Available online at www.sciencedirect.com
ScienceDirect
Polymer 49 (2008) 2055–2064
polymer
www.elsevier.com/locate/polymer

Polymer blend latex films: Miscibility and polymer diffusion studied by energy transfer

J. Pablo Tomba [a,1], Xiaodong Ye [a,2], Fugang Li [a], Mitchell A. Winnik [a,*], Willie Lau [b,**]

[a] *Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, ON, Canada M5S 3H6*
[b] *Rohm and Haas Company, 727 Norristown Road, P.O. Box 904, Spring House, PA 19477-0904, USA*

Received 5 December 2007; received in revised form 14 February 2008; accepted 16 February 2008
Available online 21 February 2008

Abstract

Fluorescence non-radiative energy transfer experiments were used to study latex blend films composed of high molar mass poly(butyl acrylate-*co*-methyl methacrylate) (PBA-*co*-MMA) and much lower molar mass PBA-*co*-MMA latex of the same chemical composition (50:50 BA:MMA by weight). These blends take advantage of the strong chain length dependence of T_g so that the particles consisting of oligomeric polymer (“low-M”) have a much lower T_g than the corresponding high-M latex. This type of blend represents a useful strategy for obtaining latex coatings with a reduced VOC content. Here we report on experiments which follow the rate at which the low-M polymer mixes via diffusion with the high-M polymer in the latex films. The high-M latex are doubly labeled, containing both donor and acceptor dyes covalently bound to the PBA-*co*-MMA backbone. Diffusion of the unlabeled low-M polymer into this phase dilutes the dyes, increasing their separation and lowering the quantum efficiency for energy transfer.

Keywords: Oligomeric latex; Emulsion polymerization; Polymer diffusion

---

1. Introduction

Concern for the environment is driving changes in coating technology. One of the major goals is a reduction in the amount of volatile organic compounds (VOCs) released to the atmosphere. Most waterborne coatings contain significant amounts of organic solvents. In latex coatings, these solvents act as fugitive plasticizers, lowering the glass transition temperature (T_g) and the modulus of the latex polymer so that the forces associated with drying are sufficient to deform the latex particles into polyhedral cells that pack to give a void-free film. These solvents also promote the rate of polymer diffusion across the intercellular boundaries, leading to the development of full mechanical strength in the coating. The challenge for the industry is to remove these solvents and at the same time obtain films with similar or even enhanced properties compared to traditional coatings.

One set of strategies for achieving enhanced properties without resorting to volatile solvents involves the use of latex blends. Latex blends are mixtures of two or more different kinds of latex particles in the dispersed state. Upon drying of the dispersion, both types of particles contribute to the properties of the film that is formed. Several authors have examined the properties of hard–soft latex blends. Hard refers to particles consisting of a polymer with a T_g above room temperature, and soft refers to particles of a low-T_g polymer. Particularly in the case where one prepares a mixture of large soft latex particles and small hard particles, packing considerations lead to percolation of the small hard particles to form a continuous phase that provides mechanical reinforcement of the film

---

* Corresponding author. Tel.: +1 416 978 6495; fax: +1 416 978 0541.
** Corresponding author.
E-mail addresses: mwinnik@chem.utoronto.ca (M.A. Winnik), wlau@rohmhaas.com (W. Lau).

[1] Permanent address: Institute of Materials Science and Technology (INTEMA), National Research Council (CONICET), University of Mar del Plata, Juan B. Justo 4302, 7600 Mar del Plata, Argentina.

[2] Permanent address: The Opening Laboratory for Bond-selective Chemistry, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China.

0032-3861/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.02.024

and good block resistance. This strategy requires particles of different compositions so that the phases remain discrete in the film.

Here we consider a different strategy, developed originally at Rohm and Haas. In this approach, one blends two types of latexes of (essentially) the same chemical composition, but very different molar mass. One takes the advantage of the strong chain length dependence of T_g so that the particles consisting of oligomeric polymer ("low-M" or "oligomeric latex") have a much lower T_g than the base latex prepared under normal emulsion polymerization conditions. Films of these blends have excellent mechanical properties and block resistance. There is a synergy between the components, and the final film properties are different from what one would predict from a simple linear relationship between the properties of the individual components and the composition of the film.

We are interested in understanding how these films achieve their properties. One can imagine, for example, that upon drying, the low-M (soft) particles will deform more readily than the high-M particles. Because the two components differ only in composition only by the concentration of end groups, one also expects the two polymers to be miscible on a molecular level. To achieve miscibility, low-M polymers must diffuse out of the low-T_g cells in the film into cells consisting of higher T_g polymer. At the same time the high-M chains must diffuse in the reverse direction to maintain the density of the solid. This situation recalls the theoretical analysis of polymer chains across interfaces in which the polymers on the two sides of the interface had very different chain lengths several years ago by de Gennes [1a], Brochard et al. [1b], and others [1c]. In the system we are considering, there is, in addition, a difference in the glass transition temperature of the two pure components. Miscibility in the final film can be inferred from differential scanning calorimetric (DSC) measurements of T_g for the blend compared to the individual components. We show here that even deeper insights into miscibility are possible through fluorescence resonant energy transfer (ET) experiments.

In this paper, we present the results of our initial investigation of films formed from blends of high-M and low-M poly(butyl acrylate-*co*-methyl methacrylate) (P(BA-*co*-MMA)) latex. We employ oligomeric latex samples synthesized by an approach that employs dodecyl mercaptan as chain transfer agent in the presence of methyl-β-cyclodextrin. We report T_g values of the latex polymer as a function of molar mass. The major result described in this paper is the use of a single sample of doubly labeled high-M (P(BA-*co*-MMA)) latex as a probe of miscibility and diffusion in films formed from blends of this latex with oligomeric latexes of the same composition.

2. Experimental

2.1. Materials

All reagents were purchased from Aldrich unless otherwise specified. Methyl methacrylate (MMA), butyl acrylate (BA), butyl methacrylate (BMA) and ethylene glycol dimethacrylate (EGDMA) were distilled under vacuum prior to use. Potassium persulfate (KPS), sodium bicarbonate ($NaHCO_3$), dodecyl mercaptan ($C_{12}SH$), sodium dodecyl sulfate (SDS) were used as-received. (9-Phenanthyl) methyl methacrylate (PheMMA) was purchased from Toronto Research Chemicals Inc. Polystep A-16 (22%) (sodium dodecylbenzene sulfonate) was purchased from Stephan (IL) and used as-received. Methyl-β-cyclodextrin (Me-β-CD) was provided by Rohm and Haas. The synthesis and characterization of the monomer 4′-dimethylamino-2-acryloxyl-5-methyl-benzophenone (NBen) is described elsewhere [2]. The distilled water used in these experiments was further purified through a Millipore Milli-Q system.

2.2. Characterization of latex particles

For the high-M doubly labeled latex, the particle size distribution was measured by capillary hydrodynamic fractionation chromatography (CHDF, Matec Applied Sciences, Model 2000). Gel permeation chromatography (GPC) was performed on a Waters liquid chromatograph equipped with a Waters 480 tunable UV–vis absorbance detector and a Waters R410 differential refractive index detector. Syringe Filters (PP Filter Membrane, 0.45 μm, Whatman) were used prior to injecting the samples in the GPC. Molecular weights were calibrated with poly(methyl methacrylate) standards from Polymer Laboratories Ltd. Glass transition temperatures (T_gs) for pure polymers and mixtures were determined by differential scanning calorimetric (DSC). Measurements in Toronto were made using a DSC 2920 MDSC V2.6A differential scanning calorimeter from TA Instruments. Samples were cooled and heated from −70 to 70 °C at rates of 10 °C/min, under N_2 atmosphere. Glass transition temperatures were determined by the instrument software as the inflection point in the second heating step. Measurements at Rohm and Haas were carried out on a TA Instruments Q1000 differential scanning calorimeter. The samples (10–15 mg) were preheated to 150 °C to ensure complete drying. After cooling back to −90 °C, the heat flow was measured upon heating at 20 °C/min to 150 °C. The T_g is reported as the inflection point of the DSC curve. The onset of the curve is generally about 10 °C below that of the inflection point.

2.3. Synthesis of the oligomer latex

These emulsion polymerizations were carried out in a three-neck 50 mL round bottom flask equipped with a mechanical stirrer, a condenser, one emulsion feed line and a nitrogen inlet. A monomer emulsion of deionized water, Polystep A-16 (22%) anionic surfactant, and monomers was prepared in accordance with the recipe given in Table 1. Deionized water, Polystep A-16, and Me-β-CD were introduced into the reaction flask at room temperature. The contents were heated to 85 °C while stirring under a nitrogen purge. At 85 °C, the monomer emulsion was introduced into the reaction flask followed by the Na_2CO_3 and $Na_2S_2O_8$ solution. After the exotherm subsided, the remainder of the monomer emulsion was fed into the reaction mixture over a period of

Table 1
Emulsion polymerization recipe for the oligomeric latex

	Chemicals/reagents	Amounts [g (mol)]
Monomer emulsion	Deionized water (DW)	10.0
	Polystep A-16 (22%)	0.205
	Butyl acrylate (BA)	7.50 (0.0585)
	Methyl methacrylate (MMA)	7.35 (0.0734)
	Methacrylic acid (MAA)	0.15 (0.00174)
	n-Dodecyl mercaptan (*n*DDM)	0.2–3 (variable)
Initial charge	Deionized water (DW)	4.0
	Polystep A-16 (22%)	0.307
	Methyl-β-cyclodextrin	0.075
	Monomer emulsion	3% of total emulsion
	Sodium persulfate/DW	0.106 in 1.0 DW
	Sodium carbonate/DW	0.106 in 1.0 DW
Feed	Monomer emulsion	97% of total emulsion
Time (min)	Seed formation	20
	Feed	180
	After feed	30

3 h. At the end of the feed, the reaction mixture was held at 85 °C for 30 min and then allowed to cool to room temperature. The latex was neutralized to pH ~ 8.5 with ammonia.

2.4. Synthesis of the doubly labeled latex

The doubly labeled poly(methyl methacrylate-*co*-butyl acrylate) (P(MMA-*co*-BA)) was prepared by seeded semi-continuous emulsion polymerization [3]. Cross-linked unlabeled latex particles, used as seeds, were first prepared from a 4/3 molar ratio of butyl methacrylate (BMA) and ethylene glycol dimethacrylate (EGDMA) by batch emulsion polymerization at 80 °C. The seeds represent 6 wt% of the final dry polymer. The recipe for the preparation of seeds (first stage) is summarized in Table 2. The polymerization was carried out under a nitrogen atmosphere in a 3.0 L three-necked glass reactor, equipped with a condenser and a mechanical stirrer. The monomers, water, surfactant and $NaHCO_3$ were deoxygenated with nitrogen (30 min) while being stirred mechanically, and then heated to 80 °C. The initiator solution (potassium persulfate (KPS) in water) was rapidly added. Stirring was continued for another 3 h under a nitrogen atmosphere. An aliquot of these particles was used as seed for the second stage of polymerization.

Table 2
Recipe for the synthesis of P(MMA-*co*-BA) latex particles doubly labeled with Phe and NBen by semi-continuous emulsion polymerization

	First stage	Second stage
Seeds	–	3 mL
H_2O	2280.00 g	98.00 g
KPS	1.67 g	0.073 g
SDS	26.96 g	0.726 g
$NaHCO_3$	1.17 g	–
BMA	55.67 g	–
EGDMA	58.33 g	–
MMA	–	12.39 g
BA	–	12.38 g
NBenMA	–	0.133 g (0.2 mol%)[a]
PheMMA	–	0.304 g (0.5 mol%)[a]
$C_{12}SH$	–	0.095 mL
Diameter	31 nm	98 nm

[a] Based on total monomer content.

In the second stage of the polymerization, an aqueous solution containing the surfactant (SDS) and initiator (KPS) and the organic solution containing the two base monomers (MMA and BA) and the two fluorescent monomers (PheMMA and NBen) were fed continuously into the reactor containing the dispersion of seed particles. The recipe is summarized in Table 2. An aliquot (3 mL) of the seed dispersion and 64 mL of deionized water were introduced into a 250 mL three-neck flask equipped with a condenser and a mechanical stirrer. The dispersion was purged with N_2 for 90 min and then heated at 80 °C, always under N_2 atmosphere. The monomer feed rate was kept at 1.4 mL/h, controlled by metering pumps (Fluid-Metering Inc Lab Pumps, Motor QSY pump head, QSYQ for the aqueous solution; Motor QC, pump head RHOCKC for the monomers). KPS and SDS dissolved in water were added into the reactor concurrently. After the addition was complete, the reaction mixture was stirred and heated for another 2 h, yielding doubly labeled particles with a mean diameter of 119 nm and 18 wt% of solids. The characteristics of this latex sample are presented in Table 3.

The distribution of dyes and presence of free dyes in our doubly labeled latex were checked by GPC measurements, using tandem UV and RI detectors [4]. These are important requirements in order to support our assumption that donor and acceptor groups serve only as tracers for the localization of the polymer. The trace for the polymer, as monitored by the RI detector, and the trace for the dyes, as monitored by the UV signal, had similar shapes and eluted at times consistent with the fact that the UV detector precedes the RI detector. No peaks corresponding to unreacted dye were found. We conclude that dyes were uniformly incorporated into the copolymer and that there are no free dyes in the system.

2.5. Preparation of films for ET measurements

Latex blends were prepared by mixing aliquots of the oligomeric P(MMA-*co*-BA) unlabeled latex (at about 50 wt% solids) and the doubly labeled P(MMA-*co*-BA) latex (at about 20 wt% solids). The resulting mixture was gently agitated for several minutes to promote mixing. Except where indicated, mixtures were prepared with a 1:1 weight ratio of doubly labeled and unlabeled oligomeric latex particles.

Table 3
Physical properties of the latex particles

Latex	Label	T_g[a] [°C]	M_n [g/mol]	Solids [%]	*d* [nm]
Unlabeled P(MMA-*co*-BA)	M_n-2.4	−48	2400[b]	52	128
	M_n-6.4	−1.5	6400[b]	52	109
	M_n-11.3	6.4	11,300[b]	50	110
	M_n-140	18	140,000[b]	52	110
Doubly labeled P(MMA-*co*-BA)	DL	12	252,000[c]	19.1	119

[a] Measured by DSC.
[b] $M_w/M_n \approx 2.5$.
[c] $M_w/M_n > 3$.

Latex films were prepared by spreading 3–4 drops of the corresponding latex dispersion onto small quartz plates (2 cm × 1 cm, used for fluorescence decay measurements). Then, the films were allowed to dry in a cold room (ca. 4 °C) overnight. The dried films, typically 50–100 μm thickness, were transparent and free of cracks. In some cases, the fresh films were annealed to investigate the influence of temperature on the rate of mixing between latex particles. The films on their quartz substrates were annealed by placing them directly onto a high-mass aluminum slab in a preheated forced air oven. The films were cooled to room temperature before energy transfer measurements were carried out. We also studied energy transfer on "solvent-cast films". To prepare these films, we placed a few drops of each mixed dispersion on a glass plate and allowed the water to evaporate at room temperature. The dry film was dissolved in tetrahydrofuran (THF) to form a transparent solution at 2–3 wt% solids. A few drops of this solution were spread on a quartz plate and then allowed to dry overnight at room temperature.

2.6. Fluorescence decay measurements

All fluorescence decay profiles were measured by the time-correlated single photon counting technique, using a deuterium lamp as the excitation source. The donor (Phe) was excited at 300 nm and the emitted light was collected in the 350–400 nm range. Two filters, a band-pass (310–400 nm) and a cut-off (335 nm) were placed in the collection path to minimize the influence of scattered light. For each measurement, the quartz plate that supports the film was placed into a quartz tube and sealed with a rubber septum. The tubes were deoxygenated with N_2 for 5 min prior to measuring the donor fluorescence decay profile. Measurements were performed at room temperature. Data were collected up to 6000 counts in the channel of maximum intensity, which usually requires 10–12 min.

3. Data analysis in ET experiments

For a dipole–dipole coupling mechanism, the rate of energy transfer (ET) between a donor and an acceptor group depends sensitively on their separation distance r [5].

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

where τ_D is the lifetime of the donor in the absence of acceptors, and R_o is the characteristic (Förster) distance over which ET takes place. The Förster distance for the Phe–NBen pair is 2.7 nm [6–8], somewhat larger than that for the phenanthrene/anthracene pair ($R_o = 2.3$ nm) that we have used in the previous experiments [9].

The Phe (donor) fluorescence decays in the absence of acceptors are exponential, but they become non-exponential when ET acceptors are present in the sample. If the donors and acceptors are homogeneously distributed in a three-dimensional medium in which edge effects are not important, the fluorescence donor decay function I_D is described by Eq. (2), first derived by Förster [10].

$$I_D(t') = A\exp\left[-\frac{t'}{\tau_D} - P\left(\frac{t'}{\tau_D}\right)^{0.5}\right] \tag{2}$$

where t' is the fluorescence decay time and A is a normalization parameter. The term containing the P parameter accounts for the influence of ET, and depends on the concentration of acceptors [A] in the medium, as well as on the averaged relative orientation of donor and acceptor transition moments $\langle\kappa^2\rangle$:

$$P = \frac{4}{3}\pi^{3/2}\left(\frac{3}{2}\langle\kappa^2\rangle\right)^{1/2} N_A R_0^3[\mathrm{A}] \tag{3}$$

where N_A is Avogadro's number (6.023×10^{23} number/mol). The orientation factor $\langle\kappa^2\rangle$ has a value of 2/3 in fluid solution, where rotation is rapid. The experiments described here involve a random distribution of dipoles that are immobile on the time scale of the donor lifetime. For this case, $\langle\kappa^2\rangle = 0.476$ [11].

The quantum efficiency of ET Φ_{ET} is a useful way to measure the extent of ET in a system,

$$\Phi_{ET} = 1 - \frac{\int_0^\infty I_D(t')\,dt'}{\tau_D} \tag{4}$$

where the integral represents the area under the donor fluorescence decay curve obtained for a film labeled with donors and acceptors. One of the ways to calculate this integral is to fit the experimental decay to a suitable equation, and then to integrate the equation analytically, from the fitting parameters obtained.

4. Results and discussion

4.1. Experimental design

In the past, we have been interested in the rate at which polymers undergo mixing as a consequence of polymer diffusion across the boundary between neighboring cells in a latex film [12]. To monitor the rate and extent of polymer diffusion through energy transfer measurements, we labeled the polymers in some of the cells with a donor chromophore D and the polymer in the remaining cells with an acceptor chromophore A. As diffusion proceeds in this type of experiment, D and A groups are brought into proximity, and the extent of energy transfer increases. In the newly formed film, with sharp boundaries between the cells, Φ_{ET} is very small. Over time, as polymers diffuse, Φ_{ET} increases to its maximum value, determined by the parameters in Eqs. (2)–(4).

Here we have a different situation. We are interested in understanding the interaction of a series of oligomeric polymers with a high molar mass polymer of a very similar composition. The system is prepared as a series of latex blend films, and the concern is the rate and extent of diffusive mixing across the boundaries separating high-M and low-M polymers. To simplify the requirements for the synthesis of dye-labeled polymer, we have designed the system in such a way that only one of the components needs to be labeled. The high-M latex particles contain a random distribution of both donor and acceptor groups. Thus, it is doubly labeled. The oligomeric latex polymers are unlabeled.

The concept of the experiment is depicted in Fig. 1. The blend in solution consists of a mixture of doubly labeled high-M particles and unlabeled particles. In the doubly labeled latex particles, donor (Phe) and acceptor (NBen) dyes are assumed to be attached at random to the polymer. In the newly formed film, if the particle deformation step is well resolved from the subsequent diffusion step, D and A groups will be confined to doubly labeled cells. The extent of energy transfer Φ_{ET} will be determined by the local concentration of A groups. This corresponds to the "no-mixing" state shown in Fig. 1. As the two polymers mix, the labels are diluted by the unlabeled polymer and the efficiency of ET will decrease.

Fig. 2 shows the expected changes in Φ_{ET} with the acceptor concentration, calculated using Eqs. (2)–(4), with $\langle\kappa^2\rangle = 0.476$ and a value for $R_o = 2.7$ nm, appropriate for the NBen–Phe pair [6–8]. As shown in Fig. 2, Φ_{ET} increases rapidly with increasing acceptor concentration for low concentrations of A, changing sensitively in the range from 0 to 0.02 M, and then levels off approaching asymptotically 1.0 at high values of [A]. Our doubly labeled latex contains 0.5 mol% Phe and 0.2 mol% of NBen. The NBen concentration in the doubly labeled copolymer (0.2 mol%) corresponds to a concentration of 0.02 M in the film. In this way, any decrease in [A] produced by the dilution with unlabeled polymers will lie in the range of maximum sensitivity.

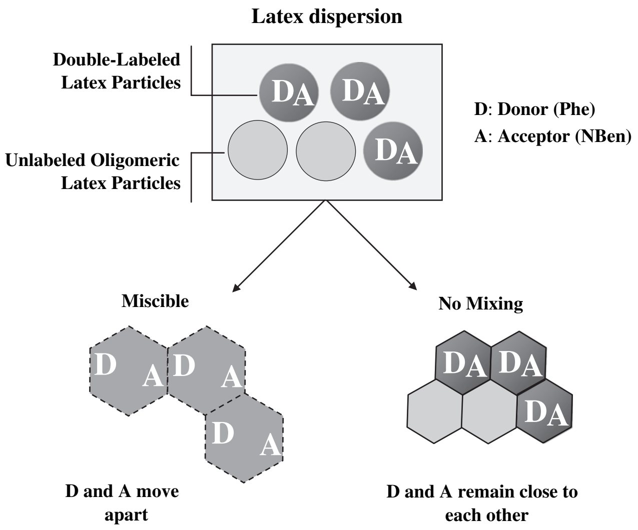

Fig. 1. Schematic representation of the two limiting cases for the mixing process between doubly labeled and unlabeled latex particles. *No-mixing state*: ET occurs mostly inside the doubly labeled latex particles. *Full-mixing state*: the presence of unlabeled polymer increases the average distance between donors and acceptors, decreasing the extent of ET.

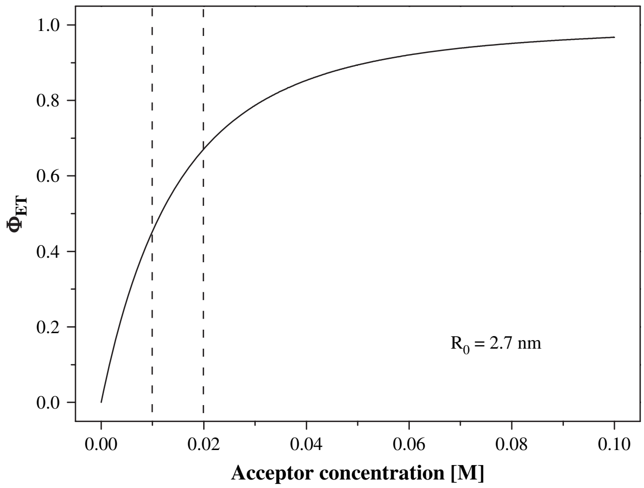

Fig. 2. Theoretical plot of the quantum efficiency of energy transfer Φ_{ET} vs. acceptor concentration [A]. For the calculations, Eqs. (2) and (3) were used. In Eq. (3), $\langle\kappa^2\rangle = 0.476$ and $R_o = 2.7$ nm were assumed. Dotted lines indicate the range of variation of [A] in our experiments.

4.2. Synthesis and properties of the components

The doubly labeled latex was synthesized by seeded emulsion polymerization under monomer starved conditions, using tiny ($D_n = 30.5$ nm and $D_w = 35.9$ nm) highly cross-linked particles as seeds and a 1:1 weight ratio of methyl methacrylate and butyl acrylate in the main feed. The fluorescent dye co-monomers were introduced along with the second stage monomers. The seed particles represent only 6 wt% of the final dry polymer. This latex polymer was characterized by a single glass transition temperature of 12 °C, which is in good agreement with that calculated from the Fox equation (10 °C), assuming random copolymerization. The final particle size distribution was narrow, with $D_n = 98$ nm and $D_w = 111$ nm.

Unlabeled low molecular weight based latex samples of P(MMA-*co*-BA), also with a 1:1 monomer weight ratio, were synthesized using the recipe described in Table 1. A series of samples were prepared employing a common recipe in which the only variable was the amount of $C_{12}SH$ added as a chain transfer agent. The key feature of the synthesis is the use of methyl-β-cyclodextrin as a carrier and *n*-dodecyl mercaptan as the chain transfer agent [13]. All the dispersions were characterized by narrow particle diameter distributions. Further characteristics, and our notation for naming the samples, can be found in Table 3.

These unlabeled P(MMA-*co*-BA) latex samples have molecular weights in the range where T_g varies sensitively with chain length. A plot of T_g vs. molecular weight for these samples, measured by DSC, is shown in Fig. 3. This plot shows the typical behavior expected for linear polymers, and predicted by the Fox–Flory equation [14]. For low molecular weights, T_g increases sharply with increasing molecular weight and then levels off to a limiting value. The filled symbols represent the latex particles used in this study. As shown in Table 3, the lowest molecular weight polymer used in this work (M_n-2.4) has a T_g well below room temperature (−48 °C). Samples

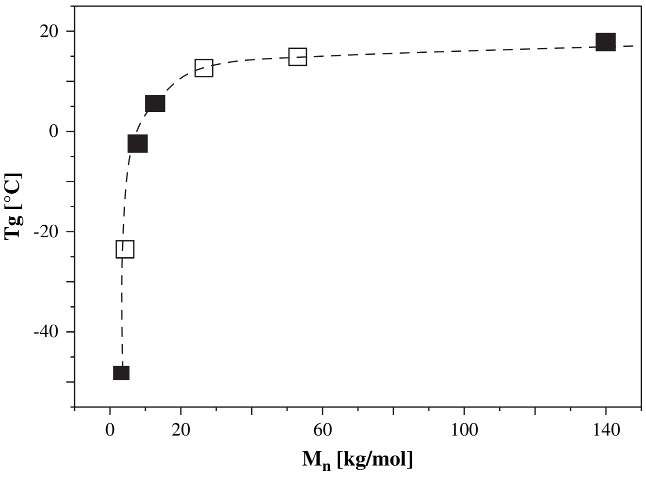

Fig. 3. Plot of glass transition temperature vs. molecular weight for the unlabeled latex polymers. The full square symbols represent the samples we used in this study.

with intermediate molecular weights (M_n-6.4 and M_n-11.3) have T_gs at around 0 °C (−1.5 and 6.4 °C, respectively). The highest molecular weight sample (M_n-140) has a T_g comparable to that of the doubly labeled copolymer. We used this sample as model to establish a reference point for the no-mixing and fully mixed states as shown in Fig. 1.

4.3. Energy transfer in latex blend films with the M_n-140 sample

The doubly labeled latex polymer and the unlabeled M_n-140 sample both consist of relatively high molar mass polymer. They have slightly different compositions (the M_n-140 sample contains 1 wt% methacrylic acid and no dye label) and similar T_g values. Blends of the two types of particles formed clear and crack-free films when dried in a cold room overnight at 4 °C. Because these films were formed below the T_g of the dry polymer, we anticipate that very little polymer diffusion occurred during film preparation [15]. The films were stored in the cold room except during fluorescent decay measurements, which were performed at room temperature. Curve (1) in Fig. 4 shows a typical fluorescence decay corresponding to a film dried as described above, prepared from a latex blend containing a 1:1 w/w mixture of the doubly labeled (DL) target and the M_n-140 particles. The fluorescence decay is non-exponential, a signature that ET has occurred.

We fitted the experimental decay to Eq. (2), using $\tau_D = 46.5$ [16]. A good-quality fit was obtained, as reflected by the randomly distributed weighted residuals and by a χ^2 value less than 1.3. This fit yielded $P = 0.22$ and $\Phi_{ET} = 0.67$. We explored a more extended range of latex blend compositions (from 1:3 to 3:1 w/w DL:M_n-140). These films gave almost identical fluorescence decay profiles, with similar fitting parameters and $\Phi_{ET} = 0.67$, irrespective of mixture composition. This is the result expected for the case of ‘‘no mixing’’ as indicated in Fig. 1. The acceptor concentration is determined only by the level of labeling in the doubly labeled latex. We refer to the ET efficiency in the no-mixing state as $\Phi_{ET}(0)$.

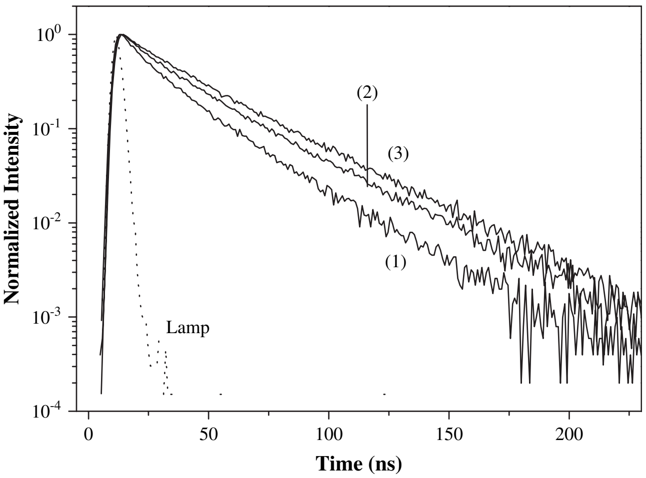

Fig. 4. Donor fluorescence decay curves for the model DL:M_n-140 latex blend. They correspond to: (1) Fresh films; (2) THF-cast films prepared from 1:1 w/w mixtures; (3) THF-cast films prepared from 1:2 w/w mixtures. For details about film preparation, see the text.

We use a solvent-cast film of the latex blend as a model for the fully mixed state. The key assumption here is that the two polymers mix completely when dissolved in a solvent like THF and that they do not demix upon drying. To prepare these model films, we dried 1:1 mixtures of the unlabeled high molecular weight latex particles (M_n-140) and the doubly labeled latex target. This mixture was dissolved in THF and cast as a film on a quartz substrate. The measured fluorescence decay profile for this film is shown as the middle curve (2) in Fig. 4. This decay also fit well to the Förster equation (Eq. (2)), yielding $P = 0.12$. From the area under this decay profile, we calculated the quantum efficiency of ET for full mixing, $\Phi_{ET}(\infty)$, obtaining a value of 0.49. This value is lower than $\Phi_{ET}(0)$ and reflects the diluting effect of the unlabeled polymer molecules on the extent of ET. When we prepared THF-cast films with increased proportions of the M_n-140 sample in the mixture, the extent of ET decreased even more. Curve (3) in Fig. 4 is the fluorescence decay profile corresponding to a 1:2 w/w DL:M_n-140 latex blends. The Förster fit for this latex blend gave $P = 0.085$ and $\Phi_{ET}(\infty) = 0.41$.

A closer examination of the values obtained for the P parameter for the sample described above shows that they are approximately equal to those expected based on Eq. (3) and the level of dye label in the DL sample. For 1:1 mixtures, P should change by a factor of 0.5 considering the diluting effect of the unlabeled chains. In our experiments with 1:1 DL:M_n-140 mixtures, we obtained $P = 0.22$ for fresh films and $P = 0.12$ for THF-cast films. Thus, the observed change in P (0.12/1.22 = 0.54) is in good agreement with our expectations. The small difference between the expected factor of 0.5 and the experimental result of 0.54 is probably within experimental error, but may also be due to a small amount of polymer mixing during the preparation of the model latex films used to determine $\Phi_{ET}(0)$. Similarly, we obtained $P = 0.085$ for THF-cast films prepared from 1:2 DL:M_n-140 mixtures. In this case, the expected change is by a factor of 0.33 with respect to the unmixed state and by a factor of 0.67 with respect to the random state in a 1:1 mixture. The observed changes, $0.085/0.22 = 0.39$ and $0.085/0.12 = 0.71$, are also in agreement with those predictions. Similar conclusions can be drawn by comparing measured values of Φ_{ET} with those expected based on Fig. 2. We conclude that the magnitude of the P parameter properly reflects the change in the local concentration of acceptors in the model system. Based on these results, we can safely assume that the no-mixing state is characterized by $\Phi_{ET}(0) = 0.67$ and the fully mixed state by $\Phi_{ET}(\infty) = 0.49$ for 1:1 latex blend films.

4.4. Energy transfer in blend latex dispersions with low molecular weight latex components

In this section, we examine polymer mixing in films formed from blends of oligomeric latex particles and the doubly labeled latex target. We prepared a series of latex blends with each of the unlabeled oligomeric latex samples (M_n-2.4, M_n-6.4 and M_n-11.3). In most of the cases, the latex blend composition was 1:1 by weight of the latex polymer. We first describe the extent of ET in THF-cast films as a way of investigating whether any factors could limit the mixing between components. We fitted the donor fluorescence decays from these films to Eqs. (2)–(4). The values obtained for $\Phi_{ET}(\infty)$ for all these films are shown in Fig. 5, where a text label on the x-axis of the plot identifies each of the four mixtures studied (we included the model DL:M_n-140 latex blend for comparison). The open circles refer to the dry as-cast blend films and the filled circles refer to the same films after they were annealed for 3 h at 75 °C.

In the three mixtures examined, the $\Phi_{ET}(\infty)$ values were similar to those obtained for the model DL:M_n-140 blend. Some local phase segregation in the solvent-cast film may explain the slightly higher Φ_{ET} values observed in the mixtures containing the two lowest molecular weight components (M_n-2.4 and M_n-6.4). This effect might be caused by the chain ends originating from the chain transfer agent. However, upon annealing at 75 °C, any remaining phase segregation was overcome, and Φ_{ET} reached the values obtained for the model system. These results indicate that the full-mixing state can be reached in all these mixtures.

In the next set of experiments, we examined the amount of polymer mixing that took place as the latex blend films were formed in freshly prepared films. For these measurements, we prepared films by drying 1:1 latex blends at 4 °C for 12 h. Fluorescence decay curves were then measured for each film. The films were kept at 4 °C except for the time needed (ca. 12–15 min) to carry out the fluorescence decay measurements at room temperature. All of the experimental fluorescence decays for these fresh films were well fitted to the Förster equation (χ^2 less than 1.3). Using Eq. (4) and the Förster fitting parameters, $\Phi_{ET}(0)$ values were calculated for each latex blend. These results are plotted as open triangles in Fig. 5. Values of $\Phi_{ET}(0)$ ranged from 0.62 (DL:M_n-11.3) to 0.49 (DL:M_n-2.4). These values are much lower than those obtained for the model system ($\Phi_{ET}(0) = 0.67$), indicating that significant mixing between the oligomeric particles and the doubly labeled latex target took place during the film formation step. The degree of mixing was different for each latex blend, increasing with the decrease of the oligomer molar mass. Remarkably, a state of full mixing was reached in the DL:M_n-2.4 blend.

As a test of miscibility in this blend, we carried out a differential scanning calorimetric (DSC) experiment to determine the T_g of the blend, taking advantage of the contrast between the T_g of the M_n-2.4 polymer and that of the DL polymer. To prepare a sample for this experiment, a few drops of the 1:1 DL:M_n-2.4 latex blend were deposited onto a glass plate and allowed to dry at 4 °C. After drying, the sample (~7 mg) was quickly transferred to the DSC pan and rapidly cooled to −70 °C. It was then heated from −70 °C with a heating rate of 10 °C/min. The corresponding DSC run (heating step) is shown in Fig. 6. The upper and lower DSC traces correspond to the pure M_n-2.4 and DL components. Fresh films of

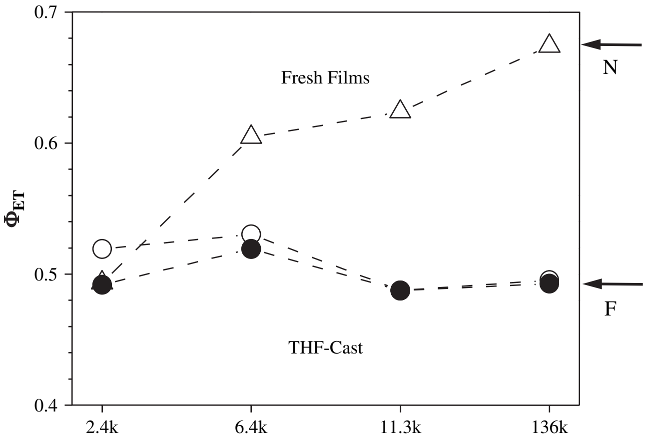

Fig. 5. Quantum efficiency of energy transfer Φ_{ET} for all the 1:1 DL:low-M latex mixtures studied. Fresh films (open triangles); THF-cast films (open circles); THF-cast films annealed at 75 °C over 3 h (filled circles). For details about film preparation, see the text. The N and F arrows indicate the no-mixing and full-mixing limits, respectively.

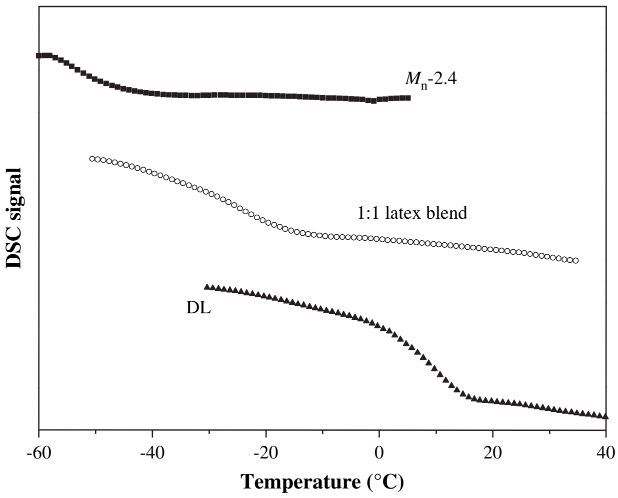

Fig. 6. DSC thermograms of freshly cast latex films. Top-to-bottom: M_n-2.4; a 1:1 DL:M_n-2.4 mixture; DL.

the 1:1 DL:M_n-2.4 latex blend exhibit only a single T_g (Fig. 6). Its value (−24 °C) is in good agreement with that calculated from the Fox equation (−22 °C) assuming full mixing between the M_n-2.4 and the DL polymer. Single values of T_g were also found when we examined a wider range of blend compositions. These values were sensitive to blend composition, and they could be nicely described using the Fox equation [17].

These results suggest that rapid interdiffusion of the polymer components takes place during the drying step. In polymer blends, the kinetics of mixing is controlled by parameters such as molecular weight and chemical composition of the polymers, thermodynamic factors and kinetic issues, represented by the monomeric friction coefficient [18]. The latter parameter is very sensitive to the $T - T_g$ difference and to the chemical structure of the monomer unit [19]. In the case considered here, except for the presence of initiator or CTA groups attached to the ends of the oligomeric chains, there are no differences in chemical composition between the latex target and the oligomeric particles. As long as there is no energetic barrier associated with an unfavorable thermodynamic interaction parameter, polymer diffusion will be controlled by entropic and kinetic factors. Since the M_n-2.4 sample consists of low molecular weight polymer, a large entropy of mixing is expected. In addition, the polymer in this latex sample has an extremely low T_g (close to −50 °C). At the temperature of the drying process (4 °C), the $T - T_g$ difference is 55 °C. Based on our previous experience, this difference is large enough to produce significant amounts of polymer mixing even in latex polymers with higher molecular weight. Therefore, the combination of a large entropy of mixing and a large $T - T_g$ difference may explain the extremely fast rate of polymer mixing observed in this blend that leads to the full-mixing state observed in its fresh films. In other cases (DL:M_n-6.4 and DL:M_n-11.3 mixtures), even though a large entropy of mixing is expected, the difference $T - T_g$ (at the temperature of the drying process) is modest, which may explain the intermediate degrees of mixing we found in their fresh films.

4.5. Homogenization times in the latex blend films

The effectiveness of the oligomeric latexes as diffusion promoters will depend on how fast they become distributed in the latex target. In this context, we measured the time required for oligomers to reach the full-mixing state in each of the blends. As full mixing implies a homogeneous distribution of oligomers, we refer to this time as "homogenization time". For these measurements, we prepared fresh films for each of the 1:1 latex blends, by drying the films on quartz substrates at 4 °C for 12 h. Then, the films were annealed at a constant temperature, and their fluorescence decay curves were measured in order to follow the evolution of Φ_{ET} with annealing time. We performed these experiments at slightly above ambient temperature (35 °C). Fig. 7 shows a plot of the evolution of Φ_{ET} with annealing time for all the latex blends studied. In this plot, the Φ_{ET} value at zero time corresponds to the measurement carried out on the fresh film.

In the 1:1 DL:M_n-2.4 latex blend (filled circles), the initial value of Φ_{ET} corresponds to the full-mixing state ($\Phi_{ET} = 0.49$), which was reached during the film drying step. Further annealing did not affect Φ_{ET} and the values remained unchanged after more than 24 h at 35 °C. We can consider that the oligomeric polymer chains contained in the M_n-2.4 latex sample reached a homogeneous distribution in the latex target almost instantaneously. In the 1:1 DL:M_n-6.4 latex blend (open triangles), Φ_{ET}, evolved from an initial value of 0.59, and reached the characteristic value for full mixing in less than 1 h at 35 °C. For the 1:1 DL:M_n-11.3 latex blend (filled squares), the homogenization time was much longer, consistent with the higher T_g and molar mass of the M_n-11.3 latex polymer. From an initial value of 0.625, Φ_{ET} for this film decreased progressively to a steady value close to that characteristic of full mixing.

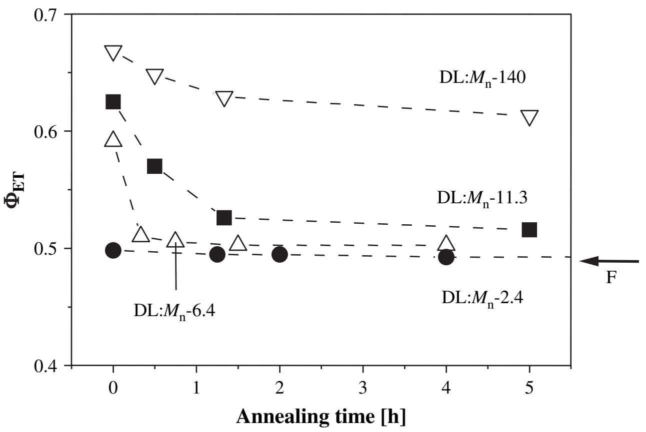

Fig. 7. Evolution of Φ_{ET} with annealing time at 35 °C for films formed from 1:1 DL:low-M latex mixtures. DL:M_n-2.4 (filled circles); DL:M_n-6.4 (open triangles); DL:M_n-11.3 (solid squares); DL:M_n-140 (open inverted triangles). The arrow F indicates the full-mixing limit.

To evaluate the efficiency of the oligomeric latex particles as diffusion promoters for the latex target, we have to compare their homogenization times with the time scale for polymer diffusion within the target. The latter process can be characterized by preparing a set of unlabeled latex particles that match the molecular weight and the T_g of the doubly labeled target, and by performing the same kind of experiments described above. Although the M_n-140 sample does not match exactly with the molecular weight of the target, it has similar characteristics in terms of T_g and particle diameter that make the samples comparable. Thus, useful information can be obtained by examining its rate of diffusive mixing with the doubly labeled target. The uppermost curve in Fig. 7 (inverted open triangles) shows the evolution of Φ_{ET} with annealing time in the 1:1 DL:M_n-140 latex blend. Here Φ_{ET} evolves slowly with time, from an initial value of 0.67, corresponding to no mixing between the latex polymers. Compared with the times for oligomer homogenization, the time scale for polymer diffusion in the 1:1 DL:M_n-140 latex blend is much longer.

5. Summary

We have examined hard–soft latex blend films in which both components have the same chemical composition (1:1

MMA:BA by weight) but different mean molar masses. As a consequence of the differences in molar mass, the latex polymers have different glass transition temperatures. In the most extreme case, the latex polymer with $M_n = 2400$ g/mol has $T_g = -48$ °C, whereas the doubly labeled sample with $M_n = 252{,}000$ g/mol has $T_g = 11$ °C. We showed using energy transfer experiments that the various oligomeric latex polymers were completely miscible with the highest molar mass sample. These experiments were carried out in a novel way. We synthesized a single sample of doubly labeled high molar mass P(MMA-*co*-BA) latex. We used this latex as a probe of its interaction with the unlabeled lower M polymer latex samples.

To establish a baseline for our experiments, we examined films of the blend of the doubly labeled high-M latex polymer with an unlabeled latex with a polymer molecular weight of $M_n = 140{,}000$ g/mol. Here, the blend dried to form a transparent film, with little or no diffusive mixing. Polymer diffusion was accelerated when the film was annealed at 35 °C, but the system was far from full mixing even after 5 h at that temperature. Polymer diffusion and mixing was more effective for the oligomeric latex samples, and the effectiveness increased as the mean molar mass and T_g of the latex polymer were decreased. For the lowest M oligomeric latex, we found that the two polymers underwent complete mixing at the molecular level in the time necessary for the latex blend dispersion to dry into a transparent film.

The interesting feature of this experiment is that the two polymers that interdiffuse in the latex film have very different T_g values. For this diffusion to take place rapidly, the low-M polymer must serve as a plasticizer for the higher M polymer. There have been a number of experiments and several theoretical treatments of polymer diffusion across an interface in which the two diffusing species had very different T_g values. For the most part, these examples involve miscible blends (like polystyrene + poly(phenylene oxide) or polystyrene + poly(vinyl methyl ether)) [20,21]. In these examples, the diffusion between the components is characterized by very asymmetric concentration profiles. This asymmetry is due to the large changes in molecular mobility experienced by the polymer chains along the diffusion path, associated with large gradients in T_g and monomeric friction coefficients across the interphase.

We end the paper with one final comment about the sensitivity of energy transfer experiments carried out by diffusion of an unlabeled polymer into a doubly labeled matrix. This diffusive mixing increases the mean separation between donor and acceptor groups. This dilution is easily detected by a decrease in the quantum efficiency of ET. From this perspective, this experimental strategy produced useful data with a minimum demand on the synthesis of many labeled polymer samples. From another perspective, experiments carried out in this way are less sensitive to the details of the polymer concentration profile across the interphase. In some experiments published by our research group, we have used the detailed shape of the donor fluorescence decay profile ($I_D(t')$) to obtain information about the polymer distribution profile across an interface. This information was accessible, because the models used to fit the $I_D(t')$ profiles were able to distinguish between uniform and non-uniform donor and acceptor distributions. In the experiments described above, we found that all of the $I_D(t')$ decays gave reasonable fits to Eqs. (2)–(4), even when there was a good reason to expect a non-uniform distribution of low- and high-M polymer in the interphase. We interpret this result to mean that the dilution experiment, which examines a blend of an unlabeled polymer with a doubly labeled polymer, does not lead to a sufficiently large change in the local donor–acceptor distribution. Thus, this particular experiment does not have the sensitivity to yield information about the polymer concentration profile along the diffusion path. We would like to explore in the future the possibility that a different experimental design will provide information about the evolution of the polymer concentration profile at the interphase in this kind of systems.

Acknowledgments

The authors thank Rohm and Haas, Rohm and Haas Canada, and NSERC Canada for their support for this research.

References

[1] (a) de Gennes P-G. J Chem Phys 1980;72:4756;
(b) Brochard F, Jouffroy J, Levinson P. J Phys Lett 1983;44:L-455;
(c) Jordan EA, Ball RC, Donald AM, Fetters LJ, Jones RAL, Klein J. Macromolecules 1988;21:23.

[2] (a) Oh JK, Wu J, Winnik MA, Craun GP, Rademacher J, Farwaha RJ. J Polym Sci Part A Polym Chem 2002;40:1594;
(b) Oh JK, Wu J, Winnik MA, Craun GP, Rademacher J, Farwaha R. J Polym Sci Part A Polym Chem 2002;40:3001.

[3] Liu R, Winnik MA, Di Stefano F, Vanketessan J. Macromolecules 2001;34:7306.

[4] Sosnowski S, Feng J, Winnik MA. J Polym Sci Part A Polym Chem 1994;32:1497.

[5] (a) Förster T. Ann Phys (Leipzig) 1948;2:55;
(b) Förster T. Z Naturforsch 1949;4A:321.

[6] Ye X, Farinha JPS, Oh JK, Winnik MA, Wu C. Macromolecules 2003;36:8749.

[7] Oh JK, Yang J, Tomba JP, Rademacher J, Farwaha RJ, Winnik MA. Macromolecules 2003;36:8836.

[8] Wu J, Oh JK, Yang J, Winnik MA, Farwaha R, Rademacher J. Macromolecules 2003;36:8139.

[9] (a) Zhao CL, Wang YC, Winnik MA. Macromolecules 1990;23:4082;
(b) Wang YC, Zhao CL, Winnik MA. J Chem Phys 1991;95:2143.

[10] (a) Förster T. Discuss Faraday Soc 1957;27:7;
(b) Baumann J, Fayer MD. J Chem Phys 1986;85:4087;
(c) For reviews of the use of energy transfer to study polymers, see: Morawetz H. Science 1988;240:172.

[11] Lakowicz JR. Principles of fluorescence spectroscopy. New York: Plenum; 1983. p. 371, 426.

[12] (a) Feng J, Odrobina E, Winnik MA. Macromolecules 1998;31:5290;
(b) Tamai T, Pinenq P, Winnik MA. Macromolecules 1999;32:6102;
(c) Kobayashi K, Rharbi Y, Winnik MA. Macromolecules 2001;34:1855.

[13] (a) Vaha-Nissi M, Kervinen K, Savolainen A, Egolf S, Lau W. J Appl Polym Sci 2006;101:1958;
(b) Lau W. US Patent 5,521,266; 1996;
(c) Lau W. Macromol Symp 2002;182:283;
(d) Lau W. US Patent Appl 2006/0183839; 17 August 2006.

[14] Fox T, Flory P. J Polym Sci 1954;14:315.

[15] Farinha JPS, Martinho JMG, Yekta A, Winnik MA. Macromolecules 1995;28:6084–8.

[16] This value represents the lifetime of the donor in the absence of acceptors and was taken as a fixed parameter in all the Förster fits.
[17] Tomba JP, Lau W, Winnik MA. Oligomeric latexes as promoters of diffusion during film formation, in preparation.
[18] (a) Kramer EJ, Green PF, Palmstrom CJ. Polymer 1984;25:473;
(b) Composto J, Kramer EJ, White DM. Macromolecules 1988;21:2580;
(c) Jordan EA, Ball RC, Donald AM, Fetters LJ, Jones RAL, Klein J. Macromolecules 1988;21(1):235;
(d) Composto RJ, Kramer EJ, White DM. Polymer 1990;31:2320;
(e) Tomba JP, Carella JM. J Polym Sci Polym Phys Ed 1999;37:3097.
[19] Ferry JD. Viscoelastic properties of polymers. New York: Wiley; 1980.
[20] (a) Composto RJ, Kramer EJ. J Mater Sci 1991;26:2815;
(b) Tomba JP, Carella JM, Pastor JM, Merino JC. Polymer 2002;43:6751.
[21] (a) Jabbari E, Peppas N. Macromolecules 1993;26:2175;
(b) Tomba JP, Carella JM, García D, Pastor JM. Macromolecules 2004;37:4940.