*Macromolecules* **1999,** *32,* 7692−7695

# Communications to the Editor

## Polymer Interdiffusion vs Cross-Linking in Carboxylic Acid−Carbodiimide Latex Films

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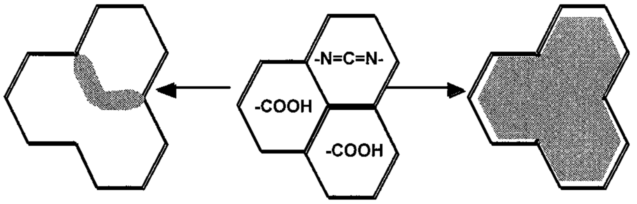
*Received April 30, 1999*
*Revised Manuscript Received September 14, 1999*

**Introduction.** In this report we consider a diffusion−reaction problem involving latex films. The films are prepared from a dispersion containing a 1:1 mixture of two similar soft copolymer latexes based on poly(2-ethylhexyl methacrylate) (PEHMA). The latex particles have similar diameters (110 nm), and their constituent polymers have similar molecular weights but contain different functional groups that react when the groups come into proximity. We assume that when the dispersion containing the latex blend dries, the resulting film contains a random distribution of the two constituents.[1] During the drying process, the individual latex particles deform into space-filling polyhedra to form a void-free film[2,3] in which the reactive functionalities are confined to different cells (see **1-A** in Chart 1).

The first copolymer latex contains 5 wt % (5.2 mol %) *tert*-butylcarbodiimidoethyl methacrylate (tBCEMA) plus 1 mol % 9-anthryl methacrylate (AnMA); the second, contains 5 wt % (11.0 mol %) methacrylic acid (MAA) plus 1 mol % 9-phenanthrylmethyl methacrylate (PheMMA). The −N=C=N− group reacts with the −COOH group to form an *N*-acyl urea. These groups cannot react until polymers from adjacent cells diffuse across the intercellular boundary. Once reactions occur, long branches and cross-links are formed. The diffusion of the branched polymers should be strongly suppressed compared to that of the original linear polymer. Thus, diffusion is necessary for the reaction to occur, but the reaction acts to suppress diffusion. This leads to a complex situation as depicted in Chart 1, in which the important issue is one of timing: How does the rate of the chemical reaction compare to the rate of polymer diffusion? If the chemical reaction is fast, essentially diffusion-controlled, the first stages of diffusion will create a cross-linked membrane at the interface of the −N=C=N- and −COOH-containing cells as shown as the gray band separating adjacent cells in part **1-I** in Chart 1. If the reaction is much slower than the rate of polymer diffusion, polymers in the two types of cells will undergo complete mixing before the reaction then locks the fully mixed structure into place. This situation is depicted as **1-M** in Chart 1, in which the three cells shown are uniformly cross-linked.

**Chart 1**



1-I 1-A 1-M

The technical implications of this competition arise from the changes in the coatings industry being driven by environmental considerations. Waterborne coatings are environmentally friendly because of reduced volatile solvent (VOC) emission, but cross-linked coatings are needed for a variety of applications in which chemical and solvent resistance, tensile strength, and hardness are important. The idea of introducing cross-linking into acrylic latex is not new, and there are a variety of strategies for introducing cross-link chemistry into waterborne dispersions.[4,5] A number of reports in the literature indicate that cross-linking improves the mechanical properties of latex films,[6−11] but excessive cross-linking can cause brittleness.[12]

The competition between polymer diffusion and reaction shown in Chart 1 is different from that in which a low molar mass cross-linking agent is added to a functional latex. In that situation, cross-linking reactions can occur locally, and the competition is with polymer diffusion to generate entanglements.[13] If the reaction is too fast, it occurs within individual cells and converts the film to an array of microgels similar to that which would be formed if the particles were cross-linked prior to film formation.[14] Zosel and Ley[15] showed this type of latex film has poor tensile strength and poor solvent resistance due to weak adhesion at the intercelluar boundaries.

One of the attractive features of blends of reactive latex is that one can prepare systems in which the two reactive groups are confined to different particles. In this way, one can prevent their reaction in the can during storage but allow the reaction to take place once the coating has dried on the substrate. For example, German et al.[16] describe films formed from a blend of epoxide-containing acrylate latex with a similar amine-containing acrylate latex. El-Aasser and co-workers[17] describe a very different blend, an acrylic latex containing isocyanate groups with a dispersion of an amino-functional polybutadiene dispersion. In the El-Aasser system in which the two polymers in the blend are very different, the reaction is confined to the interparticle interface. When the two polymers are similar, then understanding the relative rates of polymer diffusion and reaction in these blends becomes crucial. This competition is important because the mechanical properties of the films **1-I** and **1-M** in Chart 1 are expected to be very different.

The carbodiimide−carboxylic acid system is particularly amenable to study. We can use the characteristic

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10.1021/ma990677a CCC: $18.00

band at 2128 $cm^{-1}$ in the infrared spectrum[18] to follow the reaction of the $-N{=}C{=}N-$ group. In addition, we can use direct nonradiative energy transfer (ET) from Phe to An to follow the extent of polymer diffusion,[19] because the donor dye Phe is bound to the $-COOH$-containing latex polymer and the acceptor dye An is bound to the $-N{=}C{=}N$-containing polymer. Polymer diffusion brings the Phe and the An groups into proximity. ET occurs when these groups approach their characteristic (Förster) distance of $R_0 = 23$ Å. The glass transition temperature of PEHMA itself is $-10$ °C.[20] Polymer diffusion in acetoacetoxy-containing PEHMA copolymer latex films takes place at a significant rate at room temperature (23 °C).[21] In the copolymer latex films examined here, significant polymer interdiffusion requires a week at room temperature. As a consequence, we examine the competition between reaction and diffusion at 60 °C.

**Experimental Section.** All latex dispersions were prepared by seeded emulsion polymerization using a common seed representing 8 wt % of the final particle mass, with the fluorescent (1 mol %) and reactive (5 wt %) comonomers being introduced in the second stage under monomer-starved conditions. Dodecyl mercaptan was present as a chain-transfer agent. The polymerization temperature was 60 °C for the carbodiimide-containing latex {poly(ethylhexyl methacrylate-*co*-*tert*-butylcarbodiimidoethyl methacrylate-*co*-anthryl methacrylate) [P(EHMA-*co*-tBCEMA-*co*-AnMA)]} and 80 °C for the carboxylic acid-containing latex {poly(ethylhexyl methacrylate-*co*-methacrylic acid-*co*-phenanthrylmethyl methacrylate) [P(EHMA-*co*-MAA-*co*-PheMMA)]}. Both reactions yielded 30 wt % latex solids. Full details will be reported elsewhere.[22] Both latex particles have a diameter of 110 nm, with a narrow size distribution (0.02), as determined with a Brookhaven BI-90 particle sizer. Gel permeation chromatography (GPC, tetrahydrofuran (THF) eluent at 0.4 mL/min) with tandem refractive index and a fluorescent detector showed that there were no small molar mass fluorescent molecules in either latex. Molecular weight and molecular weight distributions were calculated using linear poly(methyl methacrylate) standards: $M_w = 45\,000$, $M_w/M_n = 2.73$ for the Phe/carboxylic acid-containing polymer and $M_w = 63\,000$, $M_w/M_n = 3.15$ for the An/carbodiimide-containing polymer.

Survival of the carbodiimide functionality was monitored by FTIR. Through comparison of the latex polymer with the starting monomer, we find essentially full incorporation of the $-N{=}C{=}N-$ (i.e., no significant hydrolysis) into the emulsion polymer. In films, we examined the ratio of the $-N{=}C{=}N-$ band at 2128 $cm^{-1}$ to the peak at 1380 $cm^{-1}$ (a C$-$H bending vibration[23,24]) of the polymer as an internal standard. We assume that, in a rapidly freeze-dried sample of the dispersion, all of the $-N{=}C{=}N-$ groups survive. In contrast, in films cast from water and dried slowly as described below, 2% of the $-N{=}C{=}N-$ undergo hydrolysis.[22,25]

Films were prepared at 23 °C by casting a solution of the dispersion onto a transparent substrate and then partially covering the substrate with an inverted Petri dish to slow water evaporation. The drying time ranged from 5 to 7 h. When the dispersions were mixed to form a blend, the $-COOH$-containing dispersion was first neutralized with $NH_3$ to pH 8. Films were prepared on quartz plates for energy-transfer (ET) measurements and on $CaF_2$ disks for FTIR measurements. To quantify the diffusion and cross-linking processes, films at 60 °C were cooled to room temperature. One set of films was prepared from separately freeze-dried samples of latex, which were subsequently dissolved together in THF and then cast as a film onto both $CaF_2$ and quartz substrates. Samples on $CaF_2$ disks were examined by FTIR. For those on quartz disks, fluorescence decay measurements were carried out under a $N_2$ atmosphere, with an excitation wavelength of 300 nm and an emission wavelength of 350 nm.

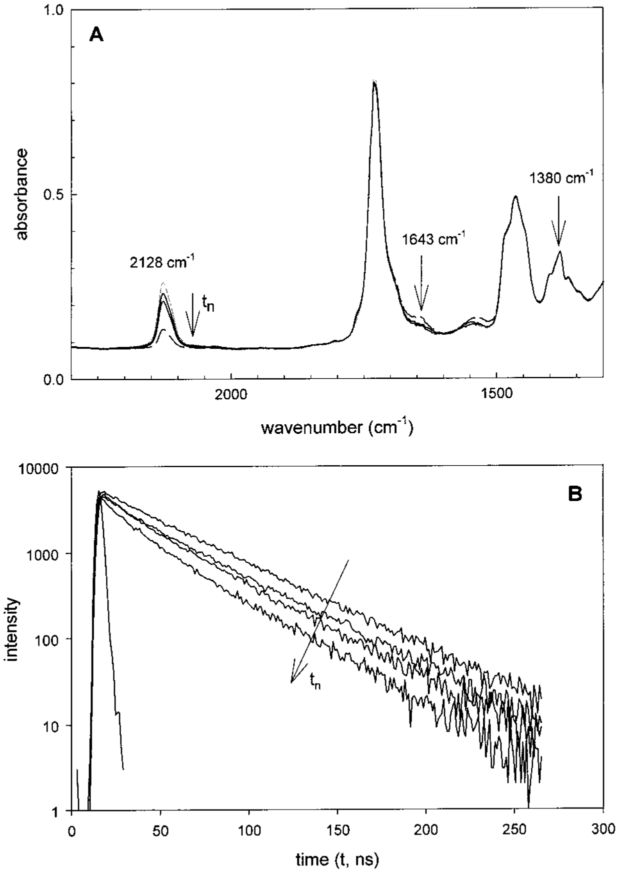

**Figure 1.** (A) FTIR spectra of a latex film prepared from a 1:1 mixture of the ammonia-neutralized P(EHMA-*co*-MAA-PheMMA)/P(EHMA-*co*-tBCEMA-AnMA) blend. These films were formed at room temperature and then annealed at 60 °C for different periods of time (0, 1, 4, and 28 h). (B) Donor fluorescence decay profiles measured for a latex film formed from the same mixed dispersion and annealed for the same times as those shown in (A).

**Results and Discussion.** Carbodiimide groups are sensitive to hydrolysis. The survival of this group during emulsion polymerization can be enhanced if the latex polymer is hydrophobic[26] and if the carbodiimide is sterically hindered. We employ *tert*-butylcarbodiimidoethyl methacrylate and 2-ethylhexyl methacrylate (EHMA) as comonomers and find that we can detect by IR essentially full incorporation of the $-N{=}C{=}N-$ groups into the latex. These groups survive extended storage of the latex at room temperature at pH 8.

When this latex is mixed with an equal number of P(EHMA-*co*-MAA-*co*-PheMMA) latex particles, previously neutralized to pH 8 with ammonia, and then dried, a fraction (17%) of the $-N{=}C{=}N-$ groups react during film formation. Representative FTIR spectra are shown in Figure 1A. If only the *N*-acyl urea was formed, we would expect the decrease in the 2128 $cm^{-1}$ band to be accompanied by an increase in intensity at 1643 cm$^{-1}$.[27] This band is weak and hard to quantify, but our spectra show that this band increases in intensity as the sample is annealed from 1 to 28 h. No gel is present in the freshly formed film, but gelation (11%) can be detected in films annealed for 1 h. Only the *N*-acyl urea product can contribute to stable cross-linking. The reactions between carbodiimides and carboxylic acids have been investigated in detail for emulsion polymers by Taylor and Bassett.[28] We infer from their results, from our FTIR measurements, and from the growth in gel content in our films that, under our annealing conditions for the dry latex films, the dominant reaction product is the *N*-acyl urea.

To examine polymer diffusion in this system, we labeled the carbodiimide-containing latex with An and the $-$COOH-containing latex with Phe. Fluorescence decay measurements on each of the films, as a function of annealing time, allow us to determine the extent of energy transfer, which in turn is a measure of the extent of mixing in the film due to polymer diffusion. Representative Phe fluorescence decay ($I_D(t')$) curves are presented in Figure 1B. The decay profiles shown were measured for samples annealed for the same times as those for which the FTIR spectra are shown in Figure 1A. In the newly formed film, the $I_D(t')$ profile is nearly exponential, consistent with little polymer diffusion during the drying process leading to film formation. But as the films are annealed for various periods of time at 60 °C, the area under the decay curves decreases, indicating a growth in energy transfer due to polymer diffusion. The quantum efficiency of energy transfer $\Phi_{ET}$ can be evaluated by integrating the fluorescence decay profiles $I_D(t')$ after normalizing them to unit intensity at $t' = 0$.

$$\Phi_{ET} = 1 - \frac{\int_0^\infty I_D(t')\,dt'}{\int_0^\infty I^0{}_D(t')\,dt'} = 1 - \frac{\text{area}(t)}{\text{area}(0)} \qquad (1)$$

We characterize the diffusion process in terms of the fraction of mixing $f_m$, which represents the fractional growth in energy transfer efficiency in the system.

$$f_m = \frac{\Phi_{ET}(t) - \Phi_{ET}(0)}{\Phi_{ET}(\infty) - \Phi_{ET}(0)} = \frac{\text{area}(0) - \text{area}(t)}{\text{area}(0) - \text{area}(\infty)} \qquad (2)$$

To model area($\infty$), we dissolve freeze-dried samples of the two latex polymers in THF and rapidly cast a film. This film was then annealed for 12 h at 60 °C to attain full mixing. The need for annealing is discussed below.

In the newly formed film, a small amount of interdiffusion may have occurred because the films are formed at 23 °C, well above the glass transition temperature of the latex polymer. In the newly formed film, examined 1 h after drying is complete, we find that $\Phi_{ET} = 0.11$. Both local interdiffusion and cross-boundary ET contribute to this value. The extent of ET increases as the films are annealed at 60 °C, reaching $\Phi_{ET} = 0.52$ for complete mixing. A plot of $f_m$ values as a function of annealing time is presented in Figure 2. In the plot $f_m$ increases rapidly to 0.6 in 1 h and then to 0.84 in 4 h, while over 4 h, only 30% of the carbodiimide groups react. This result indicates that molecular mixing due to diffusion occurs much faster than the cross-linking reaction. As we will see below, the situation is more subtle. The two polymers, MAA-11 and tBCEMA-5, have only limited misciblity, and the miscibility is driven by the chemical reaction.

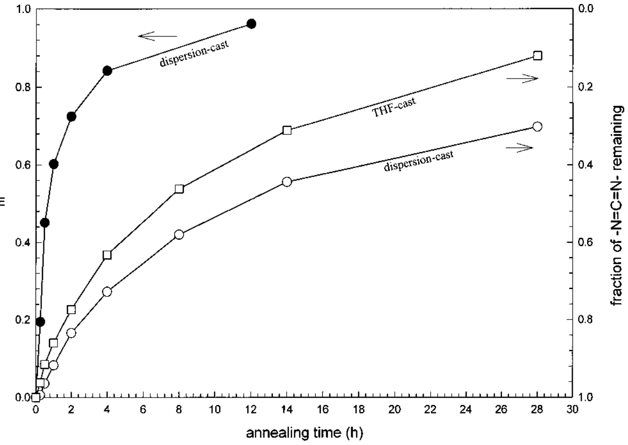

**Figure 2.** Plot of the extent of mixing ($f_m$) for the latex blend films and plots of the fraction of carbodiimide remaining in both the latex film and the THF-cast films vs annealing time at 60 °C.

In the current system, polymer diffusion and the cross-linking reaction are coupled. Polymer diffusion brings the reactive functionalities into proximity for them to react. In response, *N*-acyl urea formation increases the molecular weight of the polymer. It creates long-chain branching and gel formation in the system. One sees some of the consequences of the chemical reaction on diffusion at early times in Figure 2. For example, most of the polymer diffusion occurs in the first hour of annealing at 60 °C, during which $f_m$ reaches 0.6. Over this time, only about 10% of the $-$N=C=N$-$ groups have reacted. As the extent of reaction increases, the rate of diffusion slows. From the plot in Figure 2 we see that mixing reaches completion after about 12 h, over which about half of the $-$N=C=N$-$ groups present in the initial film have reacted.

Further important information about the system is presented in the middle curve in Figure 2, which describes the rate of consumption of the $-$N=C=N$-$ groups in a film cast from a solution of the two polymers in THF.[29] We initially imagined that we would prepare a homogeneously mixed film in this way but were surprised to discover that $\Phi_{ET} = 0.42$ for the newly formed film instead of 0.52 expected for a fully mixed film. Some demixing of the two polymers occurred. Over the first 20 min of annealing, $\Phi_{ET}$ dropped to 0.40 and then grew back to 0.46 within 2 h. Upon prolonged annealing, $\Phi_{ET}$ reached its limiting value of 0.52. These results, which are currently under investigation,[30] indicate that the two polymers have limited miscibility before the chemical reaction occurs but become miscible as the reaction takes place.

In summary, we have examined the relative rates of polymer diffusion and of covalent bond formation in latex blend films consisting of a 1:1 mixture of a carbodiimide-containing latex polymer and a carboxylic acid-containing latex polymer. In this system in which the molecular weight ($M_w \approx 60\,000$) of both components is relatively low, we have established that polymer diffusion is significantly faster than the rate of the chemical reaction between the $-$N=C=N$-$ and $-$COOH groups. A subtle feature of the system is that the two reactive copolymers have only limited miscibility but become miscible as a consequence of the chemical reaction.

**Acknowledgment.** We thank ESTAC Canada and NSERC Canada for their financial support.

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MA990677A