copolymer has a glass transition temperature of about 12 °C and is able to form transparent films under ambient conditions. We prepared five pairs of An- and Phe-labeled poly(BA-*co*-MMA) latex samples by seeded emulsion polymerization. The seed consists of a similar copolymer and represents 12 wt % of the final particle prepared by two-stage emulsion polymerization. Other monomers such as IBMA, fluorescent dye comonomers, and methacrylic acid (MAA) were introduced in the second stage. In all of the syntheses, the final latex dispersion was obtained with a solids content of about 24.0 wt %, with particle diameters in the range of 140 nm, and with a narrow size distribution. These characteristics, for each latex, are summarized in Table 2.

When we started this project, we tried to prepare P(BA-*co*-MMA) polymer without adding any chain transfer reagent to the reaction. We found by gel permeation chromatography (GPC) that a significant amount of gel had formed, in addition to a high molecular component with a very broad molecular weight distribution. We imagine that a process involving chain transfer to the polymer backbone formed the high molecular weight component. This is a common occurrence for BA-based polymers prepared by emulsion polymerization.[14] The addition of dodecyl mercaptan as a chain transfer reagent narrowed the molecular weight distribution of the polymer and also decreased the molecular weight. The high molecular weight ($M_w \cong 220\,000$) latex samples (latex 1, 4, and 5 in Table 2) and the low molecular weight ($M_w \cong 50\,000$) latex samples we describe below were prepared by the use of different amounts of 1-dodecanethiol as a chain transfer agent. The low molecular weight latex samples were used to explore the cross-linking reaction conditions. The high molecular weight samples were used to obtain information on the rates of polymer diffusion in the latex films and on the relative rates of cross-linking and interdiffusion for IBMA-containing latex films.

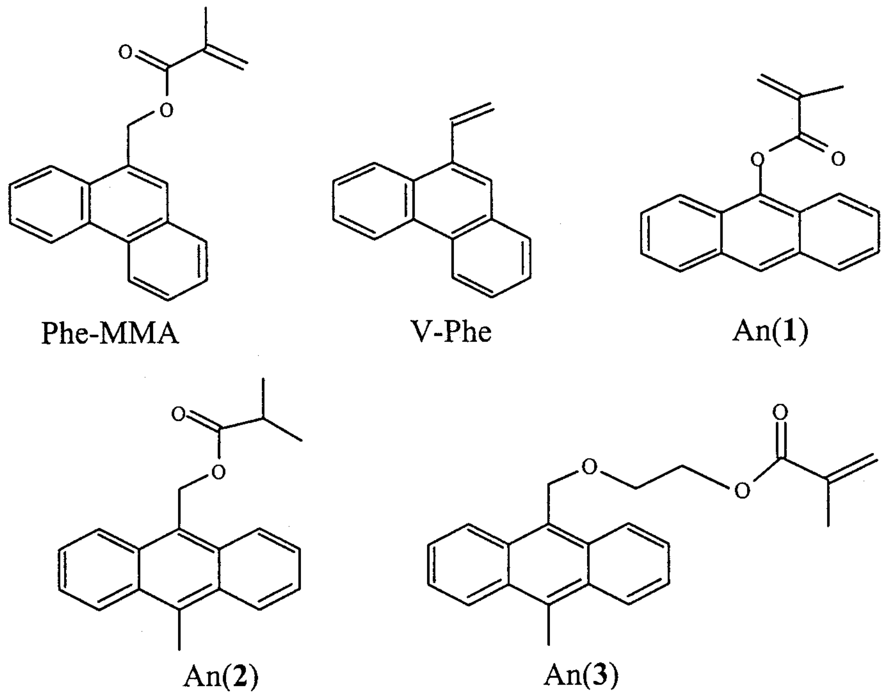
When IBMA was copolymerized with MMA and BA in the second stage of the reaction, no gel or unexpectedly high molecular weight fraction was observed by GPC, even when MAA (2 wt %) was incorporated as a comonomer. From these results, we infer that the presence of IBMA or IBMA plus MAA does not promote premature branching or cross-linking of the latex polymer.

All the experiments described here involve pairs of latex dispersions prepared from a common seed latex (d = 72 nm). In each pair, one set of particles is labeled with phenanthrene (Phe) as the fluorescent donor (D), and the other is labeled with anthracene (An) as the acceptor for direct nonradiative energy transfer (ET) experiments (see Chart 1).

In these experiments, the phenanthrene group was introduced using either 9-methylphenanthyl methacrylate (Phe-MMA) or 9-vinylphenanthrene (V-Phe). In previous experiments,[8] we introduced the anthracene group into methacrylate-rich emulsion polymers using the anthracene derivative An(**1**). When we tried to copolymerize An(**1**) with our mixture of BA and MMA, we found that An(**1**) seriously inhibited the polymerization reaction. In fact, An(**1**) turns out to be a powerful inhibitor of acrylate polymerization, and monomer mixtures rich in BA cannot be polymerized when An(**1**) is present. To explain this problem, we imagine that the more active acrylate radicals attack the 10-position of the anthracene in An(**1**).[15] As a test of this hypothesis, we synthesized An(**2**) and An(**3**) and found that they allowed us to prepare the An-labeled particles needed for these experiments. The only unfortunate feature of the two new monomers is that they both have a benzylic C−O bond. The combination of heat and acid leads to fragmentation (hydrolysis) of the dye from the polymer backbone.[16] A similar problem with polymer-bound Phe-MMA was encountered several years ago, and the problem was overcome by replacing Phe-MMA with V-Phe as a comonomer.[17] For the moment, we lack an anthracene comonomer that will survive temperatures in excess of 120 °C in the presence of acid. Copolymers containing An(**3**) are significantly more stable to the combination of heat and acid than those with An(**2**). The acid-catalyzed reactions carried out at 100 °C described at the end of this paper were carried out with latex sample 5 (Table 2) consisting of a donor-labeled latex prepared from V-Phe and an acceptor-labeled latex prepared with An(**3**). The synthesis and characterization of An(**2**) and An(**3**) are described in ref 16.

Polymer Diffusion in MMA−BA Copolymer Latex Films. As a baseline for understanding how the reactions of IBMA affect the rate of polymer diffusion in MMA−BA copolymer latex films, we first examine a model system (sample 1 in Table 2) without the reactive IBMA group. The characteristics of the latex particles in this pair of dispersions are very similar to those of sample 4 (Table 2) which contain 2 wt % (1.3 mol %) IBMA. The similarities include base polymer composition, polymer molecular weight, molecular weight distributions (MWD), and particle size. All of the sample pairs we examine form transparent and crack-free films at room temperature (22 °C).[18] From this result, we infer that as the dispersions dry, the particles deform into Voronoi polyhedral cells that fill space. The formation

Chart 1



of intimate contact between adjacent cells is a prerequisite to the polymer diffusion that leads to mechanical strength in thermoplastic latex films.

Representative donor fluorescence decays for a PheMMA-labeled P(BA-*co*-MMA) film and for a film cast from 1:1 ratio of PheMMA-labeled P(BA-*co*-MMA) latex and 9-methacryloyloxymethyl-10-methylanthracene (An(**2**))-labeled P(BA-*co*-MMA) latex (sample 1, Table 2), measured as a function of annealing time at 80 °C, are shown in Figure 1. The decay profile for the film containing only donor is exponential. In the newly formed film, the $I_{DA}(t_0)$ profile is not exponential. From the shape of the normalized decay curve, we calculate an ET efficiency (ϕ_{ET}) of 0.1. In a somewhat different system, with particles of similar size and a similar extent of labeling, we found that by preparing films at a temperature much closer to the T_g of the polymer, we could obtain transparent and crack-free films with $\phi_{ET}(0) = 0.04-0.06$. In this case, the extent of ET is typical of that expected for cross-boundary energy transfer between donors and acceptors in adjacent cells.[19] We attribute the slightly higher value of $\phi_{ET}(0)$ in the nascent film found here to a small extent of polymer diffusion at room temperature during drying process. After the film is annealed for 20 min at 80 °C, the area under the decay curve decreases, an indication of a large increase in ET due to polymer diffusion.

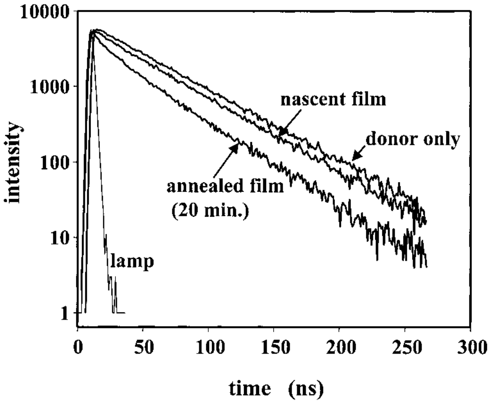


Figure 1. Donor fluorescence decay profiles of (a) a P(BA-*co*-MMA) film labeled by PheMMA only, (b) a nascent film formed at room temperature, consisting of a 1:1 ratio of PheMMA-labeled P(BA-*co*-MMA) latex and 9-methacryloyloxymethyl-10-methylanthracene-labeled P(BA-*co*-MMA) latex, and (c) the film shown in (b) annealed for 20 min at 80 °C.

To examine the rate of polymer diffusion in this system, we prepared films from 1:1 mixtures of PheMMA and An(**2**)-labeled P(BA-*co*-MMA) latex samples (sample 1, Table 2). These samples contain no IBMA groups, and hence cross-linking does not occur in this system. In Figure 2 we plot values f_m and ϕ_{ET} as a function of annealing time for films annealed at different temperatures. The data in Figures 2 indicate that, without cross-linking in the film, f_m increases as the annealing time increases, indicating that the

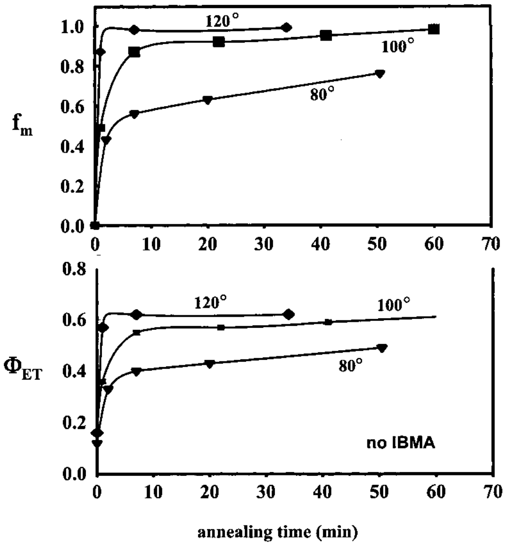


Figure 2. Plots of f_m (upper figure) and energy transfer ϕ_{ET} (lower figure) vs annealing time of the high molecular weight P(BA-*co*-MMA) latex films (sample 1, Table 2) at 80, 100, and 120 °C.

PheMMA-labeled polymers diffuse into the regions containing the An(**2**)-labeled polymers, and the An(**2**)-labeled polymers diffuse into the regions containing PheMMA-labeled polymers. From the shape of the curves, we observed that a large increase in f_m values occurs at early times, followed by a smaller increase at longer times. At 120 °C, the increase in ϕ_{ET} is extremely rapid, leveling off at a value of 0.62. This value of ϕ_{ET} is identical to that obtained from a solvent-cast film consisting of the same two polymers and corresponds to full mixing ($f_m = 1$). In an ET experiment, the extent of energy transfer reaches its maximum value when the polymer molecules in the sample diffuse a distance on the order of a particle radius.[13] Further diffusion does not lead to any increase in the extent of ET.

From Figure 2, we can also see that f_m depends strongly on the annealing temperature. For example, over 2 min, the value of f_m reaches 0.4 at 80 °C, 0.6 at 100 °C, and 1.0 at 120 °C, corresponding to $\phi_{ET} = 0.33$ at 80 °C, $\phi_{ET} = 0.42$ at 100 °C, and $\phi_{ET} = 0.62$ at 120 °C. We would like to quantify the influence of temperature on the diffusion rate. The temperature dependence of polymer diffusion rates, like that of other viscoelastic properties of polymers that depend on large-amplitude motions of the polymer backbone, is normally described in terms of models in which the temperature dependence derives from the free volume increase due to the thermal expansion of the polymer matrix.[20] When one has limited data over a relatively narrow range of temperatures, the data often fit an Arrhenius expression. From the slope, one calculates the apparent activation energy E_a for diffusion. The magnitude of E_a depends on $(T - T_g)$, where T is a temperature in the range where the measurements were carried out.

To carry out this analysis, we need more data points at intermediate extents of mixing. Therefore, we repeated the experiments described above, but at lower annealing temperatures. These experiments require patience, because at lower temperatures, the diffusion rate is rather slow. The results are shown in Figure 3, where we plot f_m values obtained from experiments carried out at 81, 67, and 51 °C. In the upper part of the figure, we show the growth in f_m over the first 7 h of annealing, and in the lower part, we show the results of following the diffusion over 100 h of annealing.

The f_m parameter itself is not very useful for examining how the rate of polymer diffusion responds to external stimuli such as a change in temperature. For this purpose, we calculate values of the apparent mean diffusion coefficient D_{app} characterizing the diffusion rate of the polymers in the samples. These values are plotted as a function of f_m in Figure 4. We emphasize that these D_{app} values are not the true center-of-mass diffusion constants for the polymers. For Fickian diffusion, these values are proportional to the true diffusion coefficients. What we assume in carrying out this calculation is that any errors in the magnitude of individual D_{app} values will cancel when we compare values obtained at different temperatures. In our experience, this assumption turns out to be reasonable if one is careful to compare different experiments at the same extent of mixing. For example, an Arrhenius plot (log D_{app} vs $1/T$) of the data in Figure 4 plotted for D_{app} values at $f_m = 0.4$ yields an activation energy of 43 kcal/mol (180 kJ/mol). Since temperature affects the rate of diffusion by a change in the microscopic friction coefficient, the magnitude of E_a should be independent of f_m. We test this idea by using the value of E_a to calculate a shift factor to create a master curve of D_{app} values at 51 °C. The shifted values calculated in this way are shown as the open points in Figure 4. From these data, we conclude that the diffusion of P(BA-*co*-MMA) with a mole ratio MMA/BA = 5/3 is characterized by an effective activation energy of 43 kcal/mol in the range 40−70 °C above T_g.

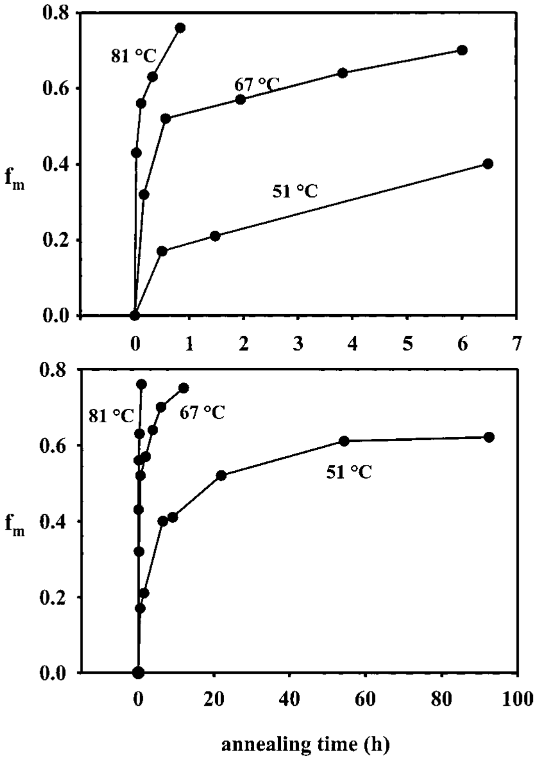


Figure 3. Plots of f_m vs annealing time of the P(BA-*co*-MMA) latex films shown in Figure 2 at lower temperatures.

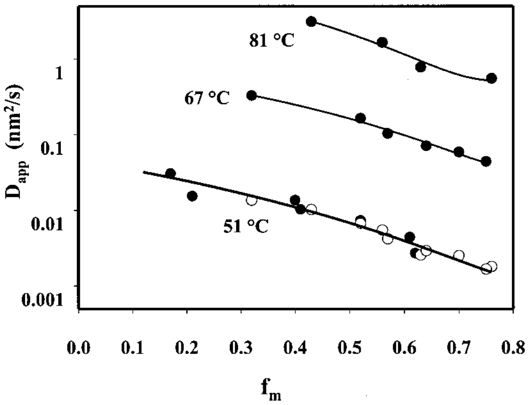


Figure 4. Values of the apparent diffusion coefficient D_{app} calculated from the data in Figure 3 plotted vs the extent of mixing f_m. The open points refer to data obtained at higher temperatures recalculated for 51 °C using $E_a = 43$ kcal/mol.

Cross-Linking Conditions. To select cross-linking reaction conditions for further examination, we carried out our first experiments on the low molecular weight latex. For the film containing IBMA but no MAA (sample 2, Table 2), we chose a composition of 6 wt % IBMA in order for the films to reach approximately the same extent of cross-linking as films cast from high molecular weight latex dispersions that contain only 2 wt % IBMA. For the film containing IBMA and MAA as copolymers (sample 3, Table 2), the composition of

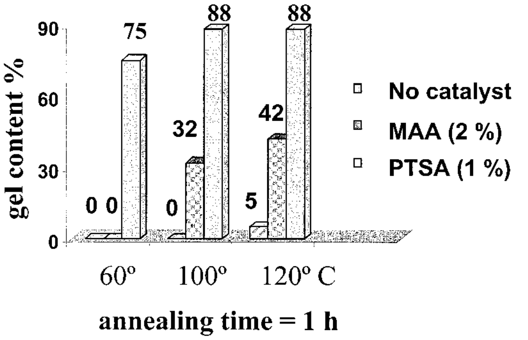


Figure 5. Gel content for samples annealed for 1 h at different temperatures. The films without acid catalyst and those containing 1 wt % PTSA were prepared from sample 2, Table 2. The films containing 2 wt % MAA were prepared from sample 3, Table 2. These films contain 2 wt % IBMA.

each is 2 wt %. We monitored the gel content of the films as a function of annealing time. Because IBMA, the cross-linker, is not present in the seed latex, the maximum gel content of fully cross-linked polymer should be the weight fraction of the second-stage polymer (88.0%). In the histogram in Figure 5, we summarize the results of experiments in which three samples were annealed for 1 h at various temperatures. In one set of experiments, sample 2 was heated without any acid catalyst. In a second set of experiments films of the same latex were prepared in the presence of 1 wt % *p*-toluenesulfonic acid (PTSA). The third set of experiments were carried out on films of sample 3, containing both MAA (2 wt %) and IBMA as comonomers. Without any acid catalyst added, the cross-linking rate of the IBMA containing films is very low. Only 5.0% gel was detected at 120 °C after 1 h annealing. With 1 wt % PTSA present in the films, the gel content after 1 h reached 75% at 60 °C and 88% at 100 and 120 °C. Recall that 88% gel represents complete cross-linking of the IBMA-containing polymer.

We see from these results that PTSA has a strong catalytic effect on IBMA cross-linking. Introduction of this acid to the P(BA-*co*-MMA-*co*-IBMA) latex film decreased the cure temperature to as low as 60 °C. This observation is consistent with the results described by Bassett et al.[7] They measured the evolution of isobutyl alcohol with annealing time at 149 °C during IBMA cross-linking in styrene−ethyl acetate−MAA−IBMA latex films in the presence of 1 wt % PTSA. Figure 5 shows that 2 wt % MAA in the polymer P(BA-*co*-MMA-*co*-IBMA-*co*-MAA) also increased the rate of the cross-linking reaction. No gel content was detected at 60 °C. The gel content reached 32% in 1 h at 100 °C and reached 42% in 1 h at 120 °C. MAA is a much weaker acid than PTSA and has a much smaller catalytic effect on the IBMA self-cross-linking reaction.

Interdiffusion vs Cross-Linking Rates at 80 °C for P(BA-*co*-MMA-*co*-IBMA) Latex Film in the Present of 0.5% PTSA. Our goal in the current project is to study the competition between the rate of polymer diffusion and the rate of cross-linking in IBMA-containing latex films. From the study of cross-linking conditions described above, we know that PTSA is a strong catalyst for the IBMA self-cross-linking reaction in P(BA-*co*-MMA-*co*-IBMA) latex films. Here we used films cast from a mixture of 1:1 PheMMA-labeled and An(**2**)-labeled high molecular weight latex dispersions (sample 4, Table 2) to study the interdiffusion and cross-linking rates of IBMA latex films at 80 °C. The polymer in these films contain 2 wt % (1.5 mol %) IBMA, and 0.5 wt % PTSA was added as a catalyst to promote the cross-linking reaction.

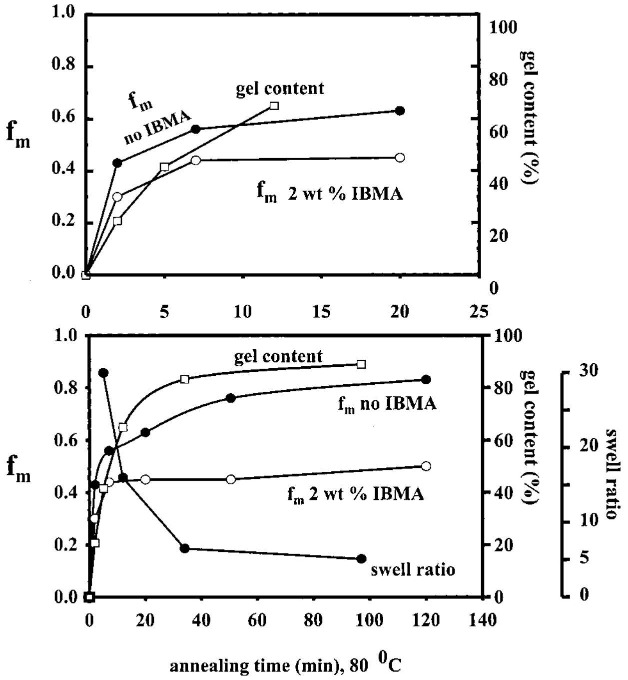


Figure 6. Plots of f_m (○) and gel content (□) vs annealing time at 80 °C for films cast from high molecular weight P(BA-*co*-MMA-*co*-IBMA) latex (sample 4, Table 2) plus 0.5 wt % PTSA. The corresponding f_m values for a film cast from the IBMA-free P(BA-*co*-MMA) latex (sample 1, Table 2) annealed simultaneously are also plotted as filled circles (●). The upper graph shows the data on an expanded time scale.

In Figure 6 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 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 (1 h), we obtained 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. In this figure, we also see that f_m increases with time, especially during the early stages of annealing. For comparison, we also present in the figure a plot of f_m vs annealing time for the IBMA-free P(BA-*co*-MMA) film (sample 1) annealed simultaneously. At early stages, as shown by the slopes of the f_m vs 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 7 min, however, the f_m value of the IBMA-containing polymer ceased to increase, an indication that polymer interdiffusion has been brought to a halt. At this point, $f_m = 0.4$, and the gel content was 42%.

We examine these results in more detail in Figure 7, where we plot ϕ_{ET} values as a function of annealing time for these same films. When these films were initially prepared at room temperature, the ϕ_{ET} values were 0.10. When the temperature was raised to 80 °C, the ϕ_{ET} values for the IBMA-free film increased more rapidly (from 0.10 to 0.33) during first 3 min of annealing than

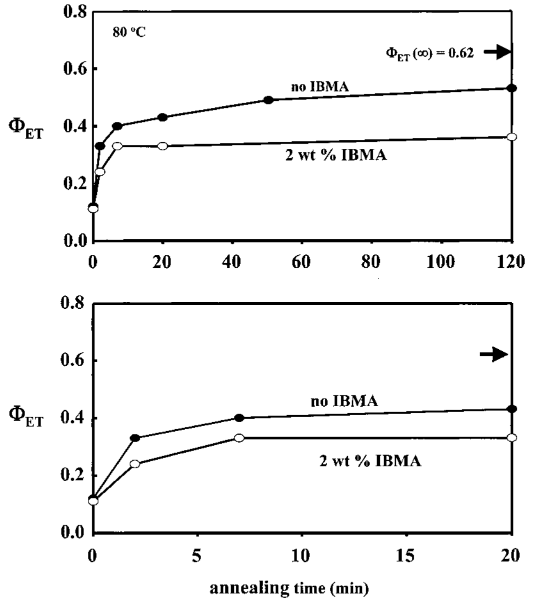


Figure 7. Plots of energy transfer efficiency ϕ_{ET} vs annealing time at 80 °C for the same films shown in Figure 6. Here the lower graph presents the data on an expanded time scale.

those of the film with IBMA plus PTSA. For both films, the rate of increase in ϕ_{ET} over the next few minutes was slower. For the film containing IBMA plus PTSA, after 7 min at 80 °C, no further increase in ϕ_{ET} occurred. Polymer diffusion appears to have ceased when the gel content was 42%, and ϕ_{ET} had reached only 0.33. With further annealing, the gel content continued to increase, and the swell ratio continued to fall as the cross-linking reaction proceeded. For the case of the IBMA-free latex shown in Figure 7, we know that with further annealing polymer diffusion will continue unimpeded. Over a period of hours (cf. Figure 3), the value of ϕ_{ET} will evolve and reach that (0.62) expected for full mixing.

Interdiffusion vs Cross-Linking Rates at 80 and 100 °C for P(BA-*co*-MMA-*co*-IBMA) Latex Film in the Presence of 0.2% Phosphoric Acid. In the past, we had no information about the relative rates of polymer diffusion and cross-linking in IBMA-containing latex films. As a consequence, there was no basis for designing composition and cure protocols to promote full mixing prior to cross-linking or to promote cross-linking at early stages of the diffusion process. For the PTSA containing P(BA-*co*-MMA-*co*-IBMA) latex film cured at 80 °C, we found that the rate of cross-linking was so fast that the interdiffusion ceased completely when f_m reached 33%. 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 the cross-linking rate. The two most straightforward variables to manipulate are temperature and the acid catalyst. Changes in temperature have different effects on the rate of the chemical reaction and the diffusion rate. While we do not know the activation energy for the reactions cited in Scheme 1, we have shown that the apparent activation energy for the polymer diffusion rate for this MMA–BA polymer composition is 43 kcal/mol. If the E_a for the chemical reaction is smaller, an increase of temperature will have a larger effect on the polymer diffusion rate. On the other hand, if the concentration of PTSA is decreased or if one uses a weaker acid as the catalyst, one expects the rate of the cross-linking reaction to be reduced.

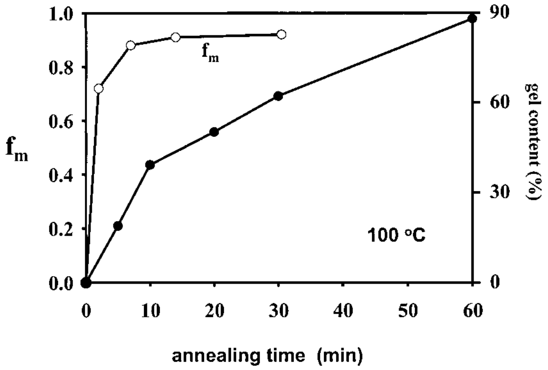


Figure 8. Plots of f_m (○) and gel content (●) vs annealing time at 100 °C for films cast from high molecular weight V-Phe and An(**3**)-labeled P(BA-*co*-MMA-*co*-IBMA) latex (sample 5, Table 2). These films contain 0.2 wt % H_3PO_4.

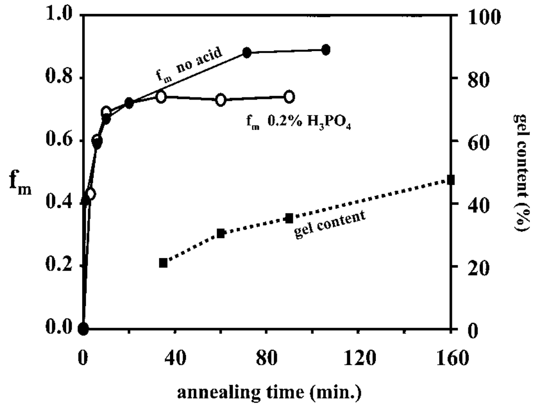


Figure 9. Effect of acid catalyst and annealing time at 80 °C on values of f_m and gel content for films cast from the same latex as in Figure 8 (sample 5, Table 2). The f_m (○) and gel content (◆) data points refer to the film containing 0.2 wt % H_3PO_4. The f_m (●) points refer to the film without any acid catalyst.

To bring this paper to a close, we summarize experiments in which we surveyed the effects of temperature and acid catalyst strength on the rates of cross-linking. For these experiments, we employ the latex sample 5 in Table 2, since the dyes in this sample are stable to acid at 100 °C. In Figure 8 we show that, at 100 °C in the presence of 0.2 wt % phosphoric acid, the rate of gel formation is much slower than that seen in Figure 6 at 80 °C for the reaction catalyzed by PTSA. The slope of the f_m vs time plot is much steeper than that of the gel content vs time plot. In only 2 min, the f_m value reached 0.72, and in 7 min, the f_m value reached 0.88. In contrast, the gel content increased slowly with annealing time. For example, in 5 min, the gel content reached 19%. After 10 min, the gel content reached 39% when f_m reached a value 0.9. It takes about an hour at 100 °C in the presence of 0.2 wt % H_3PO_4 for the system to reach full gelation (88% gel content).

We then repeated this experiment at 80 °C, and for comparison, simultaneously examined a similar latex film in which no acid catalyst was added. The results are shown in Figure 9. For the acid-free film, there was no gel detected up to 3 h at 80 °C. We can use this experiment as an example of diffusion in a film with no cross-linking. 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 slowly.

What is striking about the results in Figure 9 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 comes 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 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. When Aradian et al.[21] developed a theoretical model for the competition between cross-linking and polymer diffusion across an interface (for chains of identical length), they assumed that introduction of a single long-chain branch would stop the diffusion of the chain. If this branched polymer is formed early in the experiment, it is surrounded and interpenetrated by linear polymer containing the same fluorescent dye. As these linear polymers diffuse away, they may be replaced by linear polymer with the other label, which came from an adjacent cell in the film. In our experiment, it is likely that the diffusion of the lowest molecular weight components dominates the growth of energy transfer observed in the experiment. Only when these components have reacted to form longer polymers, particularly branched polymer and reticulated domains, will the growth of energy transfer cease.

Summary

We have synthesized IBMA containing P(BA-*co*-MMA) latex particles. The base polymer was a copolymer of 45 wt % butyl methacrylate and 55 wt % methyl methacrylate, with an estimated T_g of 12 °C. The latex particles were labeled with donor or acceptor dyes so that energy transfer experiments could be carried out. In this way we could monitor the extent of interdiffusion that occurred in each of the latex films as a function of annealing history. We monitored the cross-linking rate by measuring the increase of gel content with annealing time. With no acid catalyst, the cross-linking of IBMA groups in the latex film is very slow. We detected hardly any gel in the polymer, even with 6 wt % IBMA groups, after 1 h at 120 °C.

PTSA is a strong catalyst for the IBMA cross-linking reaction. When 0.5% PTSA was used, the cure temperature could be as low as 80 °C. Methacrylic acid as an internal catalyst at 2 wt % in the copolymer promotes the cross-linking reaction, but it has a much smaller effect than PTSA or 0.2% H_3PO_4. We monitored the interdiffusion and cross-linking rates for P(BA-*co*-MMA-*co*-IBMA) latex films in the presence of 0.5 wt % PTSA at 80 °C and in the presence of 0.2% H_3PO_4 at 80 and 100 °C. For PTSA as the catalyst, the initial stages of polymer diffusion preceded extensive gel formation, but polymer diffusion ceased at $f_m \approx 0.4$ when the gel content reached 42%. For 0.2% H_3PO_4 at both 80 and 100 °C, the cross-linking reaction was much slower. Nearly full mixing took place prior to the formation of a full cross-linked film. In this type of energy transfer experiment, full mixing corresponds to polymer diffusion over distances comparable to the radius of a latex particle.

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