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SHORT COMMUNICATION

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Preparation and characterization of crosslinked PMMA latex particles stabilized by grafted copolymer

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Abstract The preparation of polymethyl methacrylate lattices stabilized by polyhydroxystearic acid and crosslinked with ethylene glycol dimethylmethacrylate (EGDM) has been studied. Crosslinking is a new development in the synthesis of PMMA latex. The particles are monodisperse when the concentration of EGDM ranges from 0.33 to 1.44%. The lattices are stable in aromatic and aliphatic solvents. Swelling occurs due to penetration of solvent molecules into the latex. The degree of swelling is calculated by viscosity and by dynamic light scattering measurements.

Key words Crosslinked PMMA latex – dispersion polymerization – steric stability – swelling – non-aqueous polymer latex

Introduction

There has been a steady increase in work on non-aqueous polymer colloids [1–5]. Polymer particles in non-aqueous media are prevented from flocculation by steric stabilization whereby the particle is surrounded by a surface layer of a non-ionic polymeric stabilizer. Non-aqueous dispersion systems, which have been studied extensively, consist of polymer particles in *n*-alkanes stabilized by a surface layer of poly(12-hydroxy-stearic acid) (PSA) incorporated into a graft polymer. A number of papers have described the use of poly(methyl methacrylate) lattices as model systems [6–8]. A single-stage method was used for preparing monodisperse poly(methyl methacrylate) lattices stabilized by poly(12-hydroxy stearic acid) [7]. The stabilizer, which incorporates a copolymer backbone of methyl methacrylate and glycidyl methacrylate, is chemically "locked" onto the latex particle surface by base-catalyzed hydrolysis involving cleavage of the epoxide rings on the backbone. The methacrylic acid comonomer polymerized in the core particles provides the acid groups for this reaction.

We carried out this study for the following reasons:

In sedimentation studies of two component mixtures of colloidal particles, where the sedimentation velocity of one component is measured in a "sea" of the other component, it is very convenient to be able to match the density and the refractive index of the solvent and of the non-sedimenting component [9]. At least three solvents are necessary for this matching procedure. However, due to the penetration of solvent molecules such as toluene and *p*-Xylene, PMMA latex particles dissolve slowly and the dispersion becomes viscous [9].

To prevent aromatic solvents from dissolving the polymer chains and to find out whether the use of solvents other than aliphatic hydrocarbons was feasible, we decided to study the crosslinking of the core of PMMA latex with ethylene glycol dimethacrylate (EGDM). Recently, it was reported [5] that attempts to crosslink the polymer by the inclusion of multifunctional monomers were either unsuccessful or led to a high degree of polydispersity. We prepared monodisperse PMMA latex crosslinked to EGDM. This paper describes the preparation and characterization of a new type of crosslinked monodisperse PMMA latex particles which are sterically stabilized using dispersion polymerization.

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Experimental section

Materials

Methyl methacrylate (MMA) (BDH > 99.5%) and methylacrylic acid (MA) (Fluka) were distilled before use at low pressure under nitrogen. Hexane (Merck), toluene (Baker), 40/60 petroleum ether (Baker), ethylacetate (Merck), butylacetate (Janssen Chimica), butyl catechol (Ventron), methane sulphonic acid (Baker), octyl mercaptan (Purum), 1-dimetyl aminododecane (Fluka), 12-hydroxy stearic acid (Ventron, technical grade), glycidyl methacrylate (Fluka) and ethylene glycol dimethacrylate (EGDM) were used as supplied.

Exxsol D-100 which was low in aromatics (< 1%) and had a boiling-point range (235–260) was obtained from ESSO. Azo-bis-isobutyronitrile (Janssen Chimica) was recrystallized from acetone before use.

Characterization techniques

Light-scattering experiments were performed to determine the size of the particles and to estimate the degree of polydispersity. Static light-scattering measurements of diluted dispersions were done with a FICA-50 photometer [10, 11]. The dispersions were made dust-free by filtering them through fluoropore filters. From the K-dependence ($K = (4\pi n \sin \Theta/2)/\lambda$, where n is the refractive index, Θ is the scattering angle and λ the wavelength) the radius of the particles was obtained using the Guinier approximation. The scattering angles varied between $\Theta = 15°$ and 150°. All experiments were performed at 25 °C. Dynamic light scattering, which determines the diffusion coefficient from the fluctuations in the scattered light [12], was performed with a laboratory-built apparatus which has been described elsewhere [13]. An argon ion laser operating at 514.5 nm was used as light source and the data were collected with a Malvern correlator. Diffusion coefficients were obtained by a cumulant fit of the measured autocorrelation function. A hydrodynamic particle radius R_h was obtained using the Stokes–Einstein's equation $D = k_B T/6\pi\eta R_h$, with η the solvent viscosity, k_B Boltzmann's constant and T the temperature. The "Quality factor" Q [13] derived from the second cumulant gives an indication of the polydispersity. Density measurements were carried out with a precision density meter D.M.A. 02 C (Anton Paar K.G., Austria). Viscosity measurements on dilute dispersions were performed using an Ubbelohde capillary viscometer [14]. Using Einstein's equation for the relative viscosity, the volume fraction can be written as the product of the weight concentration c and the specific volume q of the particles, where q is calculated from the slope of the straight line by plotting $\eta^r - 1$ vs. C. ($\eta_r = 1 + 2.5qC$, where $\eta_r = \eta/\eta_s$ and η and η_s are viscosities of dispersion and solvent, respectively.)

To make scanning electron micrographs, we dipped carrier grids covered with carbon-coated Parlodium films into a very dilute latex dispersion and dried them in air. The carrier grid was glued to the mounting table. The grid was covered with platinum and palladium in the ratio 4:1 in a Cressington Sputter Coater 208 HR. Scanning electron micrographs were made with a Philips 30 XL FEG scanning electron microscope. The accelerating voltage used was 5 kV.

Preparation

Preparation of the stabilizer

The stabilizer was synthesized according to the method described elsewhere [7]. The stabilizer used was a comb-like graft copolymer with a backbone of methyl methacrylate and glycidyl methacrylate and "teeth" of poly(12-hydroxystearic acid). One component of the copolymer is the soluble stabilizing moiety and the other component, termed the anchor, is insoluble in the continuous phase and is absorbed onto the disperse phase. To ensure stability the stabilizer was chemically locked onto the particle surface by an esterification reaction. 12-Hydroxy-stearic acid (151 g) was put into a round-bottomed flask connected to a Dean Stark water separator and toluene (27 g) was added. The reaction mixture was kept under a nitrogen atmosphere and heated with an oil bath. When all 12-hydroxy-stearic acid had melted at an oil-bath temperature of about 100 °C, methane sulphonic acid (0.35 g) was added and refluxed at 140 °C for 24 h. The water produced by the condensation reaction was removed by azeotropic distillation. A light-brown viscous product was obtained. The acid value of poly (12-hydroxy-stearic acid) (PHS), determined by titration with alcoholic potassium hydroxide, was 35.2 mg KOH per g product. An average of 5.6 ester linkages per chain was calculated from the acid value.

To the reaction product PHS were added 30 g toluene, 16.3 g glycidyl methacrylate, 0.62 g 1-dimethylamino-dodecane and 0.23 g t-butylcatehol. The mixture was refluxed for 7 h under a nitrogen atmosphere. The reaction mixture was cooled and 110 g toluene was added. The acid value of the PHS-glycidyl methacrylate (PHS-GM) adduct was 0.32 mg per g product.

To a refluxing mixture of 102.2 g ethylacetate and 50.8 g butylacetate was added a mixture of 271.2 g PHS-GM, 133.9 g MMA, 15.7 glycidyl methacrylate and 2.26 g ADIB at a rate of about 1–2 drops per minute. The

mixture was refluxed for about 3.5 h. The oil bath temperature was kept at 105–110 °C. Reflux conditions were maintained for another 6 h during which time two additions of ADIB, each of 1.02 g were made at intervals of 1.75 h. The end product was diluted with 150 g of a mixture of ethylacetate and butylacetate (2:1 w/w) and a gold-colored comb-like grafted polymer solution containing 40% stabilizer was obtained.

Preparation of lattices

Polymer lattices were prepared by dispersion polymerization. Lattices was prepared in three stages: preparation of latex, attachment of the stabilizer to the particles and removal of excess unlinked stabilizer. The preparation was analogous to the method described by Antl et al. [7]. A three-necked round-bottomed flask attached to a reflux column was used. The column was cooled with water. A mixture of hexane/exxol D100 was used as solvent. The ADIB and a part of the MM/MA mixture were weighed in the flask and stirred with a magnetic stirrer till all ADIB had dissolved. EGDM, the stabilizer solution and the remaining MM/MA mixture were added and nitrogen was passed into the reaction vessel in order to remove the oxygen. The temperature of the oil bath was increased to 80 °C and the reaction mixture was refluxed for 2 h. After about 5 min the light-yellow solution turned to light blue and after 20 min the dispersion became milky white. During the locking stage the hexane was distilled off and exxol D100 was added until the temperature of the distillate was 120 °C. An extra amount of stabilizer solution and 2-dimethylaminoethanol was added and the dispersion was refluxed for another 2 h at 120 °C.

The dispersion was filtered through glass wool and subsequently sedimented in a preparative ultracentrifuge at 10000 RPM. The sediment was redispersed in 40/60 petroleum ether and the sedimentation procedure was repeated four times.

Results and discussion

Figure 1 is a scanning electron micrograph of latex KGG3. The latex particles were seen to melt and deform when exposed to radiation. Similar phenomena were reported earlier for PMMA particles [15]. This may be due to depolymerization at high intensities of the electron beam. The monomer concentration was kept constant and the amount of stabilizer and the amount of crosslinker EGDM were varied (Table 1). The results of static and dynamic light-scattering measurements are listed in Table 1. In the case of latex KGG1, acrylic acid was used instead of methacrylic acid. The particles were unstable in dodecane. An additional amount of stabilizer was added and the locking reaction was repeated. Thereafter, the particles were coded KGG1A and were stable in dodecane. For the preparation of lattices KGG2–KGG5 additional stabilizer was added and the locking reaction was repeated. An increasing quantity of crosslinker EGDM was used for latices KGG2–KGG5. The EGDM built into the lattices makes them more polar [1] so the stabilizer is

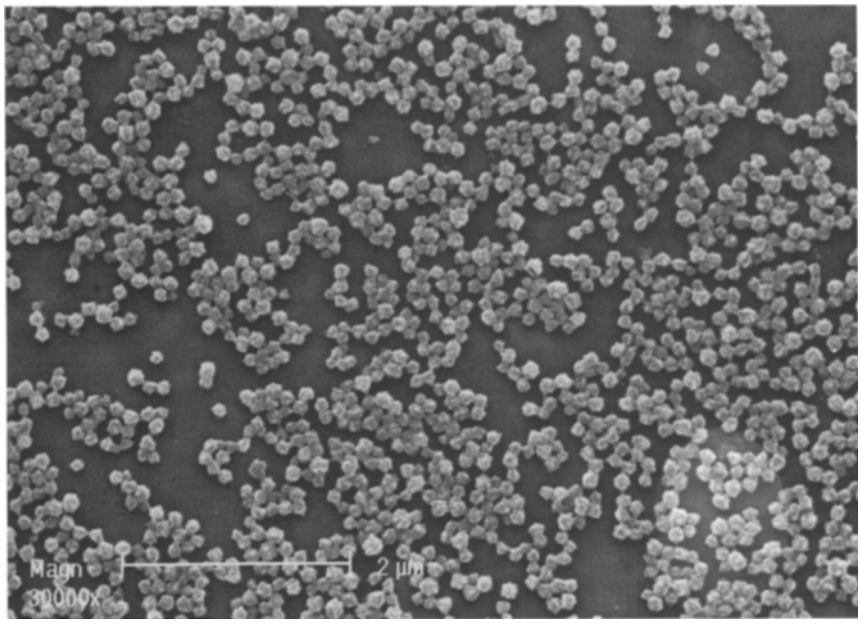

Fig. 1 Scanning electron micrograph of latex KGG2

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Table 1 Characterization of latex particles

	KGG1	KGG1A	KGG2	KGG3	KGG4	KGGG
MM	29.25	29.25	32.47	31.22	30.96	31.28
MA	0.60[1)]	0.60[1)]	0.73	0.70	0.70	0.69
EGDM	0.33	0.33	0.35	0.68	1.44	3.16
Stabilizer	9.79	9.79	10.64	13.60	13.29	13.16
EXXOL D100	16.38	16.38	17.96	17.31	17.32	16.98
Hexane	43.13	43.13	37.28	35.91	35.80	34.98
ADIB	0.35	0.35	0.39	0.38	0.37	0.36
Octyl Mercaptan	0.18	0.18	0.18	0.20	0.22	0.22
Additional stabilizer	—	1.0	5.39	2.5	2.5	—
2-Dimethyl aminoethanol	0.1	0.1	0.12	0.13	0.13	—
R (SLS) nm	80.6	73.5	67.9	101.8	120.7	—
R (DLS) nm	84.9	70.9	68.0	103.1	144.1	—
Q (DLS) quality factor	0.12	0.12	0.05	0.04	0.12	—

[1)] Acrylic acid is used instead of methacrylic acid.

Table 2 The dispersability of latex in different solvents and the hydrodynamic radius

Solvent	Time needed to disperse (min)	State after 2 days	Hydrodynamic radius (nm)
Benzene	10	stable	—
p-xylene	10	stable	81
ethyl-benzene	< 10	stable	91
toluene	20	stable	100
cyclohexane	< 10	stable	66
c-decalin	40	stable	75
hexane	20	stable	66
1-hexanol	20	stable	65
1-propanol	60	sediment	—

strongly physically adsorbed and, as a result, the stabilizer becomes built into the particle. The monomers reach the particles by diffusion. Polymerization takes place on the surface and the particle is left with only a small amount of stabilizer for stabilization. This could be the reason why a gel formed in the case of KGG5. Table 1 shows that the particle size increases with increasing EGDM concentration. It is already known from synthesis without a crosslinker that the particle size decreases [7] with increasing concentration of the stabilizer. Due to the physical adsorption of the stabilizer inside the particles at high EGDM concentration, the amount of stabilizer needed to stabilize the particles decreases and as a result the particle size increases. This can be infered from Table 1. Table 2 indicates the stability of the lattices in various solvents and the hydrodynamic radii. From Table 2 it is seen that the lattices are stable in aromatic and aliphatic solvents. The core did not dissolve but the particles swelled in aromatic solvents. From the density measurements we obtained a value of $1.113 \pm 0.004\ g\,ml^{-1}$ for the density of KGG3 latex in *t*-decalin. The corresponding poly(methacrylate) latex particles without the crosslinker was found to be $1.172 \pm 0.003\ g\,ml^{-1}$. This low value for crosslinked particles, may be due to the fact that the stabilizer is embedded in the latex particle and the solvent molecules have penetrated into the core of the particle. The hydrodynamic radius obtained from dynamic light-scattering measurements of latex KGG3 in a mixture of *t*-decaline/CCl_4/CS_2 with a volume ratio 30:20:50 was 158 nm. From viscosity measurements of latex KGG3 in a mixture of solvents *t*-decalin/CCl_4/CS_2 (volume ratio, 47:29:24) we find the density of KGG3 to be $0.372 \pm 0.004\ g\,ml^{-1}$. Even though the solvent composition is slightly different, the degree of swelling calculated from both hydrodynamic measurements $(158/103)^3$ and viscosity measurements (1.113/0.372) is near the same. No swelling occurred in similar latex particles without the crosslinker.

Conclusions

Monodisperse methyl methacrylate lattices stabilized with amphiphatic grafted copolymers poly(12-hydroxy stearic

acid) and crosslinked with ethyleneglycol dimethylmethacrylate (EGDM) in the concentration range 0.33–1.44% were prepared in non-aqueous media. The lattices were found to be stable in both aromatic and aliphatic solvents. In aromatic solvents, the solvent molecules penetrate into the core and, as a result, the particles swell. The degree of swelling of the particles can be either calculated from the hydrodynamic radius or from viscosity measurements. Further study of the synthesis is needed with regard to other monomer (MMA) concentrations.

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