

Luminescence Techniques and Characterization of the Morphology of Polymer Latices. 3. An Investigation of the Microenvironments within Stabilized Aqueous Latex Dispersions of Poly(*n*-butylmethacrylate) and Polyurethane.

I. Soutar[†] and L. Swanson*

The Polymer Centre, School of Physics and Chemistry, Lancaster University, Lancaster LA1 4YA, UK.

and

T. Annable[‡], J. C. Padget and R. Satgurunathan⁺

Zeneca Resins,

PO Box 8, Runcorn,

Cheshire WA7 4QD, UK.

*Present address and address for correspondence: Department of Chemistry, University of Sheffield, Brook Hill, Sheffield S3 7HF, UK.

l.swanson@sheffield.ac.uk

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⁺DSM NeoResins, Sluisweg 12, PO Box 123, Waalwijk, Tge, The Netherlands.

[‡]Avecia Specialities, Hexagon Ho, Old Market St, Blackley M9 8DE, UK

[†] Deceased

Experimental

Materials

Pyrene (Aldrich; 99.9%) was purified by multiple recrystallization from toluene.

Phenanthrene (Aldrich; Zone Refined), nitromethane, CH_3NO_2 , (Aldrich), benzene, methanol, toluene and diethylether (all spectroscopic grade; Aldrich) were used as received.

Water was doubly distilled prior to use.

n-Butyl methacrylate, BMA (Aldrich) was freed of inhibitor by washing with 5% NaOH (three times) followed by distilled water until the aqueous layer was neutral to litmus. The monomer was fractionally distilled, under high vacuum, immediately prior to use.

Methacrylic acid, MAA, (Aldrich) was purified by vacuum distillation.

The initiator, ammonium persulphate, AMPS, (Aldrich) and surfactant, sodium lauryl sulphate, SLS, (Aldrich) were used as received. Sodium bicarbonate was used to mediate the pH of the acrylic latex polymerization system.

Dimethylolpropionic acid (DMPA), isophorone diisocyanate (IPDI), N-methylpyrrolidone, NMP, and triethylamine, (all Aldrich) were used as received.

Polycaprolactone diol (MW 1250), PCAP1250, and polycaprolactone diol (MW 530), PCAP530, (both Aldrich) were used without further purification.

Acrylic latex polymerization

A poly(*n*-butyl methacrylate), PBMA, latex dispersion was prepared *via* a two-step seeded emulsion polymerization process: water (160 g), SLS [0.4g] and sodium bicarbonate (0.15 g) were mixed and heated to 40-45°C, stirring continuously. BMA (5 g) was added to emulsify the mixture. The reactants were subsequently heated to 60-65°C and the initiator solution (ammonium persulphate, 0.20 g; water, 15 ml) was added. The mixture was heated to 80-85°C and the rest of the BMA (35 g) was fed in over a

period of 1.5 hours under monomer-starved conditions. After a further hour the mixture was cooled and filtered.

Polyurethane polymerization

Polyurethane dispersions, PU, were prepared in the following manner: initially, PCAP530 (14.1g), PCAP1250 (37.5g) DMPA (6.5g) and IPDI (42g) were reacted as a melt, in a small amount of solvent [NMP (1.52g)/dibutyl tin dilaurate (10% v/v)]. This mixing procedure, produced isocyanate terminated prepolymer. The melt was then neutralised with triethylamine, dispersed into water and chain extended using hydrazine monohydrate.

Particle sizes, for both the PBMA and PU dispersions, respectively, were determined using photon correlation spectroscopy (Coulter N4S autosizer).

Gel permeation chromatography, GPC, was used to estimate the molecular weights of the PBMA and PU colloids. The samples were dried and dissolved in THF prior to injection into the GPC. A full description of the chromatographic system can be found elsewhere¹.

Solids contents, particle sizes and molecular weight data are listed for both PBMA and PU, respectively, in Table 2.

Free radical polymerization

Poly(methacrylic acid), PMAA, was prepared by free radical polymerization of MAA using azobisisobutyronitrile as initiator in benzene solution. Purification was by multiple reprecipitation from methanol into diethylether.

Molecular weight information for the PMAA sample (*cf.* Table 1), was determined by aqueous GPC. (A description of the procedure has been described elsewhere¹).

Colloidal dispersions were typically diluted 100-fold prior to fluorescence spectroscopic examination. The total concentration of the fluorescent probe (phenanthrene or pyrene) in each system was 10^{-5} M. (The concentration of probe when dispersed in water was kept at 10^{-6} M to prevent the occurrence of excimer formation).

Instrumentation

Steady-state emission and excitation spectra were recorded on a Perkin-Elmer LS50 spectrometer.

Fluorescence lifetime measurements were made using an Edinburgh Instruments 199 time-correlated single photon counter using a thyatron-gated, coaxial flashlamp with deuterium as the discharge medium. The instrument was modified through addition of a second detection channel to allow time-resolved anisotropy measurements (TRAMS) to be made. This channel was equipped with a “toggling” device, which periodically switched the plane of polarization of the analyzer and simultaneously addressed the detector signals to a designated memory segment in the multichannel analyzer. Details of the TRAMS experiment and associated analytical procedures have been described elsewhere².

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