Preparation and Properties of Cross-Linked Fluorescent Poly(methyl methacrylate) Latex Colloids

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We report a single step preparation of monodisperse fluorescent poly(methyl)methacrylate (PMMA) lattices cross-linked with ethylene glycol dimethacrylate with radii in the range 150−1000 nm using dispersion polymerization. The particles are applied as fluorescent cores in core−shell PMMA particles for confocal microscopy (Dullens et al. *Langmuir* **2003,** *19,* 5963). Contrary to un-cross-linked particles, these cross-linked colloids are stable in good solvents for PMMA as well. Therefore we studied the properties of the cross-linked PMMA particles in the good solvents tetrahydrofuran (THF), chloroform, and toluene using light scattering and confocal scanning laser microscopy. We show that the particles swell instantaneously and that their volume can increase up to more than seven times their volume in poor solvents. Further, it is very likely that the particles are charged in THF.

Introduction

Suspensions of sterically stabilized poly(methyl methacrylate) (PMMA) latex particles in apolar solvents are extensively used as a colloidal hard sphere model system.[1−5] When these particles are dispersed in a solvent or solvent mixture that matches the refractive index, the attractive van der Waals forces are minimized. In addition, the particle density can be matched which minimizes gravitational effects in experiments. Therefore, these colloidal particles are very suitable as model systems for molecules and atoms.[1,6] Furthermore, colloidal particles are applied in many technological areas such as paints, drilling fluids, coatings, food processing, etc. Thus, understanding the behavior of colloids is important for many applications.

Over the past few years confocal scanning laser microscopy (CSLM) has been increasingly applied in colloid science.[2,7−14] CSLM facilitates studies of the structure and dynamics of colloidal systems in real space and time. However, this technique places high demands on the colloidal model system. Therefore, fluorescent particles were developed by incorporating fluorescent dyes.[4,15,16] By

use of sophisticated tracking algorithms similar to those desribed in ref 17, the (time-dependent) particle coordinates can be obtained. However, tracking in three dimensions (3D) is seriously complicated if the particles are completely fluorescent. Van Blaaderen developed silica particles consisting of a fluorescent core and a large nonfluorescent shell.[18] The core−shell topology facilitates tracking of particles with accuracy in 3D. In a recent publication we described the development of similar core−shell PMMA latex colloids using dispersion polymerization,[5] a simple method for preparing colloidal latex particles.[4,5,19] These particles allow investigation of a model colloidal hard sphere system using quantitative CSLM in 3D with negligible effects of gravity.

Chemical cross-linking of the PMMA chains was essential to prepare the PMMA core−shell particles.[5] Pathmamanoharan and co-workers described the synthesis of cross-linked PMMA particles by a single-step procedure.[20] However, they were not able to prepare cross-linked PMMA particles with a radius larger than 120 nm, which is too small for quantitative CSLM studies. Furthermore, the resulting distribution of the cross-linking agent, ethylene glycol dimethacrylate (EGDM), throughout the particle was inhomogeneous.[21] Therefore, the important step in the development of the core−shell particles was the preparation of monodisperse large (i.e., $R \geq 200$ nm) fluorescent (homogeneously) cross-linked PMMA particles, being the fluorescent core in the core−shell particles.[5]

In this work we describe the preparation of these particles with radii in the range 150−1000 nm. The particles were fluorescently labeled by incorporating the fluorescent monomer NBD-MAEM (4-((methylamino)-ethyl methacrylate)-7-nitrobenzo-2-oxa-1,3-diazol) following the approach described in refs 4 and 5. Next to the development of the core particles, we explored the properties of the resulting cross-linked particles in good solvents,

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Table 1. Details of the Single-Step Fluorescent Cross-Linked Latex (amounts in g)[a]

	PX7	PX8	PX9	PNX4	PNX5	PNX6m	PNX10	PNX13
				Reaction Flask				
ADIB	0.108	0.105	0.104	0.11	0.101	0.107	0.104	0.104
MM	10	10.05	10.05	10	10	10.05	10	10
MA	0.202	0.202	0.23	0.22	0.207	0.205	0.204	0.207
PHS	1.06	1.03	1.07	1.05	1.065	1.005	1.02	1.09
hexane	7.24	5.78	6.06	5.98	6.54	6.74	6.2	6.16
Exssol D 100	3.77	2.91	3.1	2.94	3.34	3.26	3.21	3.21
NBD/acetone mixture[b]								0.85
octyl mercaptan[a]	0.061	0.061	0.061	0.061	0.061	0.005	0.061	0.061
				Dropping Funnel				
hexane	8.02	8.06	4.02	7.94	8	7.94	3.5	3.92
Exxsol D 100	4.08	4	2.03	4.01	4.02	4.04	1.866	2.05
EGDM[a]	0.24	0.297	0.148	0.6	0.61	0.063	0.55	0.15
NBD/acetone mixture[b]				0.71	0.72	1.5	0.78	
dropping time (min)	40	50	24	55	45	45	20	23

[a] For the determination of the amount of octylmercaptan and EGDM, the desired mass was converted to volume via the densities: $\rho_{octylmercaptan} = 0.84$ g/mL and $\rho_{EGDM} = 0.84$ g/mL. [b] The concentration of the NBD-MAEM in acetone: 11.5 mg/mL.

such as tetrahydrofuran (THF), chloroform, and toluene. Due to the cross-linked stucture, the particles swell but do not dissolve therein.[22-25] Single particle properties such as the increase in volume due to swelling and the time required to reach the swollen state were investigated using static light scattering (SLS). Since the particles are fluorescent, we were also able to study concentrated suspensions of cross-linked PMMA particles in good solvents using CSLM. In particular we focused on the interparticle interactions.

Experimental Section

Materials. Methyl methacrylate (MM, BDH, >99%) was distilled under nitrogen atmosphere before use, methacrylic acid (MA, Fluka, 98%) was distilled at reduced pressure and under nitrogen atmosphere prior to use. Exxsol D 100 (Exxon Chemical Europe Inc.), hexane (Baker, >95%), octylmercaptan (Fluka), ethylene glycol dimethacrylate (EGDM, Merck, 90%), chloroform (Merck, 99–99.4%), THF (Acros organics, >99%), and toluene (Baker, >99.5%) were used as supplied. Poly(12-hydroxystearic acid) graft copolymer (50% solution in a 2:1 (w/w) ethyl acetate/butyl acetate mixture) was obtained from ICI. This copolymer will be referred to as PHS. Azo-bis-isobutyronitrile (ADIB, Janssen Chimica) was recrystallized from acetone before use. The fluorescent monomer NBD-MAEM was prepared following the procedure described by Bosma.[4] Prior to the synthesis the NBD-MAEM was dissolved in acetone (Merck, p.a.).[5]

Preparation of Cross-Linked Fluorescent PMMA Latex Spheres. To prepare the latex particles, a standard reflux setup expanded with a dropping funnel with a water jacket was used. The 50-mL two-necked round-bottom flask was evacuated and brought under a nitrogen atmosphere. The dropping funnel was removed while an overpressure of nitrogen was present. The ADIB was added in the reaction flask. In a separate beaker the MM and MA were mixed. A small amount of this mixture was added to the reaction flask in order to dissolve the ADIB, using magnetic stirring. To the remaining MM/MA mixture PHS, hexane, and Exxsol D 100 were added. The contents of the beaker was added to the MM/MA/ADIB mixture in the reaction flask. Finally the octyl mercaptan was added. The dropping funnel was placed back, thereby closing the setup. The dropping funnel was filled with a mixture of hexane, Exxsol D 100, and EGDM that was mixed in a second beaker. In the case of the preparation of fluorescent particles, a mixture of NBD-MAEM/acetone was added to the reaction flask or dropping funnel (see Table 1).

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The contents of the round-bottom flask was subsequently heated to 80 °C using an oil bath. A few minutes after the reaction had started, the reaction mixture became turbid, indicating nucleation. The addition of the mixture in the dropping funnel was started at the moment that nucleation was observed. After complete addition, the reaction mixture was refluxed for 1 h. Next the oil bath was removed, and the contents of the flask was cooled to room temperature.

By use of the same method as described above, multiple batches of fluorescent and nonfluorescent lattices were prepared. The amounts of chemicals used and the dropping times are summarized in Table 1. All the chemicals were weighed unless stated otherwise.

Characterization of the Latex Particles. To determine the size and polydispersity of the particles SLS experiments were performed on dilute dispersions in hexane on a homemade light scattering apparatus. The wavelength λ_0 of the incident light was 632.8 nm. The diluted dispersions were made dust free by filtering them through Mitex filters. The sphere radius and the polydispersity were obtained by fitting form factors, calculated using MIE theory,[26] to experimentally obtained scattering patterns.

Scanning electron microscopy (SEM) was performed with a Philips XLFEG30 microscope to obtain information about the shape and the surface roughness of the particles. SEM samples were prepared by dipping formfar-coated grids into dilute dispersions. The grids were coated with a 5 nm thick layer of platinum/palladium to minimize particle damaging such as melting and shrinking due to the electron beam.

Single Particle Properties in Good Solvents. The radius of the PMMA particles in good solvents was obtained using static light scattering on diluted dispersions. The degree of swelling was quantified by the swelling ratio α

$$\alpha = R_{swollen}/R_{unswollen} \tag{1}$$

where the particle radius in hexane (inferred from SLS data) was taken to be $R_{unswollen}$. The samples were prepared as described before, except that the dispersions were not filtered since the filters dissolved in the good solvents. To account for the penetration of solvent in the particle, an effective refractive index, n_{eff}, which is a function of α, was used in the calculations of the form factors. This was obtained by scaling the refractive indices of the particle, $n_{particle}$, and the solvent, $n_{solvent}$, with their volume fractions in the particle while keeping the volume occupied by PMMA constant

$$n_{eff} = \frac{1}{\alpha^3}[n_{particle} + n_{solvent}(\alpha^3 - 1)] \tag{2}$$

The time required for a particle to swell to its maximum size (in

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the different solvents), the swelling time, was determined using SLS as well. The samples were prepared by adding a small amount of a dispersion in hexane to an excess quantity of the good solvent. Within a few minutes the SLS measurements were started. A custom-made DLS setup, equipped with an argon laser, $\lambda_0 = 514.5$ nm, was used as an SLS apparatus. It took approximately 1 h to complete one scan from 20° to 120°, because of the weak scattering intensity at large angles. After 5 weeks, the sample was measured again to check the swelling behavior also on a much larger time scale.

Concentrated Dispersions of Swollen PMMA Particles. CSLM was used to study concentrated dispersions of swollen PMMA particles in real space. To change the solvent, the particles were sedimented using a Beckman Coulter Spinchron centrifuge and the supernatant was removed. The particles were redispersed in the new solvent. When this procedure was repeated for the fourth time, the solvent was considered to be completely changed. The mass fraction of the samples was determined by centrifugating a stock dispersion of known mass fraction. Subsequently the (clear) supernatant was removed and the samples were diluted to the target mass fractions with a known amount of solvent. To calculate the volume fraction of the samples, one must correct for the swelling of the particles in a similar way as was done for the determination of the effective refractive index. Therefore the effective volume fraction, ϕ_v^{eff}, is a function of the swelling ratio and is calculated using the following expression[27]

$$\phi_v^{eff} = \alpha^3 \frac{\phi_m \rho_s}{\phi_m(\rho_s - \rho_p) + \rho_p} \tag{3}$$

where

$$\phi_m = \frac{m_p}{m_p + m_s} \tag{4}$$

Here ρ_s is the mass density of the solvent, ρ_p the mass density of the unswollen particle (taken as 1.172[20]), ϕ_m the mass fraction, m_p the mass of the particles, and m_s the mass of the solvent.

The sample was contained in small vial (contents ~1 mL).[28] To be able to use the cell in a CSLM setup, the bottom of the vial was removed and replaced by a thin cover glass, which was glued to the vial using an epoxy glue (Araldit AW2101 with hardener HW2951). A Leica DM IRB confocal scanning laser microscope in combination with an argon laser ($\lambda_0 = 488$ nm), a Leica TCS NT scanhead, and an oil-immersion lens (Leica 100×, NA 1.4) was used in fluorescence mode. With image analysis software similar to those described in ref 17, the coordinates of the particles in the first layer at the glass wall were determined. These were used to calculate the two-dimensional radial distribution function, g_{2D},[2] as a function of the distance r. The steepness and the position of the first peak of g_{2D} give information about the interparticle potential.[29]

Results and Discussion

Synthesis of Cross-Linked PMMA Latex. In our first attempts, we tried to prepare cross-linked PMMA particles with a radius larger than 120 nm following the method described in ref 20. As the final radius of the particles is a function of the MM concentraion,[4,19] we increased the MM concentration while keeping the MM to EGDM ratio constant. Unfortunately, all the attempts to increase the size by this approach failed. Within a few minutes after nucleation was observed, the systems irreversibly aggregated. This was probably due to presense of the final amount of EGDM in the reaction mixture. As a result, the polymerization rate increased[30−32] and the particles grew faster than those without EGDM. Consequently, a larger amount of stabilizer was needed to prevent aggregation.

However, the size of the particles is basically determined by the ratio of the amounts PHS and MM concentrations present at the moment of nucleation.[4,19,20] So if both the MM and the PHS concentrations are increased with the same fraction, their ratio remains the same and so will the resulting particle size. Another problem was that the resulting distribution of EGDM throughout the particle was inhomogeneous.[21] Due to bifunctionality, the EGDM was probably consumed more rapidly during the polymerization than the monofunctional monomers. As a result, the EGDM was mainly present in the interior of the particle.

In our new approach we added the cross-linking agent during the polymerization reaction. As a result of the dropwise addition, starting when nucleation was observed, the concentration of EGDM in the reaction mixture was always low, thereby hardly influencing the polymerization speed. Moreover, the EGDM is absent at the moment of nucleation, which has major implications for the accessible particle sizes. Since the size of the particles is only determined by the conditions at nucleation, the size of the cross-linked particles can now be tuned in the same size range as in the preparation of non-cross-linked PMMA.[4,16,15,19] Therefore, the decoupling of the cross-linking and the nucleation facilitate the preparation of large ($R > 100$ nm) cross-linked PMMA particles in a single step. Furthermore, the distribution of the EGDM throughout the particle is expected to be homogeneous, as the EGDM is added over the whole period of particle growth. This is an important property of the particles since the degree of cross-linking at the surface has a dramatic influence on the interaction potential of the particles.[25]

The addition of the EGDM (in a mixture in the dropping funnel) was started at the moment that the nucleated particles became visible. Ideally, the interval of EGDM addition should coincide with the interval of particle growth. To optimize the dropping time, we measured the time required for a particle to reach its final size. During the synthesis of PNX5, samples were taken from the reacting mixture, starting at the moment that nucleation was observed. The samples were quenched in a relative large amount of hexane at "room temparature", to prevent further growth of the particles. Subsequently SLS was conducted to obtain the radii of the particles in the different samples. In Figure 1 the radius of PNX5 is shown as a function of the time. It is observed that already after 24 min, about 93% of the final radius is reached. After 50 min more than 99% of the final radius is reached.

With a polynomial that was fitted to the experimental data in Figure 1, the relative particle volume as a function of time was calculated. This is shown in Figure 2 together with the relative volume of added EGDM for dropping times of 24 and 50 min. From Figure 2 it can be seen that initially the particle growth rate increases, before it reaches a constant value (point A in Figure 2). The largest part of the particle growth takes places at a more or less constant growth rate, i.e., between A and B in Figure 2. In the end (above B) the growth rate reduces to zero when the particles approach their final size. A qualitatively similar result was reported by Barret.[33]

By comparing the relative particle volume to the relative volume of the added EGDM, we observe that for a dropping

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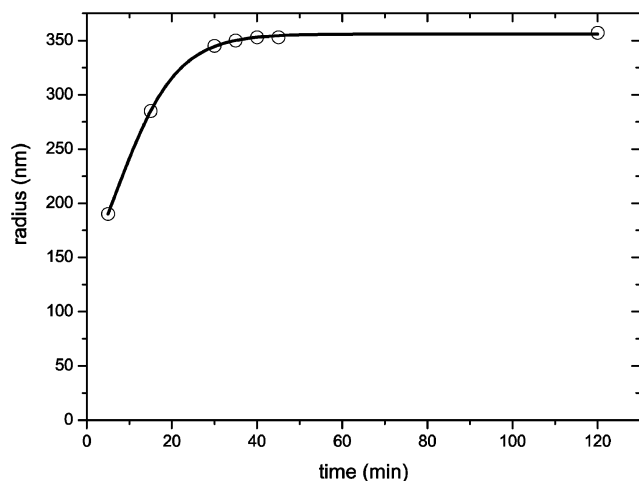(29) Hill, T. L. *An introduction to statistical thermodynamics*; Addison-Wesley: Reading, MA, 1962.

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Figure 1. The radius of PNX5 as a function of the time ($t = 0$ corresponds to moment that nucleation becomes visible). The open circles are the experimental data points, and the solid line is an polynomial fit to the data.
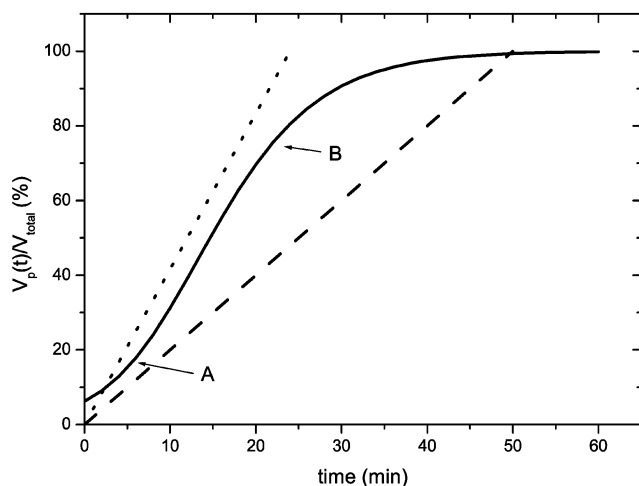
Figure 2. The relative volume of the particle (solid line) and the relative volume of the added EGDM solution as a function of time. The dotted line and the dashed line represent the dropping times of 24 and 50 min, respectively.

Table 2. Radius (*R*) and Polydispersity (σ) of Prepared Cross-Linked Lattices Obtained by Scattering Measurements in Hexane

sample no.	*R* (nm)	σ (%)
PX7	192	12
PX8	540	5
PX9	435	6
PNX4	955	8
PNX5	357	10
PNX6m	285	6
PNX10	(aggregated)	
PNX13	645	7.5

time of 24 min the EGDM addition rate is approximately equal to the particle growth rate during the largest part of the particle growth. This indicates that the particle is homogeneously cross-linked. Moreover, no secondary nucleation is expected to occur for a dropping time of 24 min. Even if the EGDM is not built in instantaneously, the generated excess amount of EGDM can be incorporated since the particle growth is not complete. Conversely, this is not the case for a dropping time of 50 min, since the particles already reached their final size by then. So if there is an excess amount of EGDM, it cannot be incorporated anymore and formation of secondary nucleii
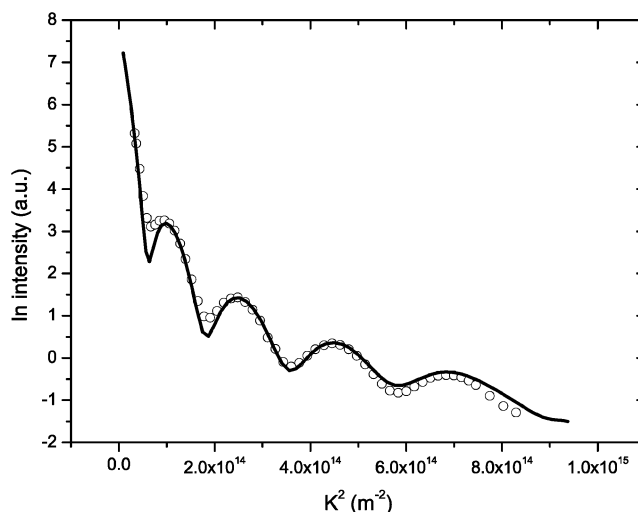
Figure 3. Experimental (open circles) and theoretical (solid line) values of the system PX8. The theoretical curve was calculated using Mie theory, with 540 nm as particle radius and 5% as polydispersity.

is expected. Furthermore, the EGDM addition rate for a dropping time of 50 min is smaller than the particle growth rate. As a consequence, the main part of the particle is not homogeneously cross-linked. Thus, using a dropping time of 24 min during the synthesis is expected to result in relatively homogeneously cross-linked particles without significant occurrence of secondary nucleation.

In our experiments we both tried dropping times of about 25 and 50 min (Table 1). The dropping speed was typically one drop every 2−3 s, which is somewhat slower than the dropping speed used in our previous work to grow the particles larger.[4] Therefore large amounts of secondary nuclei due to the fast addition of the contents of the dropping funnel are not expected. By use of the above-described procedure, large cross-linked PMMA particles with a narrow size distribution were prepared. Fluorescent cross-linked particles were prepared as well. The radii and the polydispersities of the prepared lattices are summarized in Table 2.

Figure 3 shows the scattering pattern of latex PX8 (see Table 1 and Table 2). The deep minima indicate a small polydispersity. A convenient method to obtain direct information on particle size and polydispersity is scanning electron microscopy. In addition, insight in the particle shape and surface roughness is obtained. In Figure 4 a SEM image of the system PX9 is shown. From this figure it can be seen that the particles are spherical and monodisperse. The particles are partly ordered, pointing toward a small polydispersity. Furthermore no significant amount of secondary nucleated particles is seen. While imaging the systems using SEM, the latex particles tend to shrink because of the vacuum in the SEM. Further, the PMMA spheres show rapid melting and deformation induced by the eletron beam. The effect of exposing a small spot of the sample for a longer time (in the order of tens of seconds) to the electron beam is clearly seen in Figure 5. This figure shows a SEM photograph of the PX8 particles. It is clear that the particles are not spherical anymore and have a very rough surface. Multiple particles actually coalesced into one PMMA block. Although the particles in Figure 5 are highly deformed, the presence of a significant amount of secondary nuclei in PX8 is also clearly observed. In contrast, no secondary nuclei were observed in the PX9 system (Figure 4). For PX8 the dropping time was 50 min, whereas for PX9 the EGDM
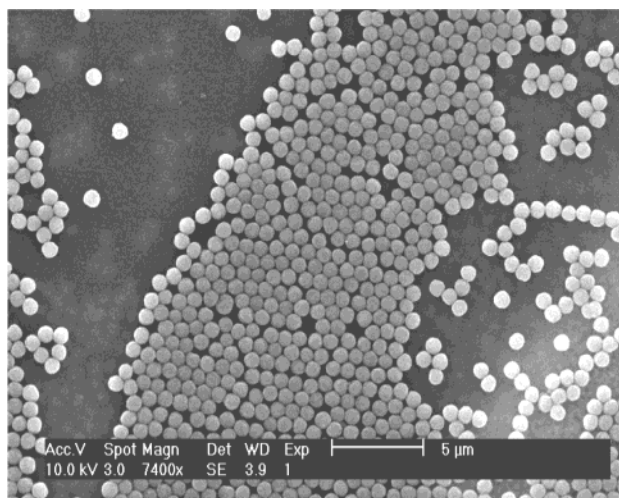
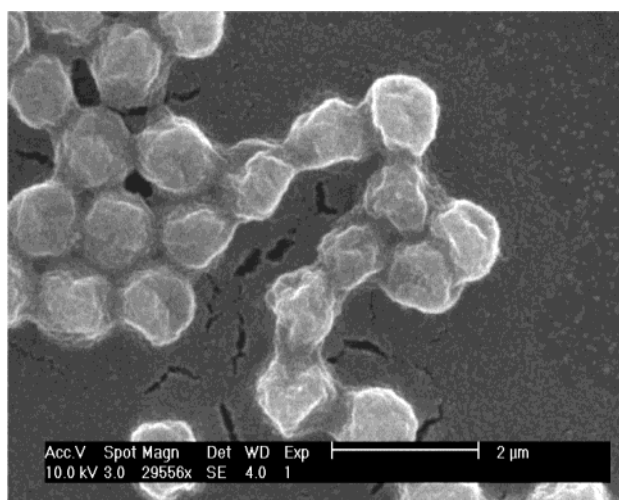**Figure 4.** SEM micrograph of the system PX9.

Figure 5. SEM micrograph of PX8. The particles in the micrograph have been overexposed to the electron beam, resulting in deformed and coalesced particles. The cracks are formed by the secondary nucleated particles.

was added over a period of 24 min. This observation is in agreement with the earlier argument that secondary nucleation was expected to occur especially if the dropping time exeeds the time needed for a particle to reach its final size.

By incorporation of a fluorescent dye, the particles are also suitable for use in real space studies using CSLM. In Figure 6 an example of a confocal image of latex PNX4 is shown. Surprisingly, it is clearly observed that these particles are not spherical. However, it appeared that they are monodisperse in volume. The same characteristic nonspherical shape was observed using SEM. In some experiments nonspherical particles were obtained, but most of the preparations yielded fairly spherical particles as confirmed by SEM and CSLM. At this time, we do not fully understand what causes the irregular shape during the synthesis. We suggest that the increased rigidity, due to cross-linking,[34] might cause irregularities in the shape of the particles.[35,36] Although the asphericity is not understood, the system itself is very interesing. Work on the properties of this volume-monodisperse, aspherical system is currently in progress.
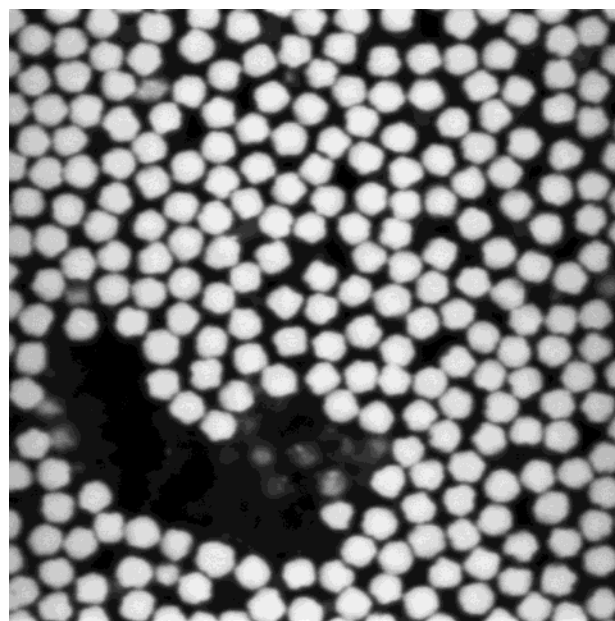
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Figure 6. Confocal scanning laser microsocpy image of the volume-monodisperse, aspherical system PNX4.
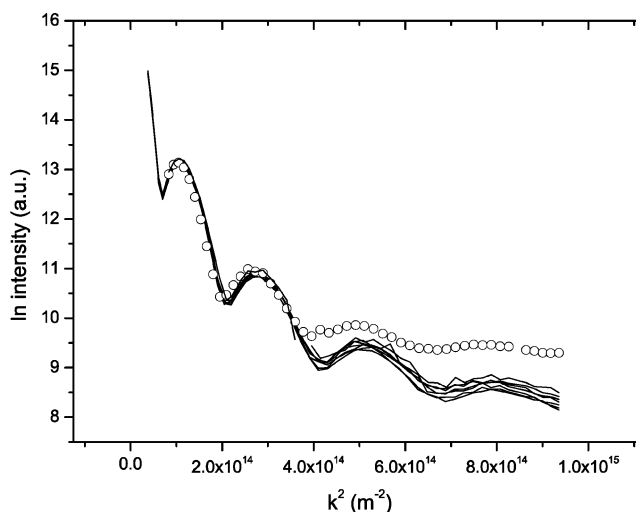

Figure 7. Scattering patterns of the system PNX6m in chloroform as a function of time. The solid lines represent the experimental data taken every hour starting at $t = 0, 1, 2, ...,$ 6 h. The open circles represent the scattering curve of the same sample measured again after 5 weeks. By fitting the curves using Mie theory, a radius of 535 nm was obtained.

Single Particle Properties in Good Solvents. As a result of the cross-linked network, the synthesized particles do not dissolve in good solvents. Using static light scattering, we explored the swelling behavior of our cross-linked PMMA particles in THF and chloroform. These properties could not be studied in toluene using light scattering, since toluene matches the refractive index of the latex particles too closely. As a consequence the intensity of the light scattered by diluted suspensions was too low to be detected. In particular, we measured the swelling time and the swell factor α, as defined by eq 1. To accurately measure the swelling factor α, the particles must have reached their final size. Therefore we first measured the swelling time. In Figure 7 the scattering patterns of PNX6m in chloroform as a function of time are

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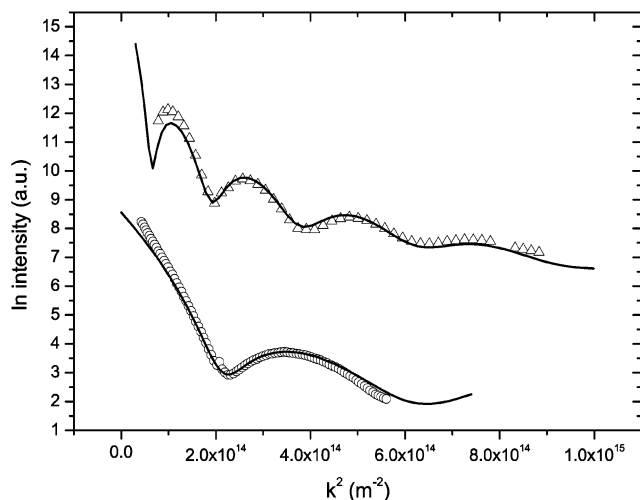
Figure 8. Scattering patterns of PNX6m in hexane (○) and THF (△). The radii obtained by analyzing the data using Mie theory were as follows: hexane, $R = 282$ nm; THF, $R = 550$ nm.

Table 3. The Radii of PNX6m in Hexane (for comparison), Chloroform, and THF and the Corresponding Swelling Factors

	R (nm)	α
hexane	282	
chloroform	535	1.90
THF	550	1.95

presented. No difference between the first measured scattering pattern and the later measured curves was observed. This implies that the particle is not swelling anymore during the first measurement. Therefore the swelling time must be equal or smaller than the time between the sample preparation and the start of the first measurement, which is on the order of a minute (or faster). The swelling time in THF is on the same order of magnitude. Furthermore, it was observed that the curve measured after 5 weeks was similar to the scattering patterns measured in the first 7 h after preparation of the sample. This indicates that the cross-linked particles are very stable in good solvents.

In Figure 8 the scattered intensity as function of the angle is shown for the PNX6m particles in hexane as well as in THF. It is obvious that the particles swell significantly in THF when comparing the scattering patterns obtained in the different solvents. The position of the first minimum shifted to lower scattering vector (k) and two additional minima appeared, implying that the PNX6m particles are much larger in THF than in hexane. The radius of the particles increased from 282 nm in hexane to 550 nm in THF, corresponding to a swelling factor α of 1.95. This implies that the volume of the swollen particle is 7.4 times the particle volume in hexane. For chloroform similar results were found (see Table 3). The swelling factor α is also a function of the cross-link density, since the density of the network determines the rigidity and thus the degree of swelling.[22−25] For example, the PX7 particles, which are higher cross-linked, have a swelling factor of 1.54 in THF, which is significantly smaller than the swelling factor of the PNX6m particles in the same solvent.

Concentrated Dispersions of Swollen PMMA Particles. Since the particles are fluorescent, we were also able to study concentrated suspensions of cross-linked PMMA particles in good solvents using CSLM. In particular we focused on the interparticle interactions. By calculating the two-dimensional radial distribution function g_{2D} and monitoring the shape and the position of the
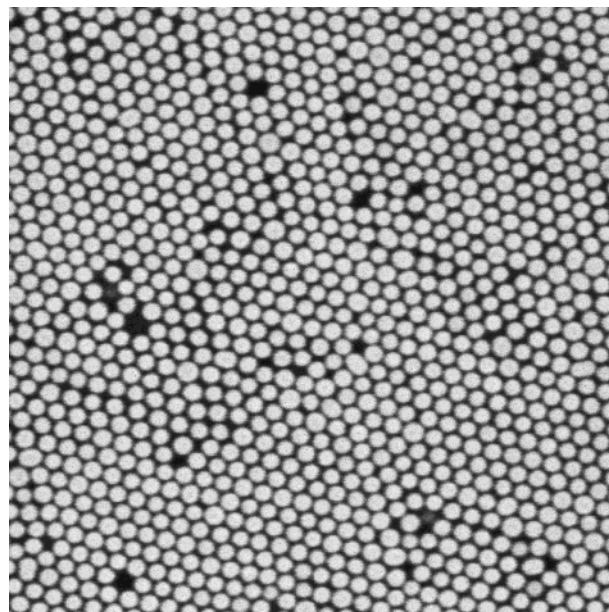

Figure 9. CSLM picture of the PNX6m particles at the glass wall in THF, $\phi_v = 0.44$. The field of view is 37.5 μm × 37.5 μm.
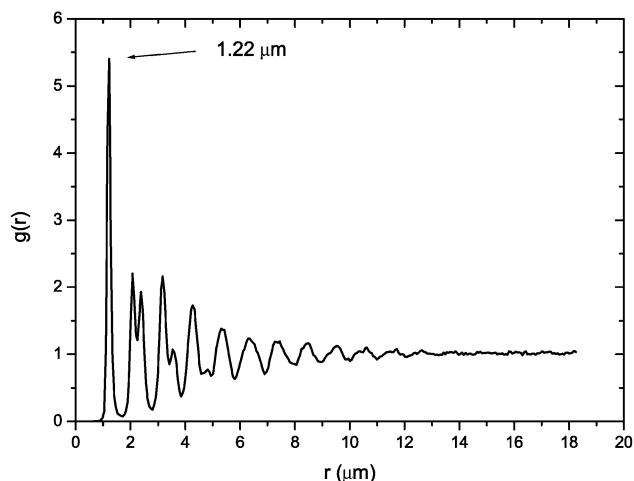

Figure 10. Two-dimensional radial distribution function for PNX6m in THF at $\phi_v = 0.44$.

first peak of g_{2D} as a function of the concentration, information about the interparticle potential is obtained.[29] Unfortunaly, it appeared that chloroform dissolved the glue that was used in the sample cell and that in hexane some particles were stuck to the glass wall. Therefore only the behavior of the cross-linked PMMA particles in THF and toluene was studied by imaging the first layer at the glass wall.

Figure 9 shows a CSLM image of the PNX6m system in THF. Local crystalline order is observed, which is reflected by the sharp peaks of g_{2D}, shown in Figure 10. The first peak, which corresponds to the average position of the nearest neighbor particles, is located at 1.22 μm. This value is 10% higher than the diameter of the particle obtained with SLS. However, since the system was ordered, the position of the first peak of g_{2D} corresponds to the crystal lattice spacing, which can exceed the particle diameter.[16] Upon dilution of the system, the first peak of the g_{2D} shifted to significantly larger distances. More specific, for $\phi_v = 0.37$ and $\phi_v = 0.17$ the peak shifted to respectively 10% and 20% larger distances (see Table 4, which is indicative for charge on the particles. Moreover, the structure remained crystalline ordered even at volume
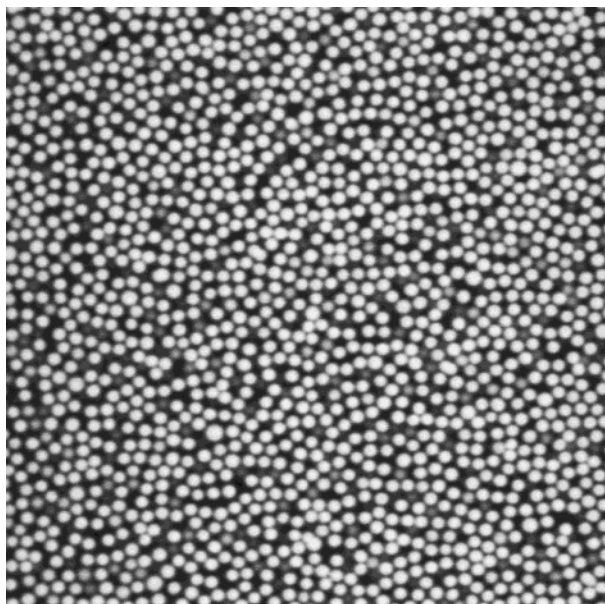
Figure 11. CSLM image of PNX6m in toluene, $\phi_v = 0.59$. The field of view is 37.5 μm × 37.5 μm.

Table 4. The Position of the First Peak of the Radial Distribution Function as a Function of the Volume Fraction for THF and Toluene

	volume fraction	position of first peak $g(r)$ (μm)	structure
THF	0.44	1.22	crystal
	0.37	1.34	crystal
	0.17	1.46	crystal
toluene	0.59	0.95	glass
	0.52	1.01	crystal
	0.42	1.01	crystal

fractions as low as $\phi_v = 0.17$. Therefore it is very likely that the PMMA particles are charged in THF. However, what actually causes the charge on the particles in THF and similar apolar solvents is unclear.[13]

Figure 11 shows a confocal image of PNX6m in toluene at $\phi_v = 0.59$ at the glass wall. The corresponding g_{2D} is presented in Figure 12. A disordered structure is observed, resulting in only two peaks in the radial distribution function. The first peak of g_{2D} was located at 0.95 μm. For disordered hard sphere systems, this value corresponds to the diameter of the particles. Applying this to PNX6m in toluene, a particle radius of 475 nm is obtained. Consequently, the swelling ratio $\alpha' = 1.68$ (in eq 1 now $R_{swollen} = 475$ nm), implying that the PNX6m particles swell significantly in toluene as well. When the system was diluted to $\phi_v = 0.52$, the system became ordered and the position of the first peak of g_{2D} was shifted to 1.01 μm. This shift can be attributed to the transition from a glassy to a crystalline state, as the first peak of g_{2D} corresponds to the lattice spacing and the (effective) particles diameter. The position of the first peak did not shift to larger distances upon further dilution, although the structure
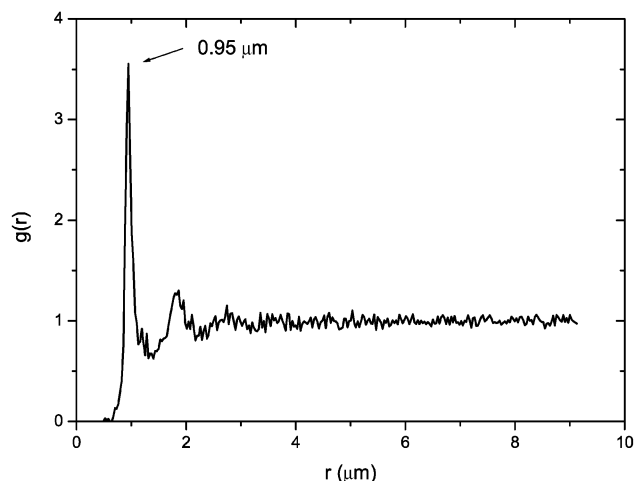

Figure 12. Two-dimensional radial distribution function for PNX6m in toluene at $\phi_v = 0.59$.

remained crystalline at a volume fraction of 0.42. Therefore, charge on the particles in toluene cannot be ruled out.

Conclusions

We have demonstrated that PMMA latex particles, cross-linked with EGDM can be prepared with radii in the range 150–1000 nm by adjusting the single-step dispersion polymerization as described in ref 20. The cross-linked PMMA particles can be fluorescently labeled following the procedure of Bosma et al.[4] Static light scattering and scanning electron microscopy measurements show that the resulting particles are monodisperse and spherical. As a result, the particles are very suitable to serve as the fluorescent cores in the preparation of core–shell particles.[5] Sometimes also nonspherical particles are obtained, although it is at present not clear what causes the asphericity. Furthermore, the particles are stable in good solvents such as THF, chloroform, and toluene, because of their cross-linked structure. We show that the particles swell instantaneously and that their volume can increase more than a factor 7. In THF it is very likely that the PMMA latex particles are charged, which is not uncommon in organic solvents,[13] whereas for toluene the situation is not clear.