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S.M. Underwood
W. van Megen

Refractive index variation in nonaqueous sterically stabilized copolymer particles

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S.M. Underwood · Dr. W. van Megen (✉)
Department of Applied Physics
Royal Melbourne Institute of Technology
GPO Box 2476V
Melbourne 3000, Australia

Abstract We present procedures for preparing sterically stabilized polymer particles whose refractive index can be controlled over a range of a few percent. Particle sphericity and size distribution are such that suspensions crystallize at high concentrations. This at least ensures that Brownian motion dominates over particle settling and that the polydispersity is no more than about 10%. Of particular interest are new particles comprising poly(methylmethacrylate-co-trifluoroethylacrylate) that can be optically matched in single solvent, namely cis-decalin.

Key words Dispersion polymerization – non-aqueous co-polymer latex – steric stability – light scattering – refractive index variation

Introduction

Dispersions of near-micrometer sized particles are generally opaque except at extremely low concentrations. Studies of concentrated dispersions by conventional light scattering rely on a dominance of singly scattered light and therefore require that the refractive index of the suspending liquid phase closely matches that of the particles. In a binary mixture of colloidal particles control of the refractive index of the liquid as well as that of each of the particle types is essential in order to measure the spatial distribution and motion of the individual components. In this paper we describe new preparations of sterically stabilized polymer particles for which the refractive index can be varied over a range of a few percent in a controlled manner.

A dispersion can be regarded as a system of superatoms whose interactions are described by the potential of mean force among the particles. Thus, as far as the thermodynamic properties are concerned a dispersion is formally equivalent to a system of atoms [1]. There are also similarities in the dynamics in spite of the fundamental difference between the ballistic motion of atoms and the diffusive motion of suspended particles [2]. Consequently, colloidal dispersions serve as an important vehicle for experimental exploration of universal dynamical processes, such as crystallization [3] and glass formation [4], that are too fast to be easily observed in simple atomic systems.

In a manner analogous to the application of neutron scattering to atomic systems, the structure and particle dynamics of dispersions of near micrometer sized particles can be studied most conveniently by light scattering. Dynamic light scattering (DLS) applied to a dispersion of identical particles probes collective particle concentration fluctuations [5]. Single particle motion can be measured in a dispersion consisting of a mixture of dynamically identical but optically contrasting particles [5].

The recently developed multiple scattering suppression spectrometer [6] extends the application of dynamic light scattering to turbid samples by effectively selecting the light that has been scattered only once. However, the singly scattered component must still be a measurable fraction of the total light scattered. Clearly, the ability to tune the refractive index of the suspending liquid, by varying its composition or temperature or by varying the wavelength of the radiation, is a prerequisite for the successful application of light scattering techniques. To resolve the partial structure factors of a binary (or more complex) mixture of particles of different size adjustment of the refractive index of the particles becomes an additional requirement. For concentrated binary mixtures of particles with comparable size and number ratios the maximum tolerable contrast limits the difference between the refractive indices of the species to less than 1%. Where the size or number ratios differ significantly a larger refractive index difference can be tolerated and may be desirable in order to achieve sufficient contrast between the species.

Non-aqueous dispersions of polymethyl methacrylate (PMMA) particles, stabilized by thin layers of poly-12-hydroxystearic acid (PHSA) [7], have been used extensively as model colloids for well over a decade [4, 8, 9]. The size distributions of the particles are generally sufficiently narrow and the particle interactions sufficiently steeply repulsive that the dispersions show a freezing-melting transition [3] which mimics that expected for a system of identical hard spheres.

In this paper we describe modifications to the polymer composition of particles prepared using procedures developed by Antl et al. [7] based on the concept of dispersion polymerization [10]. The objective is to modify the PHSA stabilized PMMA particles to produce a change in refractive index of about 1%. In addition, particles with a refractive index that matches a suitable single solvent are particularly desirable. In all cases, the particle sphericity and size distribution must be such that dispersions of a nominally single species crystallize homogeneously at the appropriate concentrations. This at least ensures that Brownian motion dominates over particle settling and that the polydispersity is no more than about 10% [2].

Background

Although, in principle, dispersion polymerization offers the scope to independently vary the monomers, stabilizer composition [11] and reaction medium [12–16], the work described in this paper is restricted to the preparation of PHSA stabilized polymer particles in apolar organic solvents [7, 10]. Dispersion polymerization involves thermally initiated polymerization of monomers in solution, in the presence of an amphipathic graft or block copolymer which becomes physically adsorbed to the precipitating polymer and protects it from coagulation.

The stabilizer used here has a comb-like structure comprising a copolymer of methyl methacrylate (MMA), glycidyl methacrylate and PHSA macromonomer [7] at molar ratios of approximately 17 : 1 : 1. The PHSA provides side-chains which are soluble in the organic diluent. Since the copolymerization reactivity ratios of the simple monomers with the macromonomer are undoubtedly asymmetric, it is likely that the distribution of side chains is skewed, although this remains to be established. It is possible that a skewed distribution is advantageous to adsorption of the stabilizer to the precipitating polymer during the particle nucleation stage of dispersion polymerization.

At least 2% methacrylic acid (MAA) by weight of total monomers is included in the formulations for the preparation of latex particles to covalently bond the stabilizer to the particle cores. The MAA copolymerizes with MMA to form acid functional core polymer to which the stabilizer can be bonded, via the glycidyl groups, in a post-polymerization base-catalyzed reaction. Note that for this reason all preparations described here contain MAA, including those referred to as PMMA.

The PHSA stabilizer has been used successfully and extensively for the preparation of PMMA particles with radii, R, ranging from about 25 nm to 1.5 μm. Particle radii, from about 0.1 μm to about 1.5 μm, with polydispersities (σ, width of the particle size distribution relative to the mean) generally less than 10%, can be obtained by varying the initial monomer concentration from about 30% to 50% (by weight of initial solution) using a stabilizer concentration of 5% by weight of monomer. In agreement with earlier work [7], an instability region is found for monomer concentrations below about 30%. As reported elsewhere [17, 18], smaller PMMA particles ($R < 0.1$ μm) can be prepared by using monomer concentrations below 30% provided that the concentration of stabilizer is increased (up to 25% by weight monomer concentration).

Generally PHSA stabilized PMMA particles have good long-term stability in a range of solvents such as decalin, dodecane, tetralin and carbon disulfide. Importantly, by careful adjustment of the composition of the suspending liquid mixture (for example, decalin and carbon disulfide), turbidities as low as about 0.01 cm^{-1} can be achieved for any concentration [3]. Unfortunately, for PMMA there does not appear to be a suitable single solvent in which this low optical contrast can be achieved without compromising the stability or integrity of the particles.

Experimental

Materials

The PHSA stabilizer was prepared at ICI-Dulux Australia on a commercial scale, using procedures similar to those reported by Barrett et al. [10] and supplied as a 50 weight percent solution in butyl acetate. The monomers and chain transfer agent were obtained from Aldrich and used as received. Azo-bis-isobutyronitrile (TCI, Japan), hexane (67–70 °C fraction, BDH) dodecane (Rhone-Poulenc), decalin (*cis/trans*, Sigma), *cis*-decalin (Aldrich) and carbon disulfide (Ajax Chemicals) were all AR grade and also used as received.

Choice of monomers

To achieve the change in particle refractive index from that ($n = 1.491$ at 20 °C [19]) of PMMA (with 2% MAA) a further monomer can be copolymerized [12, 20] with MMA using the method of preparation outlined below. The efficacy of the PHSA comb stabilizer, described above and developed for the preparation of PMMA particles, is unlikely to be affected provided that the reaction medium is not changed significantly and that the properties of the copolymer do not vary significantly from those of PMMA.

The selection of comonomer is subject to several constraints. First, the comonomer must neither impede the nucleation process nor the rate of precipitation of the stabilizer. This requires favorable copolymerization kinetics between the comonomer and MMA. Second, polymers with a polarity or glass transition temperature significantly different from PMMA are undesirable because they may hinder the adsorption of the stabilizer to the precipitating copolymer. Third, an additional requirement of the core copolymer is that ideally a single liquid, or at least a liquid mixture, of suitable viscosity and polarity and with a refractive index identical to that of the particles must be available. This medium must be a good solvent for PHSA but essentially a non-solvent for the particles which must retain their integrity at all concentrations, although some swelling can be tolerated.

Given the lack of clear direction in the literature with regard to the above constraints several different monomer combinations were selected (see Table 1) as candidates on the basis of the refractive indices of their polymers and their anticipated compatibility with MMA.

Latex preparation

The initiator (azo-bis-isobutyronitrile, ADIB) was first dissolved in the monomers in a three-necked round-bottomed flask. The stabilizer solution (50% polymer dissolved in butyl acetate) was added to the monomer solution followed by the filtered solvents (hexane and dodecane) and the chain transfer agent. A stirrer and condenser were fitted to the flask which was then immersed in a water bath at 80 °C to initiate polymerization which was continued for 2 h.

In a subsequent stage, to covalently bond the stabilizer to the particle cores, the latex was reheated to 125 °C while removing hexane and replacing it with dodecane. Once at 125 °C dimethylethanolamine catalyst was added to the latex, at a molar concentration four times that of the glycidyl functionality in the stabilizer backbone, and the reaction continued for 90 min. The duration of this reaction was established in earlier work by following the decrease in acid functionality, by titration with base, to the plateau of the change in acid value with time [7, 10].

The concentration of ADIB was 0.4% by weight of reaction mixture in all preparations. The concentration of monomer was varied between about 34% and 43% by weight of reactants as given in Table 1. As mentioned above the particle size was controlled by variation of the monomer concentration while maintaining a constant ratio of monomer to stabilizer and a near constant initiator concentration.

Refractive index determination

Each new latex was redispersed in decalin by successive centrifugation, decantation of supernatant and redispersal in fresh solvent. Stock dispersions were prepared at concentrations of about 30% weight of solids. Aliquots of each dispersion were placed in optical cuvettes of 1 cm square corss-section. Particles with anticipated refractive indices greater than about 1.49 (the refractive index of PMMA) were dispersed in *cis/trans* decalin and carbon disulfide was systematically added. Transmission coefficients were measured with a He–Ne laser (wavelength, $\lambda = 633$ nm).

At maximum sample transmission (corresponding to turbidity typically less than about 0.05 cm^{-1}) refractive indices were obtained from measurements of the angle of minimum deviation of the laser light through the corners of the cuvette. By averaging over the four cuvette corners we estimate the accuracy of the refractive index results to be ± 0.003.

Dispersions of particles with refractive index less than 1.49 were redispersed in *cis*-decalin. In these cases a more sensitive method was employed for determining the minimum turbidity. This entailed measurement of the scattered intensity, at the angle of the main structure factor peak of the dispersion, as a function of temperature. The temperature where minimum scattering was obtained corresponds to optimum match of the refractive indices of solvent and particles.

Particle characterization

Hydrodynamic radii of the particles were determined by DLS on dispersions diluted in either dodecane or

Table 1 Characteristics of a range of modified particles (see text). The DLS results are estimates from first cumulants. The DLS radii (*R*) are from first cumulants and the quality factors (Q) are from the second cumulant. The polydispersities are from electron microscopy or DLS [20] as indicated and visual observation

Preparation reference	Monomer (Wt%)	Composition	*R* (nm) DLS (Q)	Polydispersity crystallization
SMU21	39	MMA98:MAA2	210 (0.02)	6% (EM); 5%(DLS) fully xtalline sediment
XL27	37	MMA92:MAA3: Styrene5	210 (0.02)	approx 6% (EM) fully xtalline sediment
XL16	34	MMA87:MAA3: Styrene10	159 (0.05)	broad (EM) no sedimentary xtal
XL24	36.5	MMA87:MAA3: Styrene10	228 (0.07)	broad (EM) no sedimentary xtal
XL18	34	MMA77:MAA3: Styrene20	250 (0.1)	broad (EM) no sedimentary xtal
XL17	34	MMA77:MAA3: Styrene18:DVB2	235 (0.06)	broad (EM) no sedimentary xtal
XL35	37.4	MMA80:MAA10: Styrene10	250 (0.03)	6% (DLS) fully xtalline sediment
XL49	39	MMA71:MAA5: TFEA24	200 (0.02)	8% (DLS) fully xtalline sediment
XL50	43	MMA71:MAA5: TFEA24	370 (0.02)	4% (DLS) fully xtalline sediment
XL52	39	MMA79:MAA5: TFEA16	189 (0.03)	8% (DLS) fully xtalline sediment

cis-decalin. The quality factor (second cumulant of the intensity autocorrelation function) was used as an initial indication of the polydispersity. Only those latices with quality factors less than about 0.03 were subjected to further analysis of the PSD by the DLS procedure introduced by Pusey and van Megen [21] and in some cases also by analysis of electron micrographs.

The formation of sedimentary crystals, observed in several latices when left standing, provided another indication of the size and shape polydispersity of the particles. Those particles considered to be sufficiently narrow in PSD ($\sigma < 10\%$) were resuspended in appropriate index matching solvents and concentrated in order to explore their homogeneous crystallization behavior [3, 4].

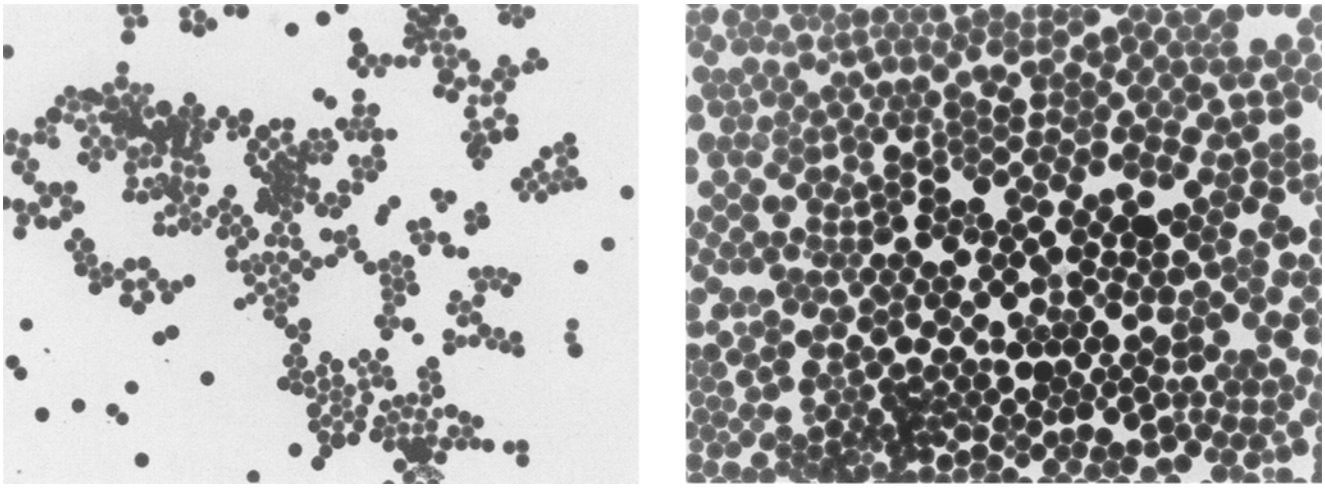
Results

Table 1 shows the particle radii, estimated polydispersities and a comment on the nature of any crystals formed in dispersions of particles modified with a range of monomers. SMU21 is a reference PMMA latex from earlier work [5].

At minimum turbidity the measured refractive index of a dispersion of PMMA particles in a mixture of decalin and CS_2 is 1.506. Partly as a consequence of CS_2 imbibition by the particles [22, 23] this value is greater than the published value [19] for bulk PMMA. Previous work [23] has established that CS_2 is absorbed by the particles to an extent of about 6% by weight. Inclusion of 10% styrene as a comonomer produced an increase in measured refractive index, at minimum turbidity, to $n = 1.52$. However, acceptable levels of polydispersity ($\sigma \lesssim 10\%$) of particles containing more than 5% styrene could only be achieved when the proportion of MAA was increased from 2–3%, used in the PMMA preparations, to 10%. This is illustrated in Fig. 1 which shows electron micrographs of SMU21 (PMMA) together with two preparations containing 10% styrene, XL24 (3% MAA) and XL35 (10% MAA).

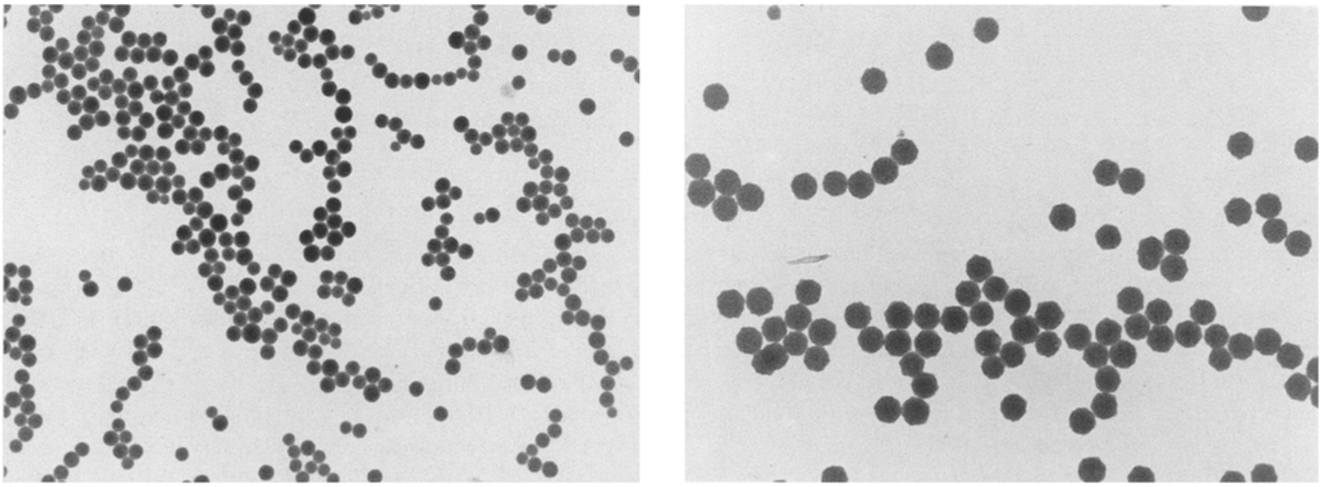
Figure 2 shows the percent transmission of 633 nm laser light at 21 °C through dispersions of particles, containing increasing proportions of styrene (Figs. 2(a)–(c)), as a function of solvent composition (CS_2 and decalin), each compared with the reference PMMA latex. We include in this figure results for equimolar mixtures of comparably sized reference PMMA particles and modified P(MMA/styrene) particles. When the modified particles contain 20% styrene the mixtures are opaque at all solvent compositions (Fig. 2c).

The refractive indices of dispersions at maximum transmission were measured for each of the styrene modified particles used for the transmission studies. The results are presented in Table 2. Refractive indices have also been calculated from the known fractions of decalin, CS_2, PMMA and polystyrene in the samples. For these calculations published values for the refractive indices of bulk



(a) SMU21

(c) XL35



(b) XL24

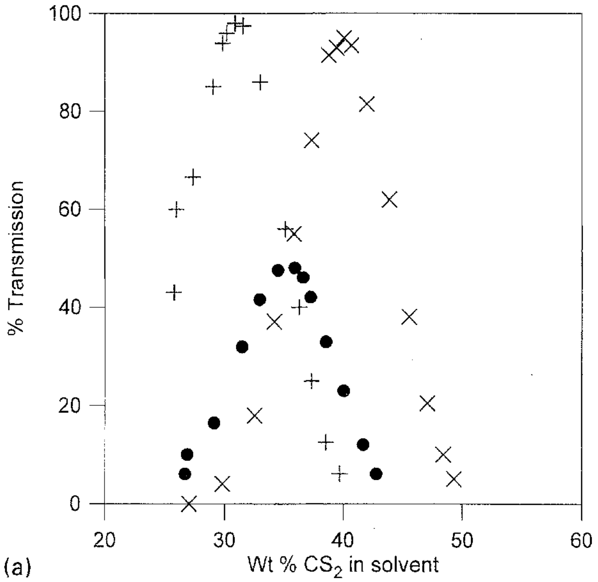
(d) XL50

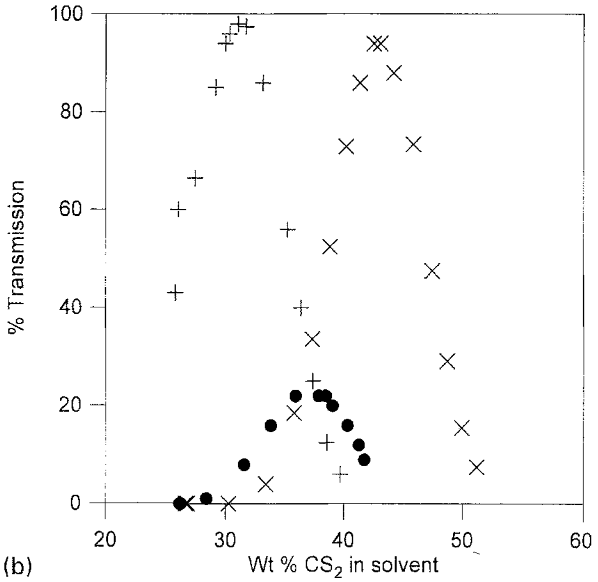
Fig. 1 Electron micrographs of PMMA and modified PMMA particles. Magnification ×5000. a) SMU21, PMMA with 2% MAA; b) XL24, P(MMA/styrene) with 10% styrene and 3% MAA; c) XL35 P(MMA/styrene) with 10% styrene and 10% MAA; d) XL50, P(MMA/TFEA) with 24% TFEA and 5% MAA

polymers were used whereas the refractive indices for the two solvents were measured (at $\lambda = 633$ nm, $T = 21$ °C, for *cis*/*trans*-decalin, $n = 1.475$ and CS_2, $n = 1.621$).

The refractive indices measured for the dispersions at minimum turbidity (i.e., when the particles are optically matched to the continuous phase) agree well with those calculated from the volume composition of the dispersions. However, the refractive indices of the dispersions at match are less than those calculated for the solvent mixture and greater than those calculated for the copolymer. The apparent discrepancy between these values can be explained by CS_2 partitioning into the particles. The amount of CS_2 absorbed into the particles (see Table 2) is readily calculated from the difference between the dispersion refractive index and that of the particle copolymer. Since CS_2 is a good solvent for polystyrene the increased absorption with increasing styrene fraction is expected. The result for the PMMA particles (11%) is larger than that (6%) determined in a previous study [23].

Interestingly, phase separation was observed in mixtures prepared from modified latices with narrower PSD's (achieved through an increased proportion of MAA) such as XL35 (Table 1) with the reference PMMA latex. As reported in detail elsewhere [24], this phenomenon can be





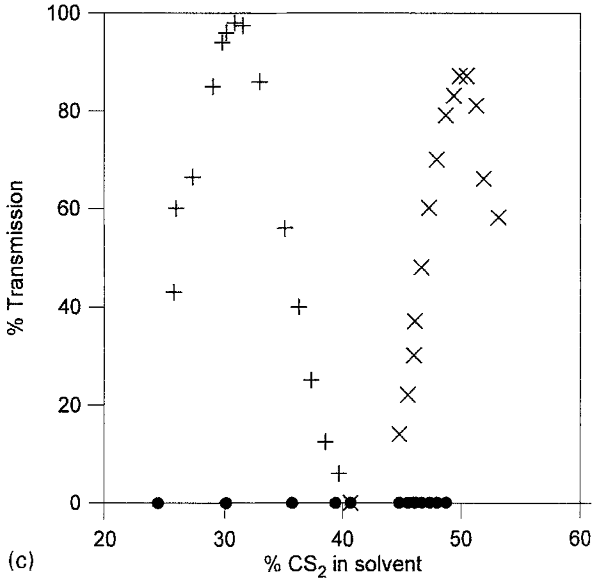


Fig. 2 Percent transmission as a function of percent CS_2 in the continuous phase of dispersions, measured in 1 cm path length cuvettes ($\lambda = 633$ nm and $T = 21\,°C$). In (a)–(c) particles modified with different amounts of styrene (×) are compared with PMMA (SMU21, +) and the 1:1 mixture of the two particle types (●). (a) × = 5% styrene, XL27; (b) × = 10% styrene, XL16; (c) × = 20% styrene, XL18

attributed to a cross-attraction between the different particles and subsequent work [25] has shown this cross-attraction appears to be associated with a significant difference in MAA concentration (e.g. SMU21, 2%MAA with XL35, 10%MAA).

Particles of refractive index lower than that of PMMA were prepared using trifluoroethyl acrylate (TFEA). Polytrifluoroethyl acrylate (PTFEA) has a significantly lower refractive index (nominally 1.407 at 25 °C [19]) than PMMA. Particles with up to 24% TFEA required only 5% MAA to achieve particle size distributions similar to those of comparably sized standard PMMA particles (see XL49, XL50, XL52 in Table 1). Surface roughness of particles containing 24% TFEA (XL50) is illustrated in the electron micrograph in Fig. 1 and suggests phase separation within the particles.

In Fig. 3 the intensities of the 488 nm (Argon laser) light scattered by two of latices (in *cis*-decalin) differing only in the fraction of TFEA are plotted as a function of temperature. The minimum turbidities of these latices are typically less than 0.05 cm^{-1}. The refractive indices of the particles determined from the refractive index of *cis*-decalin at the appropriate temperature and wavelength, are compared with those calculated from the composition of the particles (Table 3) using published values for the bulk polymers [19]. The most attractive property of these P(MMA/TFEA) particles from a light scattering perspective is that they can be optically matched in the one solvent, *cis*-decalin.

One further approach is mentioned for completeness. As described earlier, previous work has established that PMMA particles when suspended in a mixture of CS_2 and decalin imbibe CS_2 to approximately 6% of their weight [23]. This results in an increase of the radius of about 2% and a particle refractive index of about 1.506 (see Table 2). In principle, therefore, it should be possible to control the refractive index of the particles by reducing the extent of absorption. However, attempts to achieve this by crosslinking the polymer through the inclusion of

Table 2 Measured and calculated refractive indices for a selection of modified particles (from Table 1) initially dispersed in decalin (*cis/trans*) at $T = 21\,°C$ and $\lambda = 633$ nm

Sample and polymer composition	Particle vol fraction at trans$_{max}$	Vol fraction CS_2 in match solvent	Calculated *n* of match solvent	Calculated *n* of copolymer	Measured *n* of suspension at trans$_{max}$	Calculated *n* of suspension at trans$_{max}$	Vol % CS_2 partitioned into particles
SMU21, PMMA	0.202	0.244	1.510	1.491	1.506 ± 0.003	1.506	11 ± 2
XL27, 5% styrene	0.182	0.319	1.521	1.499	1.516 ± 0.003	1.517	14 ± 2
XL16, 10% styrene	0.175	0.342	1.524	1.501	1.520 ± 0.003	1.520	16 ± 2
XL18, 20% styrene	0.126	0.413	1.535	1.511	1.534 ± 0.003	1.532	21 ± 2

Table 3 Measured and calculated refractive indices for P(MMA/TFEA) particles dispersed in cis-decalin; $\lambda = 514$ nm; polymer refractive indices at 20 °C [18]

Sample	Polymer composition	Temp (C) at Scatt$_{min}$	Solvent ref index at match Temp	Calculated *n* from polymer composition
XL49	24% TFEA	22	1.482	1.475
XL52	16% TFEA	13	1.486	1.480

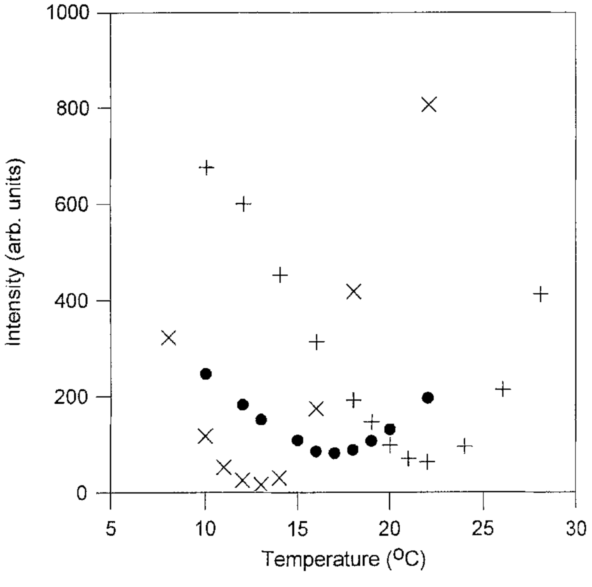


Fig. 3 Scattered intensity (arbitrary units) of $\lambda = 488$ nm laser light as a function of temperature for TFEA modified PMMA particles, 24% TFEA (XL49, +), 16% TFEA (XL52, ×) and 1 : 1 mixture (●). See text for details

multifunctional monomers, such as divinyl benzene, trimethylol propane trimethacrylate and allyl methacrylate were either unsuccessful or did not meet the required polydispersity ($\sigma \lesssim 10\%$). In the case of divinyl benzene the particles became aspherical [25].

Discussion

The accepted picture [7, 10–16] of particle formation in dispersion polymerization is as follows: Initially amphipathic stabilizer is dissolved in a solution of apolar hydrocarbon solvents and polar monomers. Initiation results in conversion of monomer to polymer causing a reduction in the polarity of the initial solution. The higher the initial monomer concentration the longer the solution remains a good solvent for both the growing polymer and the amphipathic stabilizer. A stage of conversion is reached when the polymer begins to precipitate and the stabilizer adsorbs on to the polymer creating particle nuclei. As found here and illustrated in the work of Antl et al. [7], nucleation and, therefore, the final particle size is a steep function of the monomer concentration, even when the concentration of stabilizer is increased in proportion to the monomer. In the formulating approach used here, and in refs. [7] and [10], the stabilizer is dissolved in polar solvent such that changes in stabilizer concentration cause further complications through alteration of the polarity of the reaction medium.

In order to prepare particles having a narrow particle size distribution (PSD) the particle nucleation phase must be short. This can be aided by choosing monomers, reaction medium and reaction conditions that, upon initiation, result in the polarity of the initial solution decreasing as rapidly as possible, minimizing the time interval during which the polymer precipitates, aggregates and adsorbs stabilizer.

Inclusion of comonomers of polarity lower than that of MMA, such as styrene, results in two competing effects [10]. On the one hand, the polymer will tend to precipitate earlier because of the low polarity of the reaction medium while, on the other hand, the less polar polymer will tend to stay in solution longer. This has not been studied in detail. One explanation for the broader PSD found for the P(MMA/styrene) particles is that the reduced polarity of the starting solution causes a reduction in the rate of change in polarity with monomer conversion, probably accompanied by a reduced rate of stabilizer adsorption, and resulting in nucleation over an increased time interval. Inclusion of 5% styrene increased the polydispersity only slightly and homogeneous crystallization was observed in the final latex. Particles with 20% styrene, however, had unacceptably broad PSD's (as observed by electron microscopy and suggested by an absence of sedimentary crystals). Interestingly, the polydispersity of preparations containing 10% or more styrene could be reduced to an acceptable level by using a larger proportion of MAA (e.g. XL35, Table 1 and Fig. 1). This also resulted in a reduction in particle size, presumably because the more polar polymer causes an increased number density of nuclei. An upper limit on the proportion of MAA occurs as a consequence of less favorable stabilizer adsorption when the copolymer becomes too polar.

The most successful modifications were obtained by incorporating TFEA. Data for this monomer is rather sparse but it would seem to be sufficiently similar to MMA in polarity and reactivity to have only a small effect on particle size and PSD when compared with PMMA preparations. The slight increase in particle size from incorporating TFEA can be offset by increasing the proportion of MAA to 5% (see XL49 and XL52 in Table 1) such that the final particle sizes differ little from the reference PMMA latex. As model colloids these P(MMA/TFEA) particles have the following important properties. First, their refractive index [19], in nonswelling solvents, can be varied continuously from $n = 1.491$ (no TFEA) to atleast $n = 1.475$ (24 weight % TFEA). Second, particles with levels of TFEA in excess of about 10% can be optically matched in pure *cis*-decalin at convenient temperatures; for example at 24% TFEA the match temperature is around 22 °C while at 16% TFEA it is near 13 °C. Third, despite the fact that particles with 24% TFEA show some surface irregularity (see XL50 in Fig. 1), crystallization studies performed on these particles with radii close to 200 nm (XL49 and XL52) and 370 nm (XL50) reveal the equilibrium phase behavior expected for hard spheres [3]. We surmise that the surface irregularities are sufficiently smoothed by the stabilizer layer for the particles to approximate spheres.

The 11% CS_2 absorbed by PMMA particles (Table 2) was calculated using published polymer refractive indices. This should be compared with 6% obtained in a previous study [23], without recourse to published data, from the difference in solvent composition at maximum transmission of two samples at different particle volume fractions. The discrepancy between the results of the two procedures can be explained by the possibility that published refractive indices, which apply to bulk polymers, underestimate the values appropriate to polymers in submicrometer particles. (It should be noted that the calculated dispersion refractive indices for P(MMA/styrene) particles in Table 2 are not very sensitive to the precise values of the particle refractive index at the volume fractions studied.) This possibility can also explain the discrepancy between the solvent refractive indices and the copolymer refractive indices of the P(MMA/TFEA) particles shown in Table 3.

Conclusions

It is apparent from the results in this paper that the sphericity and monodispersity established for PMMA particles, stabilized by grafted PHSA, prepared by dispersion polymerization can be retained for some other monomer combinations. We have discussed the preparation and properties of polymer particles whose refractive indices can be controlled over a range of a few percent. Aside from the obvious requirement of long-term stability, the suitability of the particles, as model colloids, is indicated by their ability to form colloidal crystals. Particles modified with trifluoroethyl acrylate are of particular interest because their refractive indices are matched by a single solvent at temperatures close to ambient.

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