The influence of nanoparticle architecture on latex film formation and healing properties

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ABSTRACT

We present a study of chain interdiffusion in films formed by specially architectured PBMA nanoparticles by Förster Resonance Energy Transfer – FRET. Polymer nanoparticles contained linear chains with narrower molecular weight distributions than other previous reports, allowing a more detailed study. Apparent fractions of mixing and diffusion coefficients, determined from the quantum efficiency of energy transfer, were used to characterize the interdiffusion mechanism in the different films. The resistance of the films to dissolution by a good solvent was finally correlated with the interdiffusion results, in order to get information about film healing. We concluded that whenever interdiffusion occurs between nanoparticles containing linear chains and fully cross-linked nanoparticles, healing becomes more effective in spite of showing slower interdiffusion. We also observed that particles with longer chains are more effective for film healing. Finally, we concluded that interdiffusion occurs both ways across interfaces in blends formed by particles swollen with linear chains of different molecular weights.

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1. Introduction

The market for emulsion polymers (latexes) is large and still growing with worldwide sales in 2007 of 12.6 billion euros [1]. There are plenty of applications for latexes, from paper coatings to adhesives and sealants, textiles, paints, etc. The water-based sector is growing at the expense of other manufacturing processes based on volatile organic compounds, VOCs [2].

The process of transforming a stable dispersion of colloidal particles into a continuous film with the same cohesive strength of the bulk material is complex and is usually described in three sequential steps: drying, particle deformation, and diffusion. There is a large literature devoted to the mechanism of film formation including some excellent reviews [3–5].

When a latex dispersion dries and is annealed above its Minimum Film Formation Temperature, MFT, its particles suffer deformation, mainly driven by capillary forces. Van der Waals attractions (especially dispersive forces) between adjacent deformed particles result in a measurable adhesion energy called interfacial wetting [3]. Transmission electron microscopy images on freshly formed films show that fractures predominantly occur along the interfaces between cells [6,7]. However, as the polymer chains adjacent to the particle surfaces adopt distorted conformations, when the film is annealed above its glass transition temperature, Tg, the entropically constrained chains diffuse and cross the interparticle boundaries [8–13]. As the cellular structure fades, fractures become more cohesive and interfaces are said to be healed. The way the chains become anchored across the interface determines most of the film properties, such as its tensile strength (the stress at which the film fails under tension) and the film resistance to solvent penetration (solvents diffuse mainly along interparticle gaps). However, a healed interface (with chains bridging adjacent particles) can still suffer rupture, either by a pullout mechanism (when a bridging chain is dragged out of one of the particles) or by chain scission (when a bond of the connecting chain breaks) [14]. When the bridging chains are either entangled or cross-linked on both sides of the interface, rupture occurs by chain scission [15]. The full tensile strength of a joint is only achieved when the diffusion length is comparable to the radius of gyration, for low molecular weight polymers, or enough to form entanglements, for long polymer chains [16–18].
The process by which chains interdiffuse across interfaces, which determines the final properties of the film, is largely dependent on the polymer molecular weight: for chains whose molecular weight is less than twice the molecular weight of entanglements, $M_w$ [19] the diffusion mechanism is Fickian [20] and the mean square displacement of a polymer chain, $(\Delta r^2)^{1/2}$, scales with time as

$$(\Delta r^2)^{1/2} \sim t^{1/2}$$

(1)

In contrast, long polymer chains have their motion constrained by the adjacent chains [21,13,22] and their diffusion occurs by reptation (inside an imaginary confining tube, defined by the adjacent chains) [23]. The reptational process can be divided into four regimes, separated by three characteristic times that depend on both temperature and molecular weight: [24] (i) the *Rouse entanglement time*, $\tau_e$, that characterizes the segmental diffusion for distances comparable to the diameter of the confining tube, below which the chain motion is not influenced by the presence of entanglements and $(\Delta r^2)^{1/2} \sim t^{1/4}$; (ii) the *Rouse relaxation time*, $\tau_R$, that refers to the time over which the motion of a segment becomes correlated over an entire chain, so that between $\tau_R$ and $\tau_e$ the segmental displacement scales with time as $(\Delta r^2)^{1/2} \sim t^{1/2}$; (iii) the *reptation time*, $\tau_D$, that is the time required for a chain to escape from its original confining tube, given by [24]

$$\tau_D = \frac{R_s^2}{3\pi D}$$

(2)

where $R_s$ is the gyration radius of the chain and $D$ the polymer diffusion coefficient (in bulk). Between $\tau_R$ and $\tau_D$, chains move by reptation and their displacement scales with time as $(\Delta r^2)^{1/2} \sim t^{1/4}$. For diffusion times larger than $\tau_D$, the process is Fickian and the displacement of the chains center-of-mass approximately follows Eq. (1).

Polymer interdiffusion between adjacent particles results in latex coatings with excellent malleability but, unfortunately, with poorer chemical resistance and lower tensile strength and hardness, when compared with solvent-borne coatings. To circumvent these disadvantages, cross-links are often introduced in the latex film formulations [25–27]. Cross-link reactions are commonly chosen to occur after a significant amount of interparticle polymer diffusion, to assure that the cross-link points become randomly distributed throughout the film [28–31]. But cross-links can also be introduced into the latex particles [32]. This strategy limits the characteristic length scale of the cross-linked networks to the diameter of the latex particles. Zosel and Ley were the first to introduce a cross-linker (2% of methallyl methacrylate, MAMA) into the feed of an emulsion polymerization of n-butyl methacrylate, BMA, and concluded that pre-cross-linked latex particles result in the formation of brittle films that are unable to develop significant tensile strength [33]. Tamai et al. produced films of substantial toughness, also from cross-linked latex particles, but at a temperature above the polymer $T_g$ [34]. All of these observations are in agreement with the classical experiments of Ahagon, who showed that when two cross-linked polymers are brought into contact above their $T_g$, the strength of adhesion decreases with increasing cross-link density [35]. They concluded that polymer diffusion across two cross-linked particles is restricted to chain segments dangling from the networks that diffuse across the interface and penetrate into the interface of the adjacent cell. The longer these dangling ends, the stronger the adhesion between particles. In spite of their good tensile strength, the films produced by Tamai et al. disintegrated when exposed to organic solvents, which led them to conclude that the dangling ends, which provide adhesion in the dry films, lose their effectiveness when swollen by solvents. In accordance with these observations, both Winnik [36] and El-Aasser [37] concluded that films formed from previously cross-linked latexes show lower strength and toughness than the corresponding un-cross-linked latexes.

Nevertheless, it is important to point that interdiffusion between two gel networks is significantly different from the interdiffusion of a free chain into a cross-linked particle. Hahn et al. [38] observed that the diffusion of linear PBMA chains into cross-linked P(BMA-co-MAMA) latex particles was significantly retarded. On the other hand, Wu et al. showed that when gel particles are blended with ordinary un-cross-linked particles, the diffusion is similar in magnitude to the diffusion in the ordinary particles, concluding that the free chains shall diffuse around the obstacles of chemical cross-links by reptation, similar to their motion through the obstacles created by entanglements [39]. This is in agreement with Antonietti and Sillescu [40] who found that the diffusion coefficients of linear chains into cross-linked networks are of the same order of magnitude of those into matrixes formed by linear entangled chains.

Actually, many commercial coating formulations contain blends of different latexes that can have either similar compositions but different sizes (to tune the rheological properties of the formulation [41]) or different compositions (either to promote a decrease in $MFT$ [42,43] or to enhance film resistance [44]).

Polymer interdiffusion in latex films has been experimentally followed by several instrumental techniques. Small Angle Neutron Scattering, SANS, has been one of the most used, allowing the observation of deuterated particles growing as the deuterated chains interdiffuse into adjacent non-deuterated particles [38]. Alternatively, Winnik and co-workers developed an approach based on Förster Resonance Energy Transfer, FRET, that has been systematically used to study the effects of temperature and molecular weight [45], polymer composition [19], influence of coalescing aids [46,47], presence of non-ionic surfactants [48], and the influence of the particle structure (different polymers) [49–51] on latex film formation.

In this work, we study the chain interdiffusion in films formed from latex particles with novel architectures, containing linear chains with narrow molecular weight distributions. Different particle architectures were used to study the influence of entanglements and cross-links on both chain interdiffusion and film healing properties. Linear chains of narrow molecular weight distributions were used to clarify the influence of chain $M_w$ on the interdiffusion process.

We prepared aqueous colloidal dispersions of nanoparticles formed by a cross-linked poly[n-butyl methacrylate-b-ethylene glycol dimethacrylate] nanogel, p(BMA-co-EGDMA), swollen by either linear dye-labeled poly[n-butyl methacrylate] chains, PBMA, of different molecular weights and very low dispersities, or interpenetrated by another dye-labeled nanogel of different mean molecular weight between cross-links. Förster Resonance Energy Transfer, FRET, was used to follow polymer interdiffusion during film formation from 1:1 molar mixtures of energy donor-labeled and energy acceptor-labeled nanoparticles dispersions in water. Films were dried and annealed at different temperatures. We showed that the linear chains interdiffusion mechanism still depends on chain molecular weight, being Fickian for linear chains of $M_w \sim 1.2 \times 10^5$ and reptational for $M_w \sim 9.0 \times 10^5$, although with lower apparent diffusion coefficients caused by the nanogel presence inside the particles. We also observed interdiffusion of linear chains independently of their $M_w$ in films formed by blends of particles containing linear chains of different molecular weights. The same is not observed in blends containing particles with a double nanogel interpenetrated network structure and particles containing linear chains, where the main contribution for diffusion comes from the linear chains. These blends show, however, the best film healing properties, tested by the films’ resistance to a good solvent for the polymer.
2. Materials and methods

2.1. Materials

All reagents used for the synthesis of 4-(phenanthren-9-yl)butyl methacrylate, Phe, and 4-(anthracen-2-yl)butyl methacrylate, Ant, were purchased from Aldrich (98%), were used as received. Water was purified through a Millipore Milli-Q purification system. Tetrahydrofuran, THF, was purchased from Aldrich (98%) and filtered through a 0.45-μm membrane when used for gel permeation chromatography, GPC.

Melting points were determined using a Electrothermal Mod. IA6304 in capillary tubes without correction. The NMR spectra were recorded on a Bruker AMX 400 in deuterated chloroform, the chemical shifts were quoted in ppm in δ-value against tetramethylsilane (TMS) as internal standard, and the coupling constants were measured in Hz. The IR spectra were recorded on a Mattson Satellite FTIR as a film, obtained by the evaporation of dichloromethane solutions on the NaCl plates, and were quoted in cm⁻¹. The microanalyses were taken on a CHNS Analyser Thermo Finnigan model Flash 1112 Series.

2.2. Synthesis of the donor- and acceptor-labeled monomers

4-(Phenanthrene-9-yl)butyl methacrylate, Phe, and 4-(anthracene-2-yl)butyl methacrylate, Ant, were synthesized from 9-(4-bromobutyl)phenanthrene or 9-(4-bromobutyl)anthracene following a reported procedure and conversion to Phe and Ant by esterification under standard conditions (Scheme 1).

4-Aryl-1-bromobutanes [52]: To a stirred solution of 9-(4-bromobutyl)phenanthrene and 9-(4-bromobutyl)anthracene in dry ether (20 ml), butyllithium as a 2.5 M solution in hexane (1.5 equiv) was slowly added at 0°C followed by 1,4-dibromobutane (4 equiv). After 2-h refluxing, the reaction mixture was extracted with ether, dried over MgSO₄, evaporated to dryness in vacuo, and purified by flash chromatography on silica gel using hexane as a mobile phase. The complete characterization of the products obtained, 4-(phenanthrene-9-yl)butyl methacrylate and 4-(anthracene-2-yl)butyl methacrylate, is presented in Supplementary Materials.

Esterification. To a solution of 4-(9-phenanthryl)-1-bromobutane or 4-(9-anthryl)-1-bromobutane (5 mmol) in dry xylene (20 ml), K₂CO₃ (10 mmol), Bu₄NI (1 mmol), and methacrylic acid (10 mmol) were added. After 4-h refluxing, the reaction mixture was extracted with ethyl acetate–brine, dried over MgSO₄, evaporated to dryness in vacuo, and purified by flash chromatography on silica gel using ethyl acetate–hexane 1:19 as a mobile phase. The complete characterization of the products obtained, 4-(phenanthrene-9-yl)butyl methacrylate and 4-(anthracene-2-yl)butyl methacrylate, is presented in Supplementary Materials.

2.3. Latex preparation

All poly(n-butyl methacrylate), PBMA, latex particles were prepared by semicontinuous emulsion copolymerization. A seed emulsion was produced introducing all reagents mentioned at the first column of Table 1 inside a previously degassed 1-L glass reactor and stirring for 2 h at 260 rpm and 80°C, under nitrogen (using a mechanical stirrer with a PTFE stirrer blade plain end). Then, ca. 25 g of the seed emulsion (ca.5 wt.%) was introduced inside a previously degassed 250-ml glass reactor, filled with nitrogen, and mechanically stirred at 210 rpm, at 80°C. Polymerizations proceeded under starved feed conditions, by continuously adding both an aqueous solution (with KPS and SDS, at a rate of 0.0375 ml/min) and an organic phase (consisted of a mixture of BMA, EGDMA, DDTh, and one of the dye-labeled monomers, Ant or Phe, at 0.0573 ml/min), according to Table 1. Both aqueous and organic phases were degassed before addition. The reactions proceeded for 7 h.

In order to remove the surfactant and other free ionic species, all latex samples were further diluted and stirred in the presence of an Ag 501-X8 mixed bed resin from Bio-Rad (20–50 mesh) for 2 h and filtered. They remained stable for more than one year.

2.4. Latex characterization

Particle sizes and size distributions were measured by Dynamic Light Scattering, DLS, in a Brookhaven instrument (BI-200SM Goniometer and BI-9000AT correlator) using a He–Ne laser (632.8 nm, 35 mW, model 127, Spectra Physics) and an avalanche photodiode detector. The measurements were taken in glass cylindrical cells in order to simplify the corrections needed for refractive index variations. The circular vat cell contained deionized water to minimize light refraction. The DLS data were analyzed using the analysis package CONTIN [55] (from Brookhaven) to determine the translational diffusion coefficient, from which the hydrodynamic radius (Rₕ) of the particles is calculated using the Stokes–Einstein equation for non-interacting spheres.

The molecular weight and molecular weight distribution of the linear chains included inside the latex nanoparticles were determined by Gel Permeation Chromatography, GPC, using two columns in series (Waters H5 and Phenomenex 10⁴) and tetrahydrofuran, THF, as eluent (0.8 ml/min). Calibration was done using several reference standards (IGE).
poly(methyl methacrylate), PMMA, standards. Two detectors (Waters 470 Fluorescence detector and Waters 2410 Refractive Index detector) were used to ensure that all dyes were uniformly incorporated into the PMMA linear chains. Latex samples were freeze-dried, dissolved in THF, and filtered (with a 0.45-μm membrane) prior to injection.

The weight fraction of solids was determined weighing four samples of each emulsion, before and after drying at room temperature till constant weight.

2.5. Sample preparation

Latex films were prepared from mixtures of phenanthrene- and anthracene-labeled particles in a 1:1 M ratio. The final dispersions were spread onto Parafilm® and allowed to dry at a slow evaporation rate (inside a closed chamber, saturated with water vapor, at 30 °C) in order to form crack-free transparent films. For a hydrophobic polymer such as PMMA, moisture has a little influence on the polymer diffusion rate of the final films [56]. Once the films were dried, Parafilm® was removed and each film annealed at a given temperature (between 80 °C and 110 °C) on aluminum foil. Samples were taken out the oven periodically and cooled to room temperature for fluorescence measurements.

2.6. Films’ resistance to solvents

Several films of different compositions but with roughly the same shape and dimensions were prepared and annealed for 90 min at 80 °C. The films were individually weighted and put on a 0.45-μm PTFE membrane of a Millipore® filtration kit. They were washed 30 min under vacuum with pure tetrahydrofuran (a good solvent for PBMA). Films were dried to constant weight. The fraction of the remaining macroscopic gel, wt.% RMG, corresponds to the ratio of the mass of the dried film at the membrane after washing to the mass of the initial film.

2.7. Fluorescence decay measurements

All fluorescence decays were measured by the time-correlated single-photon counting technique. The system consists on a diode-pumped solid-state Nd:YVO₄ laser (Vanguard, Spectra Physics) delivering 2 W of 532-nm light at a 76-MHz repetition rate with a pulse duration of ~12 ps, synchronously pumping a cavity-dumped dye laser (701-2, Coherent, delivering ~40 nJ pulses of 5–6 ps at a 3.4-MHz repetition rate) working with rhodamine 6G. Intensity decay measurements were taken by collecting both the impulses and decays with the emission polarizer set at the magic angle position. Impulses were recorded slightly away from the excitation wavelength at 295 nm with a scattering suspension. For the decays, a cutoff filter was used to effectively remove excitation light. Emission light was passed through a depolarizer before reaching the Jobin–Yvon HR320 monochromator with a grating of 100 lines/mm, which selected the 350-nm fluorescence light from phenanthrene with a bandwidth of 6 nm. The fluorescence was detected by a Hamamatsu 2809U-01 microchannel plate photomultiplier. No less than 20,000 counts were accumulated at the maximum channel.

The decay curves were analyzed using a non-linear least-squares reconvolution method [57]. All the fluorescence decay measurements were taken at room temperature in free-standing films.

2.8. Data analysis

Polymer diffusion was followed by measuring the extent of energy transfer between the energy donor and acceptor dyes, attached to the linear chains of the nanoparticles. It is well known that when a donor, D, is electronically excited, it can transfer its energy to a nearby acceptor, A. For a dipole–dipole coupling mechanism, the rate of energy transfer, w(t), between a donor and an acceptor depends on the inverse sixth power of their separation, r [58,59]:

\[
w(t) = \frac{3k^2}{2r_0^6} \frac{R_0}{r}
\]

Here, \( r_0^2 \) represents the donor fluorescence lifetime in the absence of acceptors and \( R_0 \) the Förster radius for energy transfer (a characteristic distance at which energy transfer equals the sum of all other deactivation processes, being \( R_0 = 2.3 \text{ nm} \) for the Phe/Ant pair) [60]. The term \( k^2 \) is a dimensionless parameter that considers the relative orientation of the donor and acceptor transition dipole moments [61].

When donors and acceptors are randomly distributed in a three-dimensional medium in the absence of diffusion, the donor fluorescence intensity decay after an instantaneous excitation by a δ-pulse of light is given by [58,59]

\[
I_D(t') = A \exp[-t'/\tau_D - P(t'/\tau_D)^{1/2}]
\]

where \( t' \) represents the fluorescence decay time (in order to be distinguished from the annealing time, \( t \)), and

\[
P = \frac{4}{3} \pi l^{1/2} \left( \frac{3}{2} k^2 \right)^{1/2} N_A R_0^2 / \Lambda
\]

Here, \( P \) is proportional to the acceptor concentration, \( N_A \) is the Avogadro’s number and \( |k|^2 = 0.476 \) (in the absence of diffusion) [62,63]. Annealing the latex film during a certain period of time, \( t \), induces chain diffusion across the interfaces and generates a new distribution of donors and acceptors. The efficiency of energy transfer, \( \Phi_{EF}(t) \), can be determined by

\[
\Phi_{EF}(t) = 1 - \int_0^\infty \frac{I_D(t', t') dt'}{I_D(0, t') dt'}
\]

where the decay curve of the donor fluorescence intensity in the presence and absence of acceptors is represented by \( I_D(t,t') \).
The evolution of $\Phi_{ET}$ as a function of the annealing time, $t$, can be used to calculate a normalized efficiency of energy transfer, $f_m$, which measures the extent of growth of $\Phi_{ET}$ due to the polymer diffusion

$$f_m = \frac{\Phi_{ET}(t) - \Phi_{ET}(0)}{\Phi_{ET}(\infty) - \Phi_{ET}(0)}$$  \hspace{1cm} (7)

$f_m$ values are approximately proportional to the fraction of mass that has diffused across the interface during the early stages of the interdiffusion process [64,65]. The efficiency of energy transfer in a fully mixed system, $\Phi_{ET}(\infty)$ in Eq. (7), can be easily determined using Eq. (6).

3. Results and discussion

3.1. Synthesis of the dye-labeled PBMA latex particles

Latexes were synthesized by semicontinuous emulsion polymerization from seed particles with ca. 50 nm diameter (see Table 2). During the first step, the synthesis of the seed particles, 2 mol% (based on total monomer) of a cross-linker agent, EGDMA, was added (see Table 1). As each EGDMA unit divides the chain into three segments between branch points, the average number of BMA units between two adjacent branch points, $N_{CL}$, is [66]

$$N_{CL} = N_{BMA}/(1 + 3 \times N_{EGDMA})$$  \hspace{1cm} (8)

where $N_{BMA}$ represents the average number of BMA units per chain and $N_{EGDMA}$ the average number of cross-linker units per chain (see Table 2). Cross-links are, however, not uniformly distributed over the whole particle volume, being more concentrated at the center due to microsyringesis (microphase separation in cross-linked gels) [67]. The extremely high value of $M_w$ of the released chains determined by GPC (see Table 2) agrees with the idea of nanogel-structured seed particles, as cartooned in Scheme 2A. Complete conversions were always achieved.

Dynamic Light Scattering measurements of freeze-dried seed particles dissolved in THF yielded a diameter of $D_p = 118$ nm, more than twice the diameter of the particles in water. This experiment demonstrates that the seed particles were swollen when exposed to a good solvent.

During the second step of the synthesis of LM, LM(P), LM(A), HM, HM(P), and HM(A) particles, no cross-linker was added (see Table 1). Linear chains were polymerized inside the seed nanogel particles, swollen by the BMA monomer. It should be noted that the formation of core–shell structures was prevented by the small dimensions of the seed nanoparticles [68]. The fluorescently labeled linear chains were synthesized using 1 mol% of each dye-labeled monomer (Phe for LM(P) and HM(P); Amt for LM(A) and HM(A) – see Table 1). During the second step of the synthesis of LM, LM(P), and LM(A), a small amount of chain transfer agent, DDTh, was also added to reduce the chains’ molecular weight. These Low-M particles (LM, LM(P), and LM(A)) are formed by linear chains with molecular weights of ca. $1.2 \times 10^5$ and by 7% of the p(BMA-co-EGDMA) nanogel (see Table 2), with structures similar to the one pictured in Scheme 2B.

Table 2

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$N_{N_{BM}}$ – average BMA units per chain; $N_{N_{EGDMA}}$ – average EGDMA units per chain; $N_{N_{E}}$ – average number of BMA units between two cross-links; $N_{E}$ – number of BMA units between two entanglements [19]; wt% nanogel – percentage of BMA polymerized during the first stage (nanogel) to the total polymerized BMA; Rel. Var. – D$_0$ coefficient of variation.

The molecular weight distributions of the linear chains released when the particles were dissolved in a good solvent are narrower than those generally reported for other semicontinuous emulsion polymerizations in the literature (see $M_w/M_m$ in Table 2). This could result from the presence of the p(BMA-co-EGDMA) nanogel inside the particles, which might act as a nanomembrane retaining the highest molecular weight chains (with highest $D_p$). In order to check this possibility, freeze-dried LM and HM particles were dissolved in THF and samples from each were taken periodically and injected into the GPC. Fig. 1 shows that the molecular weight of the chains released from each sample is roughly constant in time. We can also observe that the averaged $M_w$ value for the LM samples is much smaller than that obtained for the HM samples. As both LM and HM nanoparticles have the same percentage of p(BMA-co-EGDMA) nanogel, we conclude that the polymer nanogel does not act as a nanomembrane, as initially supposed. This conclusion is also supported by the work of Tobing et al. [69].
who concluded that a network would just entangle linear chains if its $N_c$ was larger than the linear polymer $N_p$. The $M_w$ and $M_n/M_w$ values determined by GPC are therefore not influenced by the presence of the $p$(BMA-co-EGDMA) nanogel, being representative of the linear chains contained inside the corresponding particles. This is an important result, as most of the previous works on polymer interdiffusion have used particles containing chains with larger molecular weight distributions.

### 3.2. Polymer diffusion in films

Phe- and Ant-labeled particle dispersions were mixed in a 1:1 M ratio, casted into a film, dried inside a closed chamber saturated with water vapor at 30 °C, and annealed at four different temperatures: 80 °C, 90 °C, 100 °C, and 110 °C. Fluorescence decay curves of the films were measured at room temperature after annealing during several periods of time.

Fig. 2 shows the phenanthrene fluorescence decay curves of several films. The decay of the $LM[P]$ film is monoeXponential, with a lifetime of $\tau_D = 47$ ns (Fig. 2, decay (1)). The film prepared from a 1:1 molar mixture of $LM[P]$ and $LM[A]$ shows, at zero annealing time, a fluorescence decay curve with just a small deviation from the strictly exponential decay (Fig. 2, decay (2)). This small deviation is caused by energy transfer from the donor- to the acceptor-labeled chains, located near the interfaces of contiguous particles. After annealing the same $LM[P]$–$LM[A]$ film at 110 °C for 30 min, the donor fluorescence decay is clearly non-exponential (Fig. 2, decay (3)). This indicates an increase in energy transfer, reflecting the chain interdiffusion between particles.

![Fig. 1. Extraction of chains from freeze-dried latexes swelled in THF followed by GPC: LM (circles) and HM (diamonds).](Image)

![Scheme 2. Cartoons representing the nanogel structure of the seed particles (A), the nanogel interpenetrated by linear chains, characteristic of both Low-M ($LM$, $LM[P]$, and $LM[A]$) and High-M ($HM$, $HM[A]$, and $HM[P]$) latex particles (B) and “double nanogel interpenetrated network” of DCL(P) latex particles (C).](Image)

![Fig. 2. Fluorescence decay curves obtained at $\lambda_{em} = 295$ nm and $\lambda_{exc} = 350$ nm with: (1) – a $LM[P]$ film; (2) a freshly formed film containing $LM[P]$ and $LM[A]$ (at a molar ratio of 1:1); (3) – the same film as (2), after annealing at 110 °C for 30 min.](Image)

![The values of the efficiency of energy transfer, $\Phi_{ET}(t)$, were calculated from the fluorescence decays using Eq. (6). The $\Phi_{ET}(\infty)$ parameter could not, however, be determined from the decay of a solvent-cast film corresponding to complete mixing between donors and acceptors, because nanogels prevent the formation of a homogeneous film [70,71]. Instead, $\Phi_{ET}(\infty)$ was estimated by Eqs. (3) and (4), with the concentration of anthracene set equal to the acceptor concentration present in the films. Finally, the apparent fraction of mixing, $f_m$, was determined from Eq. (7).](Image)
Fig. 3. Apparent fraction of mixing, $f_m$, as a function of the annealing time for two 1:1 M mixtures of $LM(P)–LM(A)$ (A) and $HM(P)–HM(A)$ (B), at four annealing temperatures: 80 °C (solid circles), 90 °C (open squares), 100 °C (solid triangles), and 110 °C (open diamonds).

Fig. 4 shows the logarithmic variation of $f_m$ with annealing time for both Low-M and High-M films (Fig. 4A and B, respectively). For the Low-M films (formed from 1:1 M ratio of $LM(P)–LM(A)$, with $M_w \sim 1.2 \times 10^5$), slopes of 0.31 ± 0.06, 0.28 ± 0.09, 0.3 ± 0.1, and 0.14 ± 0.04 were obtained at 80 °C, 90 °C, 100 °C, and 110 °C, respectively. Since linear chains molecular weight is close to the limit of the Fickian regime, values for each temperature are shown in Table 3.

Sperling et al. compared the time profile of the chains penetration depth, $d$, determined by SANS experiments for two poly(styrene) films, obtained from particles formed by chains with similar molecular weights but different dispersities [75]. The results obtained with the monodisperse sample ($M_w = 1.89 \times 10^5$; $M_w/M_m = 1.03$) showed that $d$ clearly scales with $t^{1/2}$ at early times, changing to $t^{1/3}$ at $t_d$ [17]. However, for films composed of polydisperse particles ($M_w = 2.50 \times 10^5$; $M_w/M_m = 3.6$), the scaling law had values between $1/4$ and $1/2$ [76]. This shows that chains dispersity has a strong influence on chain interdiffusion results and that the dispersivities of the linear chains contained in both high-M and Low-M particles were not low enough to give the theoretically predicted exponents.

The activation energy of 35 ± 4 kcal/mol for poly(styrene) chains [74] was used, as soon as $f_m$ is close to $f_c$ [19]. The values of $D_{app}$ are not the true center-of-mass diffusion constants of the polymer chains but are expected to be proportional to these values for $f_m < 0.7$ [64]. As polymer particles usually contain chains with large MWD, shorter chains diffuse faster and make the major contribution to the increase in energy transfer at early times. Once the mixing of the short chains is complete, high molecular weight polymer chains make increasing contributions to the growth in energy transfer leading to the decrease of $D_{app}$ values with annealing time [79]. The plots of $D_{app}$ values for both $LM(P)–LM(A)$ and $HM(P)–HM(A)$ systems as a function of $f_m$ at several annealing temperatures (presented at Fig. 5) show that the apparent diffusion coefficients are almost independent of $f_m$, which is a consequence of the low dispersities of the linear chains. The average $D_{app}$ values for each temperature are shown in Table 3.

Liu et al. [66] determined $D_{app}$ values between $10^{-1}$ and $10^{-2}$ nm$^2$/s at $T_a = 20$ °C for films formed from particles composed by linear $P(St)$ chains with $M_w = 7.8 \times 10^4$ ($M_w/M_m = 1.6$), while $D_{app}$ values between $4 \times 10^{-2}$ and $10^{-3}$ nm$^2$/s were found for films formed from similar particles, with $M_w = 3.5 \times 10^4$, annealed at 60 °C [56]. The average $D_{app}$ value of $6.4 \times 10^{-4}$ nm$^2$/s for $LM(P)–LM(A)$ films annealed at 80 °C is much lower than the reported values and can be explained by the nanogel presence inside particles, which is a physical obstacle to chain interdiffusion.

To study the effect of temperature on diffusion, the apparent diffusion coefficients, $D_{app}$, were plotted as a function of $f_m$. The activation energies for $LM(P)–LM(A)$ and $HM(P)–HM(A)$ were calculated by fitting the data at comparable fractions of mixing by a multilinear fitting procedure assuming Arrhenius behavior (see bottom line of Table 3) [74].

The activation energy of 35 ± 4 kcal/mol for $LM(P)–LM(A)$ films is in very good agreement with the $E_a = 33.5 \pm 2.5$ kcal/mol found for a...
PBMA latex film formed only by linear chains of the same molecular weight ($M_w = 1.2 \times 10^4$) [79]. This confirms that diffusion in the $LM(P)–LM(A)$ films is Fickian, being the low diffusion coefficients explained by the nanogel morphology of the particles. Contrarily, the value of $E_a = 13.3 \pm 0.4$ kcal/mol calculated for $HM(P)–HM(A)$ films (similar to $LM(P)–LM(A)$ films but containing longer linear chains, with $N_{PBA} \sim 17 \times N_c$) indicates non-Fickian chain interdiffusion. Indeed, reptational times of 8 min, 15 min, 133 min, and 375 min were calculated (Eq. (2)) for $LM(P)–LM(A)$ films annealed at 110 °C, 100 °C, 90 °C, and 80 °C, respectively, while for $HM(P)–HM(A)$ films, reptational times above ca. 5000 min were obtained at all temperatures, confirming that long chains move by reptation.

### 3.3. Diffusion in polymer blend films

Fig. 6 shows the apparent fraction of mixing for films formed by 1:1 M ratio of several blends at different annealing temperatures. The $f_m$ values for films of $LM(P)–LM(A)$ blends are intermediate between those obtained for films of pure Low-M, $LM(P)–LM(A)$, (Fig. 3A) and High-M, $HM(P)–HM(A)$, (Fig. 3B). Fig. 7 shows the plot of $D_{app}$ against $f_m$ for the $LM(P)–HM(A)$ blend at several annealing temperatures.

### Table 3

<table>
<thead>
<tr>
<th>$D_{app}$/nm² s⁻¹</th>
<th>$LM(P) + LM(A)$</th>
<th>$HM(P) + HM(A)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 °C</td>
<td>$6.4 \times 10^{-4}$</td>
<td>$1.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>90 °C</td>
<td>$1.8 \times 10^{-3}$</td>
<td>$2.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>100 °C</td>
<td>$1.6 \times 10^{-2}$</td>
<td>$1.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>110 °C</td>
<td>$3.1 \times 10^{-2}$</td>
<td>$3.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>$E_a$/kcal mol⁻¹</td>
<td>$35 \pm 4$</td>
<td>$13.3 \pm 0.4$</td>
</tr>
</tbody>
</table>
At 80 °C, $D_{app}$ values at low $f_m$ are very similar to those obtained for $LM(P)$–$LM(A)$ films (Fig. 5A), while at higher $f_m$ they become similar to those obtained for the $HM(P)$–$HM(A)$ films (Fig. 5B). At 90 °C, the plot is quite similar to the one obtained for the $HM(P)$–$HM(A)$ films (Fig. 5F) and, for higher temperatures, $D_{app}$ becomes almost constant, with values in between those obtained for the single Low-M and High-M films (Fig. 5C, D, G, and H). Tomba et al. [80] studied chain interdiffusion in films casted from blends of particles containing oligomers and particles containing high molecular weight polymers. They observed that the addition of the oligomeric particles significantly increased $D_{app}$ of the high molecular weight polymer, due to the plasticization effect produced by the lower molecular weight chains.

Our results obtained at 80 °C show that interdiffusion is asymmetrical: it begins by diffusion of the $LM(P)$ chains into the $HM(A)$ particles (that swell) at low $f_m$, followed by both $LM(P)$ and $HM(A)$ interdiffusion, possibly due to the plasticization effect. During the first step, the $D_{app}$ values are similar to the values determined for the $LM(P)$–$LM(A)$ films; at high $f_m$, both $LM(P)$ and $HM(A)$ chains diffuse and the observed apparent diffusion coefficients average the contributions from both $LM(P)$ and $HM(A)$. It should be noted that $HM(A)$ chains should diffuse faster when blended with $LM(P)$ particles than when mixed with $HM(P)$. Above 90 °C, all diffusion coefficients are higher and the first step becomes too fast to be monitored and $D_{app}$ assumes intermediate values between the $LM(P)$ and $HM(A)$ diffusion coefficients.

The activation energy determined by the multilinear fitting procedure described yields $E_a = 32 \pm 6 \text{ kcal/mol}$, a value similar to that obtained for $LM(P)$–$LM(A)$ films ($E_a = 35 \pm 4 \text{ kcal/mol}$), supporting Fickian diffusion of both short and long chains (possibly
due to the plasticization effect of the LM(P) chains on the HM(A) particles. We conclude that the linear chains present in both particles, LM(P) and HM(A), interdiffuse in the blend film. The presence of the nanogel slows down the diffusion processes, allowing the observation of two different mechanisms at 80 °C.

Fig. 6B shows the plot of $f_m$ with annealing time in films of 1:1 blends of LM(A) and DCL(P) particles. Comparing Fig. 6A and Fig. 6B, it is apparent that $f_m$ is significantly lower when LM(P) chains diffuse into cross-linked particles DCL(P) than when diffuse into particles with entangled chains HM(P). This result seems to contradict Wu et al. [39], who concluded that a linear chain diffuses similarly around an entanglement or a chemical cross-link. However, while the plasticization effect of the short chains in LM(A) particles allows HM(A) long chains to interdiffuse during annealing (increasing $f_m$), this is not possible for the DCL(P) particles due to their double nanogel interpenetrated structure (Scheme 2C). In LM(A)–DCL(P) blends, just the short LM(A) chains can diffuse since the physical cross-link points strongly restrict the network diffusion. If $N_C$ was larger than $N_e$, network would entangle the linear chains, also restricting its diffusion [81]. However, this is not the case ($N_C < N_e$) and linear chains do move similarly around an entanglement or a cross-linked chain. It is the entanglement or the cross-linked chains that behave differently, leading to different $f_m$ values. Fig. 6C shows that the apparent fraction of mixing is even lower for films of 1:1 molar blend of HM(A) and DCL(P) particles.

Fig. 8 shows the plots of $D_{app}$ as a function of $f_m$ for both LM(A)–DCL(P) and HM(A)–DCL(P) blends, at 80 °C, 90 °C, 100 °C, and 110 °C. Comparison between Fig. 8A and E and Fig. 5A and E shows that the apparent diffusion coefficients in the blend films are of the same order of magnitude as the corresponding pure Low-M and High-M films. Voyutskii and Ustinova [82] observed that the interpenetration of two adjacent particles could only result from the uncross-linked polymers and chain ends diffusion across the interface. Since the DCL(P) particles have an average number of repetitive units between cross-links of $N_C \sim 33$, the contribution of DCL(P) dangling ends to interdiffusion in the LM(A)–DCL(P) and HM(A)–DCL(P) blends is negligible. Interdiffusion is mostly due to the linear chains present in either LM(A) or HM(A) particles, which is supported by the $D_{app}$ values for the blend films (close to those determined for the pure Low-M and High-M films). Since the longer linear chains in HM(A) particles diffuse by reptation, both $f_m$ and $D_{app}$ are lower than in the case of particles composed of shorter linear chains, LM(A).

3.4. Films’ resistance to solvents

The diffusion experiments provide information on the mechanism of chain interdiffusion across the particle interfaces during film formation. However, they do not allow a direct evaluation of the degree of healing and cohesion achieved during film annealing. A strongly healed film cannot disintegrate into its original particles, either by applying tension or by swelling in a good solvent. In the present work, healing was studied by swelling films of roughly the same shape and dimensions (previously annealed at 80 °C for 90 min) in THF. The films were washed for 30 min, dried, and weighed. The fraction of remaining macroscopic gel, wt.% RMG, was calculated as the ratio between the mass of the dried film to the corresponding initial mass (Table 4).

Disintegration of a film requires the cooperative dissolution of all bridges by which a particle is connected with its neighbors. Prager and Tirrell [10] proposed that the controlling factor for healing was the number of chain segments spanning the interface, while Nguyen et al. [83] pointed to two independent healing mechanisms, one due to the interdiffusion of the sol fraction and the other to the pendant chains of the network. On the other hand, Kim and Wool [12] showed that the relevant factor for healing was the chain segment interpenetration distance, which is supported by the fact that polymer chains only need to interpenetrate around one entanglement distance to provide a good adhesion [84].

In Table 4, we can see that the least healed film is the one formed only by LM chains, which, surprisingly, has the highest $f_m$ and $D_{app}$ values. The molecular weight of the linear chains contained inside LM particles is roughly twice the value of $M_e$, allowing Fickian interdiffusion. However, polymer chains are too short to form entanglements at both sides of the interface and, upon swelling by a good solvent, chain pull out occurs leading to the film disintegration (Scheme 3A).

The linear chains contained inside the HM particles have much higher molecular weights. During annealing, they can only diffuse by reptation, leading to lower $f_m$ and $D_{app}$ values (Figs. 3 and 5). Slower diffusion apparently leads to less effective interparticles mixing; however, the corresponding wt.% RMG value is twice the one obtained for the film formed by LM particles (see Table 4). The HM particles’ linear chains are sufficiently long to form entanglements across the interface. Wool postulated that the maximum molecular weight at which disentanglement can occur corresponds to $M \sim 8 \times M_e$ [85] and the polymer chains in the HM particles are well above this limit ($N_{BAM} \sim 17 \times N_e$). In addition, the nanogel incorporated in the particles can also improve the anchoring of the chains bridging the interfaces, in both the LM and the HM films (Scheme 3B).

The values in Table 4 show that the LM–HM blend films have intermediate wt.% RMG values between those obtained with the pure LM and HM, but closer to the HM system. This confirms that both shorter and longer chains have diffused during annealing (due to the plasticization effect of the short chains). In spite of the higher $D_{app}$ and $f_m$ values (compared to those of the pure HM system), the bridges between particles are less effective because some of them correspond to chains from the LM particles and cannot form entanglements at both sides of the interface between particles (Scheme 3C).

The swelling tests show that the strongest healing is obtained for films of 1:1 molar blends of linear (LM or HM) and double nanogel interpenetrated network particles (DCL). We concluded that the dangling ends from DCL(P) particles give a negligible contribution to chain interdiffusion between particles in both LM(A)–DCL(P) and HM(A)–DCL(P) blend films, because $N_C < N_e$ [69], but swelling results show that the double nanogel interpenetrated network structure of DCL(P) particles plays a decisive role in healing the blend films. Geogehegan and co-workers [86] studied the interdiffusion between two polymeric layers by SANS, observing that whenever one of the layers is a network, diffusion between contacting polymer layers is enhanced. Networks (with $N_C > N_e$) are more heterogeneous than films of entangled polymers, because the distance between cross-link points is more variable than the distribution of entanglements, which is dictated by $N_e$ [86]. Inside a network, there are regions with higher and lower cross-link densities and diffusion is consequently faster into the less cross-linked regions (also called soft regions) [86]. According to these authors, interdiffusion between linear chains and networks occurs asymmetrically: linear chains diffuse into the soft regions of the network and become entropically trapped there (chains can adopt more conformations inside a soft region than in a more cross-linked region), while network relaxation occurs in a second slower stage [86].

We conclude that, during annealing of the LM–DCL(P) blend film, linear chains from LM particles diffuse into the soft regions of DCL(P) particles, with an apparent diffusion coefficient close to the observed for LM(P)–LM(A) films. The double nanogel interpenetrated network slowly relaxes, anchoring the LM linear chains. Although linear chains from LM particles are not long enough to form entanglements inside the network, the mechanism of chain
pull out is kinetically delayed, as it involves reversing the relaxation of the network. The 30 min of the swelling experiment was, perhaps, not enough to complete the back relaxation process, and LM-DCL(P) films showed 100% healing at the end of the test (Scheme 3D).

Compared with the LM–DCL(P) blend film, the HL–DCL(P) sample revealed a slightly lower wt.% RMG. Although this small difference can be attributed to experimental errors, it can also reflect the lower number of bridges in the HM–DCL(P) film, due to the slower reptational diffusion mechanism and residual $f_m$ values (Figs. 6C, 8E and Scheme 3E).

### Table 4

<table>
<thead>
<tr>
<th>Film composition</th>
<th>RMG (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LM</td>
<td>37</td>
</tr>
<tr>
<td>HM</td>
<td>89</td>
</tr>
<tr>
<td>LM + HM (1:1 M)</td>
<td>79</td>
</tr>
<tr>
<td>LM + DCL(P) (1:1 M)</td>
<td>100</td>
</tr>
<tr>
<td>HM + DCL(P) (1:1 M)</td>
<td>93</td>
</tr>
</tbody>
</table>

4. Conclusions

Unlike most reports in the literature, we have used nanoparticles containing narrow molecular weight distributions of linear chains, which allowed us to understand the diffusion mechanism in more detail. We observed that chain interdiffusion followed a Fickian regime in films casted from Low-M particles, LM(P)–LM(A), although with lower $D_{app}$ values than those found for films that do not contain the $p$(BMA-co-EGDMA) nanogel. Contrarily, during the annealing of...
the films formed by particles containing higher molecular weight chains, \(HM(P)\)–\(HM(A)\), interdiffusion occurred by reptation, with lower \(D_{\text{app}}\) values than expected, again due to the presence of the \(p(BMA-co-EGDMA)\) nanogel. These conclusions support the results of the chemical resistance assays in films formed by \(LM\) or \(HM\) particles. The films formed by \(LM\) particles showed lower resistance to solvent because the molecular weight of the linear chains in the particles is too short to form entanglements across the healed interfaces, with swelling of \(LM\) films occurring by a chain pullout mechanism. The higher molecular weight of the linear chains in \(HM\) particles allows the formation of entanglement at both sides of the interfaces. In this case, film disintegration can only occur by chain scission and was only observed in a small extent.

Chain interdiffusion studies performed in films casted from 1:1 molar blends of particles containing linear chains of different molecular weights, \(LM(P)\)–\(HM(A)\), show that the longer chains become plasticized by the shorter, both contributing for chain interdiffusion. These films exhibit intermediate \(f_m\) and \(D_{\text{app}}\) values from those observed for \(LM(P)\)–\(LM(A)\) and \(HM(P)\)–\(HM(A)\) films.

The best healing properties were obtained in blends containing double nanogel interpenetrated network particles, \(DCL(P)\), because the network relaxation process needed to release the anchored chains is very slow. The incorporation of a nanogel structure inside the particles slows down interdiffusion during film formation but improves the healing properties of the final films, especially in the case of the double nanogel interpenetrated particles.

The nanogel presence in all particles, although slowing down interdiffusion, improves the healing properties of the films made from those novel architectured particles.

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**Appendix A. Supplementary material**


**References**