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Preparation of polymethylmethacrylate latices in non-polar media

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Abstract: The dispersion polymerization of methylmethacrylate stabilized by poly(12-hydroxy-stearic acid) in hydrocarbon media has been investigated. Unlike earlier results [7] it was found that stable latex particles can be prepared in the initial monomer concentration range 8.5 % to 34 %. To obtain stable particles varying amounts of stabilizer were used.

Key words: Dispersion polymerization in non-aqueous media, polymethylmethacrylate latex, poly(12-hydroxy stearic acid).

Introduction

A research topic currently of importance in colloid chemistry is the behavior of particulate dispersions in non-aqueous media [1]. Such dispersions form a significant proportion of colloidal systems produced on an industrial scale. Within this group there is a substantial range of systems involving a core particle with a surrounding layer of polymer molecules. The latter are needed to maintain the stability of the system in a non-aqueous environment, i.e., to provide steric stabilization.

The preparation of polymer colloids using dispersion polymerization in non-aqueous media has been the subject of extensive investigation [2–6]. Recently, a single-stage polymerization method for preparing latices of polymethylmethacrylate (PMMA) with a covalently surface-linked stabilizer (PHSA) moiety of poly(12-hydroxy stearic acid) has been reported [7]. Antl et al. [7] performed experiments in order to study whether the stability of PMMA latex in hydrocarbon media could be affected by varying the initial monomer concentration. They varied the initial monomer concentration between 5 % and 50 % using a stabilizer (PHSA) concentration of 5 % by weight monomer concentration. Antl et al. [7] noticed that there were three distinct regions within the initial monomer concentration range, and that the latices prepared in the middle region (8.5 % to 34 % monomer) were unstable.

In our laboratory a study was undertaken to prepare latex particles following the method of Antl et al. In this note we describe the results of preparing latex particles when we varied the initial monomer concentration between 5 % and 44 %. We found that stable latex particles can be prepared in the whole concentration range provided a sufficient amount of stabilizer is used. A range of monodisperse particles with radii between 40 nm and 900 nm was obtained.

Experimental

Materials

Toluene (Baker), hexane (Merck), dodecane (Merck), 40/60 petroleum ether (Baker), ethyl acetate (Merck) and butyl acetate (Janssen Chimica) were used as received. Exxsol D-100 which was low in aromatics (< 1 %) and has a boiling point range (235–260 °C) was obtained from ESSO. Octyl Mercaptan (Purum) and 1 dimethyl aminododecane were Fluka AG materials. Azo-bis-isobutyronitrile (Janssen Chimica) was recrystallized from acetone before use.

Methylmethacrylate (MMA) (BDH) and methylacrylacid (MAA) (Fluka) were distilled before use under nitrogen at low pressure.

12-hydroxy stearic acid (Ventron, technical grade), glycidyl methacrylate (Fluka) were used as supplied.

Table 1

Sample	% monomer[a])	% stabilizer	% dodecane	% hexane	Static light scattering R/nm	Dynamic light scattering R_h/nm	Quality factor Q
KS 15	5	28	30	61	58	52	.08
KS 19	15	26	25	50	44	42	.06
KS 20	25	27	19	38	40	39	.06
KS 16	29	28	17	33	72	68	.06
KS 17	32	15	18	37	51	50	.06
KS 23	34	15	17	35	89	87	.02
KS 22	36	15	16	33	107	107	.02
KS 36	42	14	14	28	ca. 400	–	–
KS 21	44	15	13	26	ca. 900	–	–
KS 23	34	15	17	35	89	87	.008–.034
KS 24	35	10	18	36	81	79	.06–.10
% Exxsol D-100							
KS 28	33	13	18	37	80	–	–
KS 27	34	15	17	35	112	112	.02
KS 26	35	12	17	36	100	100	.002

[a]) 98 parts of MMA and two parts of MAA. All % quantities by weight. ADIB in all preparations 0.39 % by weight. Octyl mercaptan in all preparations 0.5 % by weight. Stabilizer is % by weight monomer.

Preparation

The stabilizer

The preparation of the stabilizer has been outlined in Ref. [7]. The acid value of polyhydroxy-stearic acid (PHS) determined by titration with alcoholic potassium hydroxide ws 35.2 mg KOH per g product. The acid value of the PHS-glycidyl methacrylate adduct PHSA was 0.32 mg KOH per g product. After reaction with methyl methacrylate the comb-like graft copolymer was diluted with ethyl acetate/butyl acetate mixture until the solution contained 40 % of the stabilizer.

Latex dispersion

PMMA latices were prepared by dispersion polymerization. The reagents were added in the sequence reported [7]. The solution was purged with nitrogen for 10 min., then the reaction mixture was heated to 353 K under constant stirring. The reaction was allowed to continue for a further 2 h under an atmosphere of nitrogen. The octyl mercaptan added was a 10 % solution in dodecane. The stabilizer was covalently linked to the particle surface (locking reaction) whenever the latices were to be used as a model system for further studies. The latices were cleaned by sedimentation.

Characterization

The particle size was determined by static and dynamic light scattering in dilute dispersions [8]. The size of the particle was found by static light scattering from a plot of the logarithm of the scattered intensity vs. the square of the wave vector K (a so-called Guinier plot). The slope of this plot equals $-(Rg2/3)$ where Rg is the (optical) radius of gyration, which for a homogeneous sphere of radius R according to the Rayleigh-Gans-Debye approach, is equal to $(\sqrt{3/5})\,R$. The hydrodynamic radius R_h of the particle was calculated from the diffusion coefficient obtained with dynamic light scattering using the Stokes-Einstein equation $D = kT/6\pi\eta R_h$ in which k is the Boltzmann constant, T the temperature and η the viscosity of the solvent. The quality factor (Q) [9] obtained from the dynamic light scattering reflects the degree of polydispersity.

Results and discussion

The preparations were carried out using a range of methyl methacrylate monomer concentrations as listed in Table 1. At the outset some experiments were performed to determine the minimum stabilizer concentration necessary for two initial monomer concentration, one of 5 % and the other of 35 %. It appeared that the concentration of stabilizer needed for the formation of stable monodisperse latex particles was 28 % and 10 %, respectively (Table 1). For the other initial monomer concentrations the stabilizer concentration was chosen roughly. The latex particle obtained varied between 40 nm and 900 nm in size within the monomer concentration range studied. The Guinier plots yielded a straight line except for monomer concentrations 42 % and 44 %. The particle size for the aforementioned two latices was calculated from the minimum in the Guinier plot. The diffusion coefficient was wave vector independent and the quality factor *Q* was low. This implies that the particles are reasonably monodisperse.

In our experiments we did not find the unstable region observed by Antl et al. when they varied the initial monomer concentration from 8.5 % to 34 %. It was possible to prepare monodisperse latices with varying particle sizes in the monomer concentration range 5 % to 44 %. The high amount of stabilizer (10 %) needed compared to 5 % used by Antl et al. may be due to the short poly-hydroxy stearic acid chains present in the stabilising graft copolymer.

For high initial monomer concentration, the monomers present unitially provide a good solvent for polymethylmethacrylate and as a result the particle size increases dramatically with increasing monomer concentration. This is found for monomer concentrations from 32 % to 44 % (Table 1). In this range the particle size of the latex is closely related to the solvency of the medium [7]. The trend in the particle size is not clear in the monomer concentration range from 5 % to 29 %, where a high stabilizer concentration was used. In this monomer concentration range small particles were formed. The addition of a high amount of stabilizer leads to a high concentration of ethylacetate and butylacetate which would have affected the overall solvency and the polarity of the medium for both polymethylmethacrylate and stabilizer. This may be an additional complicating factor that hampers our understanding of the mechanism of particle formation [10]. When Exxsol D-100 was used instead of dodecane, the general trends of the particle size were similar. Further study is needed to investigate the mechanism that operates in the formation of latex particles by varying parameters such as overall solvency and polarity of the reaction medium and stabilizer concentration. We conclude that stable monodisperse dispersions of PMMA latices stabilized by PHSA in nonaqueous media can be prepared in the initial monomer concentration range from 5 % to 44 %.

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