

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231677784>

Internal Structure of Core–Shell Latex Particles Studied by Fluorescence Nonradiative Energy Transfer

ARTICLE *in* LANGMUIR · JUNE 1996

Impact Factor: 4.46 · DOI: 10.1021/la9509357

CITATIONS

21

READS

9

2 AUTHORS, INCLUDING:



Elías Pérez

Universidad Autónoma de San Luis Potosí

79 PUBLICATIONS 546 CITATIONS

SEE PROFILE

Internal Structure of Core–Shell Latex Particles Studied by Fluorescence Nonradiative Energy Transfer

Elías Pérez and Jacques Lang*

Institut Charles Sadron (CRM-EAHP), CNRS-ULP Strasbourg, 6, rue Boussingault, 67083 Strasbourg Cédex, France

Received October 25, 1995. In Final Form: March 18, 1996

Latex particles have been synthesized in two-steps emulsion polymerizations under starving conditions, and the internal structure of these particles has been investigated by fluorescence nonradiative energy transfer (NRET), in order to check for the formation of core–shell particles. The polymers were based on methyl methacrylate (MMA) and butyl methacrylate (BMA) as monomers. The energy donor monomer was introduced during the first step of the polymerization, and the energy acceptor monomer during the second step. The T_g of PBMA is too low, compared to the polymerization temperature T_p ($T_p = 80^\circ\text{C}$), to observe a separation between the donor- and acceptor-labeled PBMA chains inside the particles. On the contrary the T_g of PMMA is larger than T_p , and a separation between energy donor- and energy acceptor-labeled PMMA chains is observed with this polymer. The separation has the structure of a diffuse interface between the two labeled PMMA polymers. The study of other particles shows that the apparent fraction of mixing, f'_A , between donor- and acceptor-labeled polymer chains inside the particle decreases, as expected, as the incompatibility and the T_g of the polymers increase. Addition of a cross-linking agent during the first step of the polymerization leads to a decrease of f'_A , even in the case of the PBMA latex particles. Annealing of latex films and dispersions at temperatures above the T_g of the polymers allowed phase separation or mixing inside latex particles to be observed.

Introduction

Core-shell latex particles are composite particles made of two different polymers; one theoretically composes the core and the other the shell of the particles. These particles are usually synthesized by an at least two-step emulsion polymerization. However, it is known that in practice core–shell particles are difficult to obtain. This happens for instance when the compatibility or the polymer glass transition temperature, T_g , is favorable to a partial mixing of the two polymers or when there is no appreciable difference between the affinities of the two polymers for the water phase. Other parameters like the relative solubility of the monomers in the water phase and the relative interfacial tensions between the three phases, namely the two polymers and water, or swelling of the core by the monomer used in the second stage of the polymerization, can also affect their morphology. Thus, other structures than the expected core–shell are often found. Moreover, it is likely that a neat interface between the core and the shell rarely occurs. In most cases a composition gradient forms between the center and the periphery of the particle. In order to reduce penetration of one polymer phase into the other, cross-linking agents are sometimes used.

Core-shell particles have many current and potential applications in the chemical, biological, and pharmaceutical industries. They are for example used to confer to a material two kinds of properties, one being given by the core and the other by the shell of the particle, as for instance mechanical resistance and hydrophobicity. Another example is that of shells carrying active groups in the field of biology. Therefore a great deal of studies have been done, using a variety of methods, in order to determine the shape and the internal structure of core–shell latex particles.

Transmission electron microscopy (TEM) methods have been employed in the early seventies to study the morphology of polystyrene latex particles synthesized by

a two-stage seeded emulsion polymerization.^{1,2} A small quantity of butadiene was added to the styrene in the second stage of the polymerization. Thin cross sections of the particles embedded in a resin were obtained by ultramicrotomy, exposed to osmium tetroxide to stain the butadiene, and finally examined in an electron microscope. The core–shell structure of the particles was clearly visible. This morphology was confirmed in another experiment made on the same polystyrene latex particles, where tritiated styrene was used as a tagging agent in the seed and autoradiography as a detecting method.² Thus, the possibility that incompatibility between the polystyrene of the seed and the poly(styrene-*co*-butadiene) of the second stage could be at the origin of the morphology observed in the first experiment was discarded by the authors. They concluded that in the second stage of the polymerization the monomer did concentrate at the periphery of the swollen particles rather than swelling the particles uniformly.

Transmission electron microscopy, in conjunction with the osmium tetroxide staining method, has been used for the morphological characterization of polystyrene particles embedded in a poly(isobutyl acrylate) phase.³ Foamlike structures were observed where beads of polystyrene were surrounded by a film or a shell of poly(isobutyl acrylate). The structure of poly(vinyl acetate)–poly(butyl acrylate) latex particles has been investigated by other authors^{4,5} using the staining method described in ref 3. It has been shown that the batch-polymerized particles have a relatively large butyl acrylate-rich core surrounded by a vinyl acetate-rich shell, whereas particles synthesized by semicontinuous polymerization under starving conditions have a more homogeneous composition. These structures were in agreement with dynamic mechanical spectroscopy.

(1) Grancio, M. R.; Williams, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 2617.

(2) Keusch, P.; Williams, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 143.

(3) Kanig, G.; Neff, H. *Colloid Polym. Sci.* **1975**, *253*, 29.

(4) Misra, S. C.; Pichot, C.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 567.

(5) Misra, S. C.; Pichot, C.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2383.

* To whom correspondence should be addressed.

† Abstract published in *Advance ACS Abstracts*, June 1, 1996.

copy,^{4,5} differential scanning calorimetry,⁵ and tensile strength measurements⁵ made on the same systems and were attributed to the difference in the copolymerization reactivity ratios of the two monomers.⁴

Transmission electron microscopy has been next widely used to investigate the morphology of several types of composite latex particles. Different authors have investigated particles made of poly(butyl acrylate) and polystyrene using TEM alone⁶ or in conjunction with other methods.⁷ Core-shell⁷ or "anomalous" structured⁶ particles were found, depending on the emulsion polymerization method used. Polystyrene (PS)-poly(methyl methacrylate) (PMMA) latex particles, synthesized with PS as seed particles, were found to have nonuniform morphologies,⁸ whereas PMMA-PS latex particles, synthesized with PMMA as seed particles, were found to have a core-shell structure.⁹ The existence of particles with a core-shell structure was demonstrated by TEM for several other types of latexes as for instance particles made of silicon oils-poly(glycidyl methacrylate)¹⁰ or particles based on various combinations between vinyl acetate and acrylates monomers^{11,12} or particles made of polymers with different affinities for water, as for instance the hydrophobic PS and the amphiphilic poly(hydroxyethyl methacrylate).¹³

Other methods have been used for the study of the morphology of core-shell particles. Small angle neutron scattering (SANS) analysis made for PMMA-PMMA,^{11,14} PMMA-PS,¹⁴ and PS-PMMA¹¹ composite particles, synthesized using perdeuterated monomers (methyl methacrylate or styrene) in the second stage of the polymerization, gave evidences of the presence of the deuterated polymers at the surface of the particles. SANS experiments on poly(methyl methacrylate-co-styrene)-PMMA particles with again a deuterated monomer in the second stage of the polymerization also showed evidences of a core-shell structure for these particles.¹⁵ High-resolution NMR has been employed to characterize polybutadiene-PMMA core-shell particles.^{16,17} Small-angle X-ray scattering has been employed to study, directly¹⁸ or by a contrast variation method^{19,20} the internal structure of PS-PMMA latex particles. Evidences of a core-shell structure with a small interfacial region between PS (core) and PMMA (shell) were found.^{19,20} It has also been shown that the internal structure of core-shell latex particles

could be studied using light scattering.²¹ Dynamic mechanical spectroscopy measurements^{4,5,22} and atomic force microscopy²³ gave arguments for the existence of structured core-shell particles. Titration methods can also be carried out for the study of latex particles bearing functional groups at the surface or in the shell of the particles.^{24,25}

Recently, fluorescence nonradiative energy transfer (NRET) has been used by Winnik et al.²⁶ for the investigation of the structure of core-shell latex particles. The use of NRET for the investigation of colloidal polymer particles was introduced by Winnik and co-workers for the study of the further gradual coalescence of latex particles in latex films.^{27,28} They studied the polymer chain migration between adjacent particles in films composed of energy donor-labeled polymer particles and energy acceptor-labeled polymer particles. In the case of core-shell latex particles, an adequate labeling of the polymer chains with the donor and the acceptor inside the same particle was expected to give information on the extent of mixing between the core and the shell. Winnik et al.²⁶ studied PMMA-PMMA core-shell particles synthesized by different emulsion polymerization methods. They found great differences in the core-shell morphology, depending on the type of polymerization. In particular a quasicomplete mixing was found when the methyl methacrylate and acceptor monomers were added as a batch process to the PMMA-donor seed, whereas much less mixing was found when these two monomers were added under starving conditions to the seed.

Since 1990 a rationalization of the morphology of composite particles has been suggested by Sundberg and collaborators,^{29,30} in terms of the interfacial energy between the polymer phases and between the polymers and the aqueous phases. The morphologies of composite latex particles, including core-shell structure, obtained from different types of polymerization, have been discussed along this line.^{8,30-32} However, most of the above studies have shown that, besides the nature of the monomers used and of the polymers formed, the morphology of core-shell particles is very dependent on the experimental conditions of the polymerization.³³ We present here a study of the morphology of core-shell latex particles investigated by NRET, with a special emphasis on the effect of the relative values between the glass transition temperature T_g of the polymers and the temperature T_p of polymerization on the extend of mixing between the core and the shell of the particle. We also give some results on the further gradual coalescence of core-shell latex particles in films, which are compared to those obtained

(6) Okubo, M.; Katsuta, Y.; Matsumoto, T. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 45.

(7) Min, T. I.; Klein, A.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2845.

(8) Chen, Y.-C.; Dimonie, V.; El-Aasser, M. S. *Macromolecules* **1991**, *24*, 3779. Chen, Y.-C.; Dimonie, V. L.; Shaffer, O. L.; El-Aasser, M. S. *Polym. Int.* **1993**, *30*, 185.

(9) Jönsson, J.-E.; Hassander, H.; Törnell, B. *Macromolecules* **1994**, *27*, 1932.

(10) He, W.; Tong, J.; Wang, M.; Pan, C.; Zhu, Q. *J. Appl. Polym. Sci.* **1995**, *55*, 667.

(11) Hergeth, W.-H.; Bittrich, H.-J.; Eichhorn, F.; Schlenker, S.; Schmutzler, K.; Steinau, U.-J. *Polymer* **1989**, *60*, 1933.

(12) Vandezande, G. A.; Rudin, A. *J. Coat. Technol.* **1994**, *66*, 99.

(13) Kamei, S.; Okubo, M.; Matsumoto, T. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 3109.

(14) O'Reilly, J. M.; Melpolder, S. M.; Fischer, L. W.; Wignall, G. D.; Ramakrishnan, V. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24* (2), 407. Fischer, L. W.; Melpolder, S. M.; O'Reilly, J. M.; Ramakrishnan, V.; Wignall, G. D. *J. Colloid Interface Sci.* **1988**, *123*, 24.

(15) Wai, M. P.; Gelman, R. A.; Fatica, M. G.; Hoerl, R. H.; Wignall, G. D. *Polymer* **1987**, *28*, 918.

(16) Tembou Nzudie, D.; Delmotte, L.; Riess, G. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 251.

(17) Tembou Nzudie, D.; Delmotte, L.; Riess, G. *Macromol. Chem. Phys.* **1994**, *195*, 2723.

(18) Grunder, R.; Urban, G.; Ballauff, M. *Colloid Polym. Sci.* **1993**, *271*, 563.

(19) Dingenouts, N.; Ballauff, M. *Acta Polym.* **1993**, *44*, 178.

(20) Ballauff, M. *Macromol. Symp.* **1994**, *87*, 93.

(21) Manzur, A. *J. Colloid Interface Sci.* **1994**, *162*, 197.

(22) Cavaillé, J. Y.; Jourdan, C.; Kong, X. Y.; Perez, J.; Pichot, C.; Guillot, J. *Polymer* **1988**, *27*, 693.

(23) Sommer, F.; Tran Min Duc; Pirri, R.; Meunier, G.; Quet, C. *Langmuir* **1995**, *11*, 440.

(24) Dobler, F.; Pith, T.; Holl, Y.; Lambla, M. *J. Appl. Polym. Sci.* **1992**, *44*, 1075.

(25) Murro, S.; Hashimoto, H.; Hosoi, K. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1365.

(26) Winnik, M. A.; Xu, H.; Satguru, R. *Makromol. Chem., Macromol. Symp.* **1993**, *70/71*, 107.

(27) Pekcan, Ö.; Winnik, M. A.; Croucher, M. D. *Macromolecules* **1990**, *23*, 2673.

(28) Zhao, C.-L.; Wang, Y.; Hruska, Z.; Winnik, M. A. *Macromolecules* **1990**, *23*, 4082.

(29) Sundberg, D. C.; Casassa, A. P.; Pantazopoulos, J.; Muscato, M. R.; Kronberg, B.; Berg, J. *J. Appl. Polym. Sci.* **1990**, *41*, 1425.

(30) Sundberg, E. J.; Sundberg, D. C. *J. Appl. Polym. Sci.* **1993**, *47*, 1277.

(31) Chen, Y.-C.; Dimonie, V.; El-Aasser, M. S. *J. Appl. Polym. Sci.* **1991**, *42*, 1049; **1992**, *45*, 487.

(32) Lee, S.; Rudin, A. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 865, 2211.

(33) Daniel, J. C. *Makromol. Chem., Suppl.* **1985**, *10/11*, 359.

Table 1. Recipe and Polymerization Conditions for the Homogeneous (H1 and H2) and Core–Shell (CS1 to CS8) Latex Synthesis

step	composition	H1	H2	CS1	CS2	CS3	CS4	CS5	CS6	CS7	CS8
seed (batch) (80 °C)	water (mL)	45	45	45	45	45	45	45	45	45	45
	KPS (g)	0.0430	0.0428	0.0428	0.0428	0.0422	0.0425	0.0420	0.0430	0.0430	0.0427
	SDS (g)	0.0204	0.0201	0.0203	0.0348	0.0351	0.0355	0.0352	0.0345	0.0350	0.0349
	NaHCO ₃ (g)	0.0815	0.0815	0.0817	0.0815	0.0816	0.0818	0.0813	0.0814	0.0817	0.0821
	MMA (mL)	3.25	3.25	3.25				3.25	3.25		
first slow step (5 h) (80 °C)	BMA (mL)				3.25	3.25	3.25			3.25	3.25
	water (mL)	20	20	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64
	KPS (g)	0.036	0.036	0.018	0.016	0.015	0.017	0.017	0.016	0.016	0.016
	SDS (g)	0.345	0.345	0.186	0.049	0.150	0.160	0.075	0.076	0.076	0.076
	MMA (mL)	24	24	10.38				10.38	10.38		
	BMA (mL)				10.38	10.38	10.38			10.38	10.38
	AMA (mL)							0.2	0.5	0.2	0.5
	PheMMA (g)	0.417		0.204	0.217	0.216	0.216	0.217	0.218	0.218	0.219
second slow step (5 h) (80 °C)	AnMA (g)		0.396								
	water (mL)			11.36	11.36	11.36	11.36	11.36	11.36	11.36	11.36
	KPS (g)			0.024	0.020	0.021	0.022	0.022	0.021	0.021	0.021
	SDS (g)			0.245	0.065	0.200	0.210	0.099	0.100	0.100	0.100
	MMA (mL)			13.66	13.66	6.83		13.66	13.66		
	BMA (mL)					6.83	13.66			13.66	13.66
	AnMA (g)			0.203	0.201	0.200	0.201	0.201	0.201	0.201	0.201

with homogeneous particles. Finally we show that NRET can evidence phase separation which occurs inside core–shell particles upon annealing of the dispersion.

Materials and Methods

Materials. Butyl methacrylate (BMA) and potassium persulfate (KPS) were purchased from Aldrich, allyl methacrylate (AMA, cross-linking agent) from Fluka, sodium hydrogen carbonate (NaHCO₃) from Prolabo, and sodium dodecyl sulfate (SDS) from Touzard and Matignon. All these compounds were of the best grade available. SDS was recrystallized thrice from mixtures of water and ethanol. Methyl methacrylate (MMA) was a gift from the EAHP (Strasbourg). The donor, (9-phenanthryl)methyl methacrylate (PheMMA), and the acceptor, 9-anthryl methacrylate (AnMA), were synthesized following the recipe given elsewhere.²⁸ Water was freshly deionized and distilled before use.

Latex Synthesis. The latex particles were synthesized by semicontinuous free radical emulsion polymerization using potassium persulfate as initiator and following a procedure described by Zhao et al.²⁸ For the synthesis of the homogeneous particles a latex seed was first prepared and the rest of the components, including the donor (PheMMA) or the acceptor (AnMA), were next slowly (starving conditions) added to the seed. For the synthesis of the composite (core–shell) particles a latex seed was first prepared and next the rest of the components was slowly added in two steps. The core of the particle was supposed to originate from the seed and the first slow step, and the shell of the particle was supposed to originate from the second slow step. The donor was added during the first slow step following the seed, and the acceptor during the second slow step. Slow addition of the donor or of the acceptor with the monomer was necessary to insure a uniform repartition of the probes in the core and in the shell of the particles. The second slow step was started 1 h after the end of the addition of the components of the previous step, to let all the monomer of the core be consumed before starting to build up the shell. During this period of time the emulsion was maintained at the temperature of the polymerization, which was 80 °C. Thus, in the composite particles synthesized here the phenanthrene-labeled polymer should be at the center of the particles and the anthracene-labeled polymer at the periphery. About 1 mol % of donor and acceptor relative to the current monomers was used.

Ten kinds of latex particles were synthesized, all based on methyl methacrylate and butyl methacrylate as monomers: (i) two homogeneous latexes made of PMMA, one containing the donor (H1) and the other the acceptor (H2); (ii) four core–shell latexes made respectively of PMMA(Phe)–PMMA(An) (CS1), PBMA(Phe)–PMMA(An) (CS2), PBMA(Phe)–Poly(BMA-co-MMA)(An) (CS3), and PBMA(Phe)–PBMA(An) (CS4); and (iii) four core–shell latexes prepared by adding a cross-linking agent

(allyl methacrylate) during the first slow step (synthesis of the core) at a volume percent relative to the monomer equal to 1.9% (CS5 made of PMMA(Phe)–PMMA(An) and CS7 made of PBMA(Phe)–PBMA(An)) and 4.8% (CS6 made of PMMA(Phe)–PMMA(An) and CS8 made of PBMA(Phe)–PBMA(An)). The recipe and polymerization conditions are given in Table 1. In each of the slow steps, the aqueous phase (containing the KPS and the SDS) and the organic phase (the monomers) were added separately to the reactor. These slow steps were performed in about 5 h each; next the dispersion was stirred gently at 80 °C for an additional 10 h. For the homogeneous particles the two slow steps were replaced by only one slow step, in which methyl methacrylate and the donor or methyl methacrylate and the acceptor were introduced for the synthesis of latex H1 or H2, respectively. Proper labeling of the polymer chains was checked using an UV detector coupled to a GPC apparatus. The main characteristics of these latexes are reported in Table 2.

Latex Particle Size Measurements. Particle diameters were determined from the height profile (see Figure 1) on latex dry films by atomic force microscopy (AFM) working in the height mode, which means that the force exerted on the film by the cantilever during scanning was kept constant. The model used was a Nanoscope III from Digital Instruments, Inc., Santa Barbara, CA. The piezoelectric translator could scan a maximum surface area of $12 \times 12 \mu\text{m}^2$. The spring constant of the cantilever was $0.58 \text{ N}\cdot\text{m}^{-1}$. Besides the determination of the size of the particles, the AFM allowed us to appreciate the shape and the polydispersity of the particles. It also allowed us to follow the evolution of the size (an example is given in Figure 2) and thus of the number of particles in the course of the latex synthesis. All particles investigated in this study had a spherical shape and a very low-size polydispersity (see Figure 2). Their size was determined from height profiles as the one shown in Figure 1. The value of the particle diameter given in Table 2 is an average of at least 30 measurements of the center to center distance between adjacent particles. In the case of particles with a PMMA shell, a rough surface was observed. This will be discussed below.

Particle diameters were also determined in dispersion, at a latex particle concentration of about $5 \times 10^{-6} \text{ g/cm}^3$, by quasielastic light scattering (QELS), using a home-made apparatus described elsewhere.³⁴ QELS measurements were performed at 25 °C. The full homodyne correlation function of the scattered intensity, defined on 192 channels, was obtained by using the ALV-3000 (ALV-Langen, Germany) autocorrelator in its multi- τ mode. In this mode the correlation functions cover seven decades in delay times going from 1 μs to 63 s. The homodyne intensity autocorrelation function $G^{(2)}(q, t)$ was analyzed using the constrained regularization method (CONTIN) developed by Provencher.³⁵ The base line of the scattered function

(34) Duval, M.; Coles, H. J. *Rev. Phys. Appl.* **1980**, *15*, 1399.

(35) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.

Table 2. Symbols Used in the Text, Composition, Glass Transition Temperature, and Size of the Synthesized Latex Particles

latex	theoretical structure [vol %]	chemical composition	T_g (°C) (DSC)	core of CS particle (nm) (AFM)	particle diameter (nm) (AFM)	particle diameter (QELS) (nm)	
						$\langle D \rangle_n$	$\langle D \rangle_w / \langle D \rangle_n$
H1	homogeneous [100]	PMMA(Phe)	110		183 ± 13	180	1.01
H2	homogeneous [100]	PMMA(An)	110		190 ± 18	192	1.01
CS1	core-shell [50-50]	PMMA(Phe)-PMMA(An)	110	143 ± 9 ^b	169 ± 12	131	1.16
CS2	core-shell [50-50]	PBMA(Phe)-PMMA(An)	34-110	198 ± 5	257 ± 9	252	1.08
CS3	core-shell [50-(25-25)]	PBMA(Phe)-Poly(MMA-co-BMA)(An)	34-80	242 ± 7	295 ± 22	301	1.03
CS4	core-shell [50-50]	PBMA(Phe)-PBMA(An)	34-34	186 ± 8	226 ± 10	256	1.01
CS5	core-shell [50-50]	PMMA(Phe)-PMMA(An) [1.9% ^a]	114	118 ± 10	146 ± 5	141	1.07
CS6	core-shell [50-50]	PMMA(Phe)-PMMA(An) [4.8% ^a]	110	120 ± 11	152 ± 11	166	1.01
CS7	core-shell [50-50]	PBMA(Phe)-PBMA(An) [1.9% ^a]	38	191 ± 8	231 ± 17	246	1.02
CS8	core-shell [50-50]	PBMA(Phe)-PBMA(An) [4.8% ^a]	41	182 ± 7	221 ± 8	234	1.01

^a Allyl methacrylate in the core (vol %). ^b Calculated from the diameter of the final particle measured by AFM and from the quantity of monomer introduced for the shell synthesis.

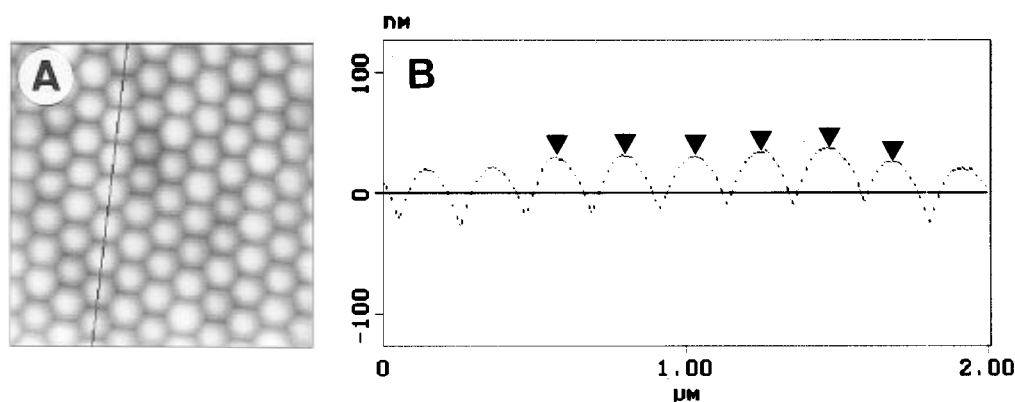


Figure 1. AFM top view (A) (size: 2 $\mu\text{m} \times 2 \mu\text{m}$) and height profile (B) of CS4 latex film. The height profile is taken along the line shown on the top view image. The diameter of the particles (226 nm) is obtained from the average distance between two adjacent triangles, which indicate the center of the particles, using the AFM software. For each latex studied, at least 30 values have been measured to obtain the average diameters given in Table 2 for the core and for the whole particle.

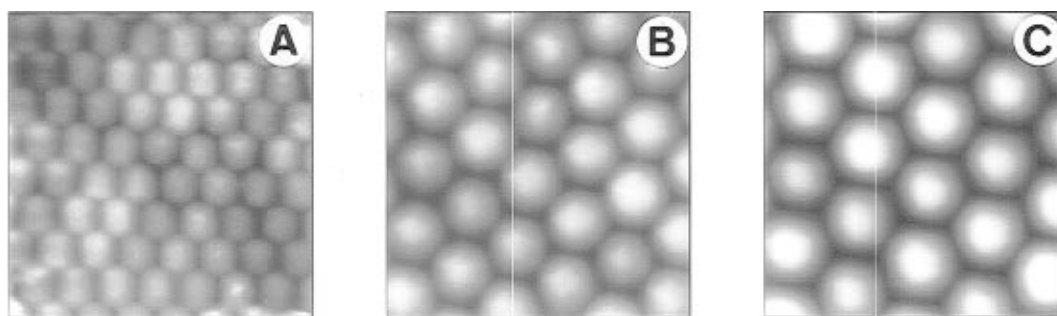


Figure 2. AFM top views of CS4 latex films obtained after solvent evaporation from dispersions taken from the reactor during synthesis: image size, 0.9 $\mu\text{m} \times 0.9 \mu\text{m}$; A, seed particles; B, particles after formation of the core; C, core-shell particles at the end of the synthesis. The increase in size of the particles of the seed has been found to be in agreement with the amount of monomer introduced during the first and second slow steps of the polymerization.

was allowed to float in the fitting procedure, and any measurement with a base line different from zero was rejected. The distribution functions of the radii of gyration as a result of the CONTIN analysis are monomodal and sharp for all the systems investigated, which indicates a rather narrow particle size distribution.

Table 2 shows that the diameters of the particles found by AFM and by QELS are very close, except perhaps for latex CS1, which is slightly less monodisperse (see last column) than the other latexes. We have given here the number average diameter, $\langle D \rangle_n$, measured by QELS, since the same average was used to determine the AFM diameter. The QELS values of $\langle D \rangle_w / \langle D \rangle_n$ also indicate a small polydispersity in size of the particles, in agreement with the observation made by AFM.

Latex Particles for Energy Transfer Measurements. The core-shell morphology of the particles was studied under two different conditions: with latexes dispersed in water at a very low concentration, about 0.2 wt %, and with the particles forming

a dry film. Films were prepared by casting 2-3 drops of the dispersion (25 wt % solid content) onto freshly cleaved mica plates and were allowed to air dry. Dry films were about 100 μm thick. Latex films used for the study of the further gradual coalescence of the particles were prepared in the same manner. Films were kept under argon during annealing at 90 °C or at 140 °C. Latexes annealed in dispersion were placed in an autoclave and heated during various periods of time at 90 °C or at 140 °C. After the dispersion was annealed, some coagulum was found at the bottom of the autoclave. Only the supernatant was used for the fluorescence measurements. Using QELS, we have checked that, in the most drastic conditions used in this work (16 h at 140 °C for CS1 and 8 h at 140 °C for CS2), the size of the particles in the supernatant had not been modified. Only a small increase of the polydispersity in size has been found in the case of the particles CS2, due probably to the formation of few aggregates during annealing.

Fluorescence Decay Measurements. Donor (phenanthrene) fluorescence decay traces were recorded with a single photon counting apparatus.³⁶ Latex dispersions, placed in a squared cell, and film samples, mounted on a home-made solid holder, were excited at 298 nm. The emission light was collected through a band-pass filter (Schott) centered at 366 nm to minimize the uptake of scattered and acceptor (anthracene) emitted light. All measurements were performed at 10 °C, i.e. below the T_g of the polymers, to avoid any kind of evolution in the particles and in the films during the illumination time.

Two methods have been employed so far for the analysis of the decay profile data; one is directly derived from the Förster equation³⁷ of nonradiative energy transfer,^{28,38} and the other uses the area under the donor fluorescence decay curves.^{39,40} Both analyses are based on the fact that the donors and the acceptors are static during the fluorescence measurements. The efficiency of the energy transfer is governed by the relation $E = R^6/(R^6 + r^6)$, where R is the characteristic distance between the chosen donor and acceptor, equal to 23 Å for the couple phenanthrene–anthracene, which are the probes used in the present study, and r is the distance between a donor and an acceptor. Thus, the energy transfer depends only on the average donor–acceptor distance in the range 0–50 Å, which is small compared to the particle size (see Table 2).

In the first analysis the donor fluorescence decay $I(t)$ is expressed by the sum of two contributions, weighted by the preexponential factors B_1 and B_2 , one which comes from the domains where the donor is mixed with the acceptor and the other which comes from the domains where the donor is without any acceptor in its vicinity, respectively:

$$I(t) = B_1 \exp(-t/\tau) - p(t/\tau)^{1/2} + B_2 \exp(-t/\tau) \quad (1)$$

In eq 1, p is a time-independent parameter proportional to the local concentration of acceptor and τ is the donor fluorescence lifetime that was found equal to 46 ns in dispersion or in film containing only donor-labeled particles. The parameters B_1 , B_2 and p are obtained by fitting eq 1 to the fluorescence decay data using a nonlinear weighted least-squares procedure. An apparent volume fraction of mixing f'_m has been defined from B_1 and B_2 , which is equal to

$$f'_m = B_1/(B_1 + B_2) \quad (2)$$

This fraction was corrected for energy transfer taking place through a perfectly neat interface between the donor- and acceptor-labeled domains ($f'_m(i)$) and for energy transfer which occurs when the donor and acceptor domains are fully mixed ($f'_m(\infty)$), and was replaced by a normalized volume fraction of mixing f_m given by eq 3:

$$f_m = (f'_m - f'_m(i))/(f'_m(\infty) - f'_m(i)) \quad (3)$$

However, in some cases the fluorescence decay data could hardly be fitted correctly with eq 1, especially when low-energy transfer occurred. Moreover the value found for p was then incorrect. Similar difficulties have already been mentioned by Winnik and co-workers.^{39,40} Therefore the method which involves the area under the decay curve has been adopted in the present study for the analysis of the fluorescence decay data. Indeed, from a theoretical point of view the energy transfer quantum yield is related to the area under each $I(t)$ curve and the apparent volume fraction of mixing, f'_A , has been calculated according to the relation

$$f'_A = (A - A_D)/(A(\infty) - A_D) \quad (4)$$

where the areas A , A_D , and $A(\infty)$ were determined after normalization and integration of the decay curves. A_D is the

area under the decay curve corresponding to latex labeled with the donor only, and $A(\infty)$ is the area under the decay curve obtained from a film formed after dissolution in THF of latexes made of the same, compatible polymer (H1–H2, CS1, or CS4). This provides conditions where donor and acceptor domains are fully mixed. A_D and $A(\infty)$ were found equal to 46.20 ± 0.53 and 21.82 ± 0.64 ns, respectively. With this procedure, the fraction of mixing f'_A was not corrected for the fraction of mixing through a neat interface. The surface area under the decay curve was determined using a numerical integration procedure which will be described elsewhere.⁴¹

Results and Discussion

Morphology and Internal Structure of the Composite Particles. All the composite particles were investigated by AFM in order to check for their shape and for the possible existence of a second nucleation which could have occurred during synthesis. Images such as those presented in Figure 2 have been taken for latexes CS1 to CS8 (see Table 2). All the particles have been found to have a rather spherical shape. No irregular structure, as for instance double hemisphere, was observed. However, the particles made of PBMA present a very smooth surface, whereas particles made of a shell of PMMA present some surface roughness, identical to the roughness shown by homogenous PMMA particles. This difference can be attributed to the higher water solubility of methyl methacrylate compared to the water solubility of butyl methacrylate, which leads to the formation of PMMA oligomers and of tiny heterocoagulated PMMA particles originated by homogeneous nucleation⁴² which later adsorb on the growing particles, and also to the higher T_g of PMMA than of PBMA, which means that at the temperature of the polymerization (80 °C) PBMA polymer chains can reorganize in, or at the surface of, the particle, whereas PMMA polymer chains cannot. Such roughness of PMMA-covered particles was already observed by TEM using a freeze fracture technique⁴³ and by AFM²³ and was assumed to originate by homogeneous nucleation. Nevertheless, all these particles synthesized for this study were found very monodisperse in size, and most often long range hexagonal packing was observed by AFM (see Figure 2), which is a good indication that the particles were very monodisperse in size and that a second nucleation had not occurred during synthesis. Indeed, it is very likely that the size of the particles resulting from a second nucleation would have been different from the size of the primary particles. We have further checked that the growth of the particles was regular from the seed to the end of the second step, by calculating the number of particles from the known quantity of monomer introduced in the reactor and the measured particle size by AFM. The number of particles during synthesis was found to be constant. This elementary work was necessary to give a reliable interpretation to the fluorescence data. Indeed, a small energy transfer could have originate from the labeled donor and acceptor polymer chains in different particles and not in different domains of the same particle. The AFM measurements show that all the particles, from a given synthesis, are identical in shape and composition, but it does not give any indication concerning the internal structure of the particles. Information on the internal structure of our core–shell particles was obtained from the NRET measurements, as is now discussed.

Table 3 shows the apparent volume fraction of mixing f'_A found for the various composite particles synthesized.

(36) Pfeffer, G.; Lami, H.; Laustriat, G.; Coche, A. C. R. *Hebd. Séances Acad. Sci.* **1963**, 257, 434.

(37) Förster, Th. *Ann. Phys. (Leipzig)* **1948**, 2, 55; *Discuss. Faraday Soc.* **1959**, 27, 7.

(38) Wang, Y.; Zhao, C.-L.; Winnik, M. A. *J. Chem. Phys.* **1991**, 95, 2143.

(39) Wang, Y.; Winnik, M. A. *Macromolecules* **1993**, 26, 3147.

(40) Kim, H.-B.; Wang, Y.; Winnik, M. A. *Polymer* **1994**, 35, 1779.

(41) Pérez, E.; Lang, J. To be published.

(42) Fitch, R. M.; Tsai, C. H. In *Polymer Colloids*; Fitch, R. M., Ed.; Plenum Press: New York, 1971; p 103.

(43) Winnik, M. A.; Zhao, C.-L.; Shaffer, O.; Shivers, R. R. *Langmuir* **1993**, 9, 2053.

Table 3. Theoretical Volume Fraction of Mixing, f'_{At} , and Experimental Volume Fraction of Mixing, f'_A , between the Donor- and the Acceptor-Labeled Polymer Chains Measured in a Dry Film and in a Dispersion for Latexes CS1 to CS8

latex	f'_{At}	f'_A	
		film	dispersion
CS1	0.093	0.52 ± 0.05	0.48 ± 0.05
CS2	0.068	0.34 ± 0.04	0.39 ± 0.05
CS3	0.056	0.50 ± 0.05	0.51 ± 0.05
CS4	0.072	1.00 ± 0.07	1.00 ± 0.07
CS5	0.112	0.40 ± 0.05	0.37 ± 0.04
CS6	0.111	0.35 ± 0.05	0.35 ± 0.04
CS7	0.071	0.70 ± 0.06	0.75 ± 0.06
CS8	0.074	0.69 ± 0.06	0.71 ± 0.06

Note first that, within the experimental errors, the same value of f'_A was obtained in the film and in the dispersion. This result will be discussed later.

We compare now the results for the latexes CS1 and CS4 given in Table 3. In both latexes the expected core and shell are made of the same polymer, PMMA for latex CS1 and PBMA for latex CS4. Whereas latex CS1 gives a fraction of mixing of 0.52, latex CS4 gives a fraction of mixing of 1. This means that, in the final PBMA particles, the polymer formed during the second step of the polymerization is completely mixed with the polymer formed during the first step. There is no separation between core and shell in these particles. There are two reasons for this: (i) the perfect compatibility between the polymer chains which were supposed to form the core and the shell of the particles and (ii) the T_g of PBMA, which is much lower than the temperature at which the polymerization was done and which allows a great mobility of the polymer chain during the synthesis. On the contrary, the result found with latex CS1 shows that a polymer with a T_g higher than the polymerization temperature can more or less remain in different domains inside the particle, presumably the core and the shell of the particle, even though the polymer chains formed during the two steps are almost perfectly compatible (the fluorescence probes represent only 1% of the monomers in the chains). However, the value of the fraction of mixing, 0.52, indicates that there is a partial mixing of the donor- and acceptor-labeled PMMA polymers. Therefore, there is not a neat separation between the core and the shell of the particles. Rather, there is presumably a composition gradient from the center to the surface of the particle. One can assume, from the labeling procedure adopted (phenanthrene in the first step and anthracene in the second step), that the center is richer in phenanthrene-labeled polymer and the surface richer in anthracene-labeled polymer. Some experimental arguments for this will be given in the following. Finally, the fraction of mixing of 0.52 found here for latex CS1 is in good agreement with the value of 0.61 found by Winnik et al.²⁶ using eq 2 for PMMA core-shell particles prepared with a slightly different procedure.

As one goes from latex CS1 to latex CS2, f'_A decreases in spite of the fact that the core of PMMA in latex CS1 is replaced by a core of PBMA in latex CS2, which has a very low T_g compared to the polymerization temperature, which should favor the penetration of monomers and of polymer chains during the second stage of the polymerization. The decrease of f'_A from latex CS1 to latex CS2 must therefore be attributed to the incompatibility between PBMA and PMMA in the latex CS2. When one goes from latex CS2 to latexes CS3 and CS4, the cores of the particle are all made of PBMA but the shell is of a different nature; it goes from pure PMMA to a copolymer of MMA and BMA and finally to pure PBMA. Thus, the second-stage polymer has an increasing compatibility with the core and a

decreasing T_g , which both contribute to the increase of f'_A . Experiments will be performed in the future in which the T_g of the shell will be kept constant and only the compatibility between the core and the shell will be varied.

The results obtained with the PMMA latexes CS1, CS5, and CS6 and the PBMA latexes CS4, CS7, and CS8 show the effect of a cross-linking agent (AMA) on the fraction of mixing. As AMA is introduced during the first stage of the polymerization (cross-linked core), the value of f'_A decreases from 0.5 (CS1, without AMA) (here values of f'_A are averages between film and dispersion values) to 0.39 (CS5, with 1.9 vol % AMA) and 0.35 (CS6, with 4.8 vol % AMA) for the PMMA particles and from 1 (CS4, without AMA) to 0.73 (CS7, with 1.9 vol % AMA) and 0.70 (CS8, 4.8 vol % AMA) for the PBMA particles. These results are in agreement with a lower penetrability of the cross-linked core by the polymer of the second stage of the polymerization as more AMA is added during the first step of the synthesis. It is worth noting that without cross-linking agent the PBMA particles (CS4) are fully mixed ($f'_A = 1$), whereas a fraction of mixing of only 0.70 is obtained upon addition of AMA, in spite of the fact that the particle T_g (about 40 °C) remains much below the polymerization temperature. This shows the efficiency of the cross-linking agent for synthesizing core-shell particles.

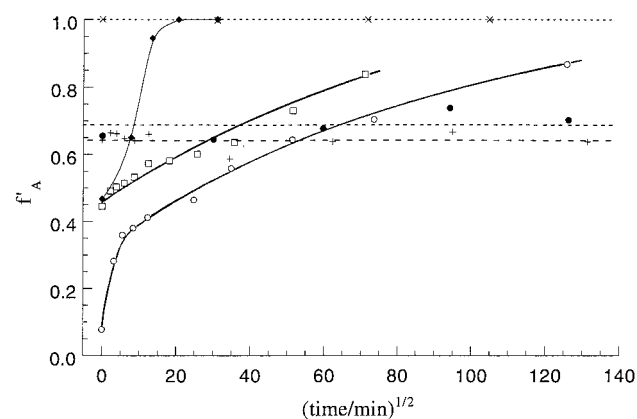
We have previously pointed out that perfect core-shell structures are sometimes difficult to obtain. In Table 3 we have reported the theoretical value of f'_A , f'_{At} , calculated assuming a neat interface between the core and the shell of the particles, i.e., assuming no mixing at all between the core-polymer and the shell-polymer. Comparison of the values of f'_{At} with the experimental values shows that f'_{At} is always much lower than f'_A . In fact the lower experimental fraction of mixing is equal to 0.35. This value indicates that, even in the best situation encountered here, a concentration gradient of the donor- and acceptor-labeled polymers takes place in the particles. Moreover, from the previous results it cannot be excluded, although this seems rather improbable in view of the procedure adopted for the synthesis, that the donor- and acceptor-labeled polymer are not confined in microdomains more or less randomly distributed. One of the questions which then arises is to know if phenanthrene labeled polymer chains can be found at the surface of the particles.

The answer to this question is partly given by the results shown in Table 3. In the dry film the particles touch each other. If phenanthrene-labeled polymers are close to the surface, some phenanthrene groups will transfer their energy to anthracene groups belonging to polymer chains which lie at the periphery of neighboring particles. This energy transfer will be included in the measured value of f'_A . If now the particles are pulled apart, this component of energy transfer will disappear and f'_A will decrease. Pulling apart the particles is done when one goes from the film to the dispersion. With the concentration of latex used for our fluorescence measurements the distance between particles in the dispersion is about 1500 nm, if one assumes particles regularly spaced. Therefore, the distance between the surface of neighboring particles is more than 1200 nm, which is much larger than the Förster characteristic distance. As already mentioned, no difference between the values of f'_A in the film and in the dispersion has been found (see Table 3). This indicates that there is probably not many phenanthrene-labeled chains at the surface of the particles.

This result was confirmed by another experiment in which CS1 to CS4 latex samples were mixed in equal quantity with H2 samples which contained homogeneous PMMA particles only labeled with the acceptor (an-

Table 4. Surface Area, A , under the Fluorescence Decay Curves Recorded for a Dry Film and a Dispersion of Particles CS1 to CS4 Mixed in Equal Weight with Particles H2

latex	A (ns)	
	film	dispersion
CS1-H2	30.82 \pm 0.30	31.34 \pm 0.29
CS2-H2	35.08 \pm 0.20	36.62 \pm 0.16
CS3-H2	31.03 \pm 0.25	31.82 \pm 0.24
CS4-H2	20.37 \pm 0.24	20.78 \pm 0.22

**Figure 3.** Apparent volume fraction of mixing versus annealing time at 140 °C for a dry film (\square) and a dispersion (\blacklozenge) of latex CS1, for a dry film of a 50/50 wt % mixture of latex H1 and latex H2 (\circ), and at 90 °C for a dry film of latex CS4 (\times), and a dry film ($+$) and a dispersion (\bullet) of latex CS8.

thracene, see Table 2). This experiment was therefore much more drastic than the previous one to detect the presence of phenanthrene-labeled polymers at the surface of the composite particles. The fluorescence decay curves of a dry film and of a low concentration of these latex mixtures as a dispersion were recorded. The values of the areas, A , under the decay curves are given in Table 4. The values of A for the films and for the corresponding dispersions are almost identical, within the experimental errors. One can however notice a very small systematic increase of A , going from the film to the dispersion, which indicates a small decrease of energy transfer. This would mean that in the film one detects the presence of some donor-labeled polymer chains at the surface or close to the surface (in the 0–5 nm range) of the composite particles. This is naturally not surprising for the latex CS4, which has a volume fraction of mixing equal to 1. For latexes CS1 to CS3 it means that the concentration gradient of the phenanthrene-labeled polymer chain extents probably down to the surface of the particle.

Film Formation. The further gradual coalescence of homogeneous latex particles has already been widely studied by NRET.^{27,28,38–40,44–49} In some of these studies the influence of coalescing aids on film formation has also been investigated.^{44,45,47–49} Only a few investigations have been done by NRET on film formation with composite particles.^{40,49,50}

In Figure 3 we compare the volume fraction of mixing $f'_A(t)$ between donor- and acceptor-labeled polymer chains

versus annealing time for films made with PMMA core-shell (CS1) and homogeneous (H1–H2, 50/50 wt %) particles. The variations of $f'_A(t)$ for the films of homogeneous particles (H1–H2) and of core-shell particles (CS1) parallel each other. Note that, for a given annealing time, the fraction of mixing is slightly larger for the CS1 film than for the H1–H2 film. This is due to the fact that in the core-shell particles a diffuse interface between donor- and acceptor-labeled chains already exists before annealing. On the other hand, Figure 3 shows that there is a great difference in the variation of f'_A for the CS1 particles annealed in the film and in the dispersion. It seems that in the dispersion the migration of the polymer chains inside the particles is much faster than that in the dry film. Some results seem to indicate that there is no plasticization of poly(isobutyl methacrylate) latexes by water.⁵¹ This conclusion has been obtained from samples which were apparently heated during a much shorter period of time than in our experiment, and it might not be valid in our case. Nevertheless, if it is also true that there is no plasticization of the PMMA latex particles by water, the origin of the apparent higher diffusion rate of the polymer chains in the case of the dispersion must be found in the structure of the system itself. In the dispersion the polymer chains can migrate only in a limited space, the sphere formed by the particle, whereas in the film the migration occurs not only inside the same particle but also across the interface between adjacent particles. Thus, even with the same diffusion coefficient of the polymer chains in a dispersion or in a film, the complete mixing might be faster in isolated particles than in the film. Modelization of chain migration inside isolated particles compared to chain migration when particles are embedded in a film will probably help to understand this difference.

Figure 3 reveals also that the NRET method is very useful to appreciate the efficiency of cross-linking agents. Annealing of a CS8 film and a CS8 dispersion shows no variation of the value of $f'_A(t)$ even after one week at 90 °C, i.e., 56 °C above the T_g of PBMA. This indicates that since the chains in the core are cross-linked, there is no possibility for the chains which form the shell to migrate into the core. This would only occur if the core could swell or if some chains could leave the core, which is apparently not possible.

Finally, Figure 3 shows that introduction of the donor and of the acceptor along the polymer chains does not induce phase separation under our experimental conditions. Indeed annealing at 90 °C, for a long period of time, of a film of PBMA, in which the donor- and acceptor-labeled chains are initially uniformly mixed (CS4), lead to a value of $f'_A(t)$ which remains constant, equal to 1. If phase separation would have taken place, $f'_A(t)$ would have decreased with annealing time, as is the case for other systems, as shown in Figure 4. This result indicates that phase separation which may occur between phenanthrene- and anthracene-labeled chains is due to the nature of the polymers themselves and not to the presence of the fluorescence probes along the chains.

Figure 4 shows the variation of the volume fraction of mixing versus annealing time for particles CS2 in a dry film and in a dispersion. Contrarily to the variations presented so far for latex films studied by NRET, one observes here a decrease of the fraction of mixing during annealing of the film and of the dispersion. This is due to the chemical composition of the particles which are made of two polymers not entirely compatible, PBMA and PMMA. Annealing of the particles above the T_g of PBMA

- (44) Wang, Y.; Winnik, M. A. *Macromolecules* **1990**, *23*, 4731.
 (45) Winnik, M. A.; Wang, Y.; Haley, F. J. *Coat. Technol.* **1992**, *64* (811), 51.
 (46) Wang, Y.; Winnik, M. A. *J. Phys. Chem.* **1993**, *97*, 2507.
 (47) Juhué, D.; Wang, Y.; Winnik, M. A. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 345.
 (48) Juhué, D.; Lang, J. *Macromolecules* **1994**, *27*, 695.
 (49) Juhué, D.; Lang, J. *Double Liaison—Phys. Chim. Pein. Adhès.* **1994**, 464–465, 3.
 (50) Juhué, D.; Lang, J. *Macromolecules* **1995**, *28*, 1306.

- (51) Lin, F.; Meier, D. J. *Langmuir* **1995**, *11*, 2726.

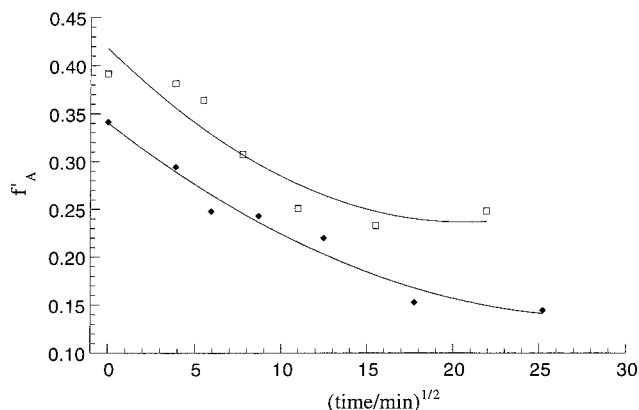


Figure 4. Apparent volume fraction of mixing versus annealing time at 140 °C for a dry film (◆) and a dispersion (□) of latex CS2.

and PMMA produces phase separation between the phenanthrene-labeled PBMA and the anthracene-labeled PMMA. In the film the fraction of mixing becomes very low at long annealing time, close to 0.15, which is the lowest value found in this work and is not far from the theoretical fraction of mixing (0.068, see Table 3), which seems to indicate that the interface between the copolymer and the shell-polymer becomes narrower. However, the apparition of microphases upon annealing cannot be completely excluded. Unfortunately it is not possible to distinguish between transfer due to partial mixing of PBMA and PMMA polymer chains and transfer through the interfaces between PBMA and PMMA microdomains. This last contribution increases when the size of the microphases decreases and can be relatively important for microphases with a diameter of only a few tens of nanometers, which corresponds to about ten polymer chains in a microdomain. The low value found here for f'_A at long annealing times seems to indicate that there is certainly not a great number of such small microdomains inside the particles. Nevertheless, it is not possible to determine, from the value of f'_A , the size of the PBMA and PMMA microdomains, if they exist. Moreover, as already pointed out in a NRET study of the further gradual coalescence of blends of donor- (acceptor-) labeled PBMA particles and acceptor- (donor-) labeled poly(amy methacrylate) particles,⁵² for partially miscible polymers one must distinguish at least three types of domains in the film, for the analysis of the fluorescence decay data: domains rich with the first polymer, domains rich with the second polymer, and domains which contain only the donor-labeled polymer (domains which contain only acceptor-labeled polymer do not participate in the fluorescence decay). Even with a such simplified model the analysis would be difficult, if not impossible, owing to the great number of parameters to be introduced in the fluorescence decay equation. A reliable analysis of the decay data would eventually be possible with completely incompatible polymers, which is not the case for PBMA and PMMA. However, a qualitative interpretation of the data can be made. One can see for instance in Figure 4 that, at long annealing time, the value of f'_A is larger when measurements are done with the dispersion than with the film. This is perhaps due to the formation of smaller microdomains in the isolated particles than in the film and therefore to a larger contribution of the energy transfer through the microdomain interfaces in the isolated particles. Indeed, in the film, phase separation

can perhaps involve several particles and the ratio of the surface which separates the microdomains over the polymer volume might be lower in the case of the film, and therefore a smaller contribution to the overall energy transfer is observed in the film.

Compatibility between polymers was extensively studied in polymer blends by Morawetz et al.,^{53–55} using NRET, followed by others.^{54,56} In these studies also only qualitative discussions of the NRET results were possible. Nevertheless, they gave some interesting indications on the effect of parameters, like composition of the blend, nature and molecular weight of the polymers, chemical composition and structure of the copolymers, or nature of the solvent used for the casting of the film, on the polymer miscibility. Such indications are also of great importance for film formation with composite particles, since the film strength and permeability may depend not only on the intrinsic nature of the polymers but also on the extent of their miscibility. Therefore, further studies on film formation with composite particles are currently being performed in our laboratory.

Conclusions

We have obtained information on the internal structure of composite particles using the NRET method. The desired core-shell particles were made of polymers not very highly incompatible. This allowed us to test, under unfavorable conditions, the possibility of the NRET method. Also, with rather compatible polymers the synthesis of core-shell particles is most difficult to achieve. There is then a real doubt about the existence of a core-shell structure which needs to be verified. For particles having a T_g much lower than the polymerization temperature and for donor-labeled polymers and acceptor-labeled polymers of the same nature (PBMA in latex CS4) there is no separation between core and shell in the particles ($f'_A = 1$). For particles with f'_A below 1 we have found that the internal structure is likely that of a polymer core separated from a polymer shell by a diffuse interface. The NRET method shows that, as expected, the size of this interface increases (f'_A increases) when the T_g of the polymers decreases and the compatibility between the core and the shell increases. Addition of a cross-linking agent in the core reduces this interface. We are presently attempting to modelize the internal structure of the composite particles, taking into account the fluorescence decay data, in order to obtain the concentration profile of the donor- and acceptor-labeled polymer chains from the center to the surface of the particles.

We have also shown that the NRET method is sensitive to phase separation which occurs in isolated particles made of two different polymers and in films formed with such particles. We have for the first time reported the observation, using NRET, of polymer phase separation in isolated latex particles during annealing. More work is presently being carried out on polymer phase separation in latex films.

Acknowledgment. The authors are extremely grateful to Dr. Michel Duval (Institut Charles Sadron, Strasbourg) for the QELS particle size determination. E.P. thanks the *Coopération Scientifique et Technique franc-mexicaine (Sfere-Conacyt)* for its financial support.

LA9509357

(52) Boczar, E. M.; Dionne, B. C.; Fu, Z.; Kirk, A. B.; Lesko, P. M.; Koller, A. D. *Macromolecules* **1989**, *22*, 159; **1993**, *26*, 5772.

(53) Amrani, F.; Hung, J. M.; Morawetz, H. *Macromolecules* **1980**, *13*, 649.

(54) Morawetz, H. *Science* **1988**, *240*, 172.

(55) Chen, C. T.; Morawetz, H. *Macromolecules* **1989**, *22*, 159.

(56) Zhao, Y.; Prud'homme, R. E. *Macromolecules* **1991**, *24*, 2103.