Characterisation and properties of purely acrylic latex with submicro particle size prepared with mixed surfactants of sodium dodecyl benzene sulphonate and allyloxy nonylphenoxy propanol polyoxyethylene ether

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The purely acrylic latex with submicro particle size was prepared via semi-continuous seeded emulsion polymerisation of butyl acrylate and methyl methacrylate in water phase initiated with potassium persulphate and emulsified with mixed surfactants of sodium dodecyl benzene sulphonate and allyloxy nonylphenoxy propanol polyoxyethylene ether (ANPPE). The structure of the resultant latex is confirmed with Fourier transform infrared spectroscopy spectrum. Differential scanning calorimetry also confirms that the resultant latex is a type of random copolymer and the consistency among the chain segment is fairly good. Influences of the amount of ANPPE on the properties of the resultant latex and its film were investigated in detail. Results show that the contact angle of the film first is increased and then decreased with the increase of the amount of SN-10. The glass transition temperature of the film is decreased with the increase of the amount of SN-10. However, the particle size of the latex is increased with the increase of the amount of SN-10.

1. Introduction: Purely acrylic latex (PAL), which is prepared by emulsion polymerisation of acrylates such as methyl methacrylate (MMA) and *n*-butyl acrylate (BA) and emulsifier conventional surfactant such as sodium dodecyl benzene sulfonate (SDBS) and polyoxyethylene octylphenol ether, is mainly used as the binder for coatings. However, the conventional emulsifiers can migrate during the course of film-forming, which has a negative effect on the properties of the latex, for example, mechanical properties, optical properties and the water-resistance of the latex film are decreased clearly. Besides, conventional emulsifiers can desorb, which can lead to many drawbacks of the latex, such as generation of gel at high shear rate, poor freeze–thaw stability, mechanical stability and storage stability [1]. The polymerisable emulsifiers for emulsion polymerisation have been examined recently. Xiao and Wang [2] synthesised and prepared an emulsifier-free fluorinated polyarcylate emulsion via a seed emulsion polymerisation method from MMA, BA and hexafluorobutylmethacrylate in the presence of a polymerisable emulsifier-ammonium allyloxtmethylate nonylphenol ethoxylates sulphate (DNS-86). Bunio *et al.* [3] synthesised a novel polymerisable surfactant (so-called surfmer). Polymeric micelles (size of 6 and 130 nm) appeared in the polyreaction initiated by free radicals from VA-044. In the presence of the monomer (i.e. MMA) microemulsion systems were formed that in turn were transformed into latex entities (size 40 nm) [3]. Yang *et al.* [4] prepared St-BA copolymer emulsions prepared by using novel cationic maleic dialkyl polymerisable emulsifier. Taniguchi *et al.* [5] studied miniemulsion polymerisation of styrene (St) in the presence of a hydrophobe (liexadecane:HD) using a cationic polymerisable surfactant (N, N-dimethyl-N-n-dodecyl-N-2-methacryloyloxyethylammonium bromide:C12Br) and a cationic initiator (2, 2′-azobis(2-amidinopropane) dihydrochloride:V50), called St/C12Br/V50 and hereafter, proceeded efficiently when compared with using sodium dodecyl sulphate (SDS) and potassium persulphate (KPS), that is, St/SDS/KPS, providing monodisperse polystyrene latex particles with a narrower particle size distribution. Ovando-Medina *et al.* [6] used semi-continuous heterophase polymerisation to copolymerise MMA with reactive surfactant HITENOL BC10 (HBC10) at 60°C and used SDS as a pre-stabilising agent and KPS as on initiator. Our research group had also prepared a series of acrylic latexes or fluorinated acrylic latexes by the method of semi-continuous seeded emulsion polymerisation in the presence of a polymerisable emulsifier-sodium 2-hydroxy-3-(methacryloyloxy) prop- ane-1-sulfonate [7–9]. The above reports have highlighted two advantages of polymerisable emulsifiers: (i) hydrophobicity of the film of the latex is improved; (ii) polymerisable emulsifiers exhibit an efficient steric hindrance.

However, the previous studies focused on the latexes prepared in the presence of the ionic polymerisable emulsifiers. The latexes that are prepared in the presence of the non-ionic polymerisable emulsifiers are strongly neglected. Chern *et al.* [10] carried out the emulsion copolymerisation of MMA and BA stabilised by a non-ionic polymerisable surfactant NE-40 (Asahi Denka Kogyo) and initiated by NaPS. In this Letter, we report a convenient method to prepare a series of PAL with submicro particle size in the presence of a novel non-ionic polymerisable emulsifier, which is allyloxy nonylphenoxy propanol polyoxyethylene ether (ANPPE), for example, SN-10. The molecular structure of SN-10 is shown in Fig. 1. The emphasis is put in the present Letter on the characterisation of the resultant PAL and the influence of the non-ionic polymerisable emulsifier on the properties of the PAL.

2. Experiment

2.1. Materials: BA and MMA were obtained from Shanghai Chemical Reagents Supply Procurement of Five Chemical Plants (China) and were distilled under reduced pressure prior to polymerisation. KPS was bought from the Second Chemical Reagent Factory in Yixin (China). SDBS was supplied by the Shanghai Yingpeng Chemical Reagent Co. Ltd (China). Non-ionic polymerisable emulsifier, which is ANPPE, for

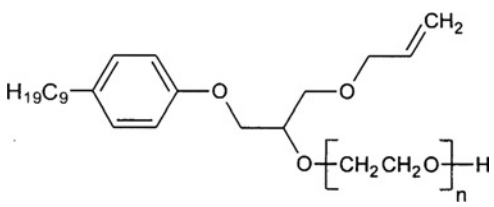


Figure 1 *Molecular structure of SN-10*

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example, SN-10, is a gift from the Foshan Kodi Gas Chemical Industry Co. Ltd (China). Sodium bicarbonate ($NaHCO_3$) was obtained from Shanghai Hongguang Chemicals (China). The water used in this experiment was distilled followed by deionisation.

2.2. Preparation of PAL: The PAL was synthesised by the seeded emulsion polymerisation technique [11]. The seeded emulsion polymerisation was carried out under in a 250 ml four-neck flask equipped with a reflux condenser, a mechanical stirrer, dropping funnels and heated with the water bath. First, all the mixed emulsifier of SDBS and SN-10 and $NaHCO_3$ was introduced into the four-neck flask charged with 80 ml of deionised water. The flask was then placed in a water bath at 80°C with a stirring rate of 200 rpm. In the study, the mixed monomers were composed of 20.00 g of MMA, 20.00 g of BA and 2.00 g of MAA. The concentration of KPS aqueous solution was 0.90 g of KPS that was dissolved in the 20.00 g of deionised water. After complete dissolution of the mixed emulsifier and $NaHCO_3$ in water, 8.00 g of mixed monomers and 4.00 g of the KPS aqueous solution were dropped into the above flask within 15 min simultaneously via two different dropping funnels. The reaction was maintained for another 15 min. Thus, the seeded latex was obtained. Then the mixture of the residual monomer and the rest of the KPS aqueous solution were fed into the flask containing seed latex under starved-feed addition simultaneously within 3.0 h via two dropping funnels. The reaction temperature was ~80°C. When the mixed monomers and KPS aqueous solution were completely fed, the temperature was raised to 90°C and maintained for another 30 min. Finally, the mixture in the flask was cooled to 40°C and its pH was adjusted to ~8.0 with ammonia water and filtered. Thus, the PAL was obtained.

2.3. Characterisation: A Fourier transform infrared (FTIR) spectrometric analyser (Thermo Nicolet AVATAR370, USA) was used to analyse the chemical structures of the latex film. The contact angle between film and water was determined with the DataPhysics contact angle meter (OCA-20, Germany) at room temperature. Differential scanning calorimetry (DSC Q100, USA) was applied to determine the glass transition temperature (T_g) of the film of the latex. The heating temperature was in the range from −50 to 80°C. The heat rate was 10°C/min. The particle size of the latexes was determined by a Zetatrac dynamic light scattering detector (Microtrac Limited Corporation, USA) at 25°C. The power and the wavelength of the diode laser used in the dynamic light scattering measures were 3 mW and 780 nm, respectively. Transmission electron microscopy (TEM) images of the latex were obtained at 60 kV using a TEM-100SX (JEOL, Japan). The latexes were negatively stained with an aqueous solution of 2% uranyl acetate.

3. Results and discussion

3.1. FTIR of film: The FTIR of the film of the latex is given in Fig. 2 when the latex was prepared with SN-10. In Fig. 2, 2955 and 2873 cm^{-1} were the characteristic stretching peaks of C–H (CH_3, CH_2); 1727 cm^{-1} was stretching vibration peak of C = O; 1449 cm^{-1} was the distortion vibration peak of –COO-; 1385 cm^{-1} was the symmetrical deformation vibration peak of $–CH_2$; 1236 cm^{-1} was the stretching vibration peak of C–O–C; 1143 and 1065 cm^{-1} were the characteristic absorption peaks of C–O–C; 988 cm^{-1} was the stretching vibration absorption peak of C–O; 842 cm^{-1} was the stretching vibration absorption peak of C = O in the acrylic group. The stretching vibration of C = C disappeared within the range of 1500 and 1700 cm^{-1}. The FTIR spectrum shows that BA and MMA are copolymerised to form the latex.

3.2. Contact angle of film: The influence of the amount of SN-10 on the contact angle of the film is shown in Fig. 3. Fig. 3 indicates that the contact angle of the film is increased with the increase of the amount of SN-10 when its amount is < 1.50 g. These show that

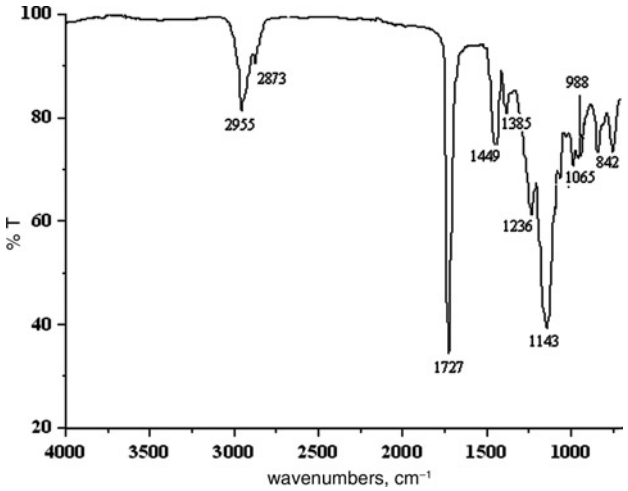


Figure 2 *FTIR of film of latex*

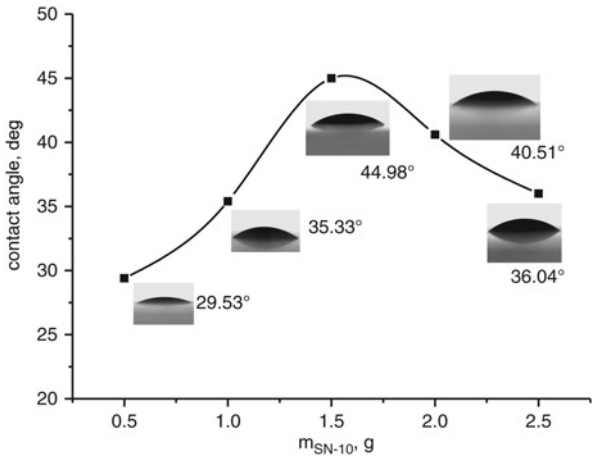


Figure 3 *Influence of amount of SN-10 on contact angle of film*

the water resistance of the film can be improved when the moderate amount of SN-10 is added. This is caused by the fact that SN-10 can copolymerise with the adsorbed matrix and be bonded onto the surface of the matrix permanently. It can emulsify the matrix and be a part of the matrix. However, Fig. 3 also shows that the water resistance of the film is decreased with the increase of the amount of SN-10 when its amount is more than 1.50 g. The function of the excessive SN-10 is consistent with that of the conventional emulsifier. It does not take part in the copolymerisation with the monomers. The excessive SN-10 may be mingled among particles of the latex. The hydrophilic group of SN-10 is migrated to the surface of the film of the latex, thus causing the poor water-resistance.

3.3. Glass transition temperature of film: The effect of the amount of SN-10 on the T_g of the film is shown in Fig. 4. Fig. 4 indicates that T_g is decreased with the increase of the amount of SN-10. This phenomenon can be explained by the fact the double bond in the molecule of SN-10 is the same with the one of BA, which implies that SN-10 also belongs to a type of monomer. The glass transition temperature of the homopolymer of the flexible monomer is lower than the one of the homopolymer of the rigid monomer. For two kinds of copolymerised monomer, the FOX equation can be turned into

$$\frac{1}{t_g} = \frac{m_1}{t_{g1}} + \frac{m_2}{t_{g2}} \quad (1)$$

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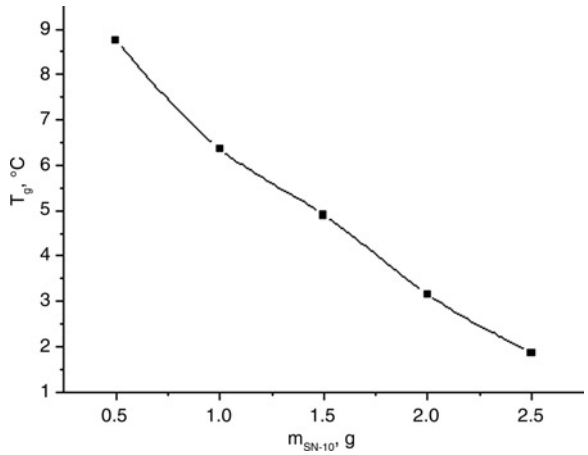


Figure 4 *Effect of amount of SN-10 on T_g of film*

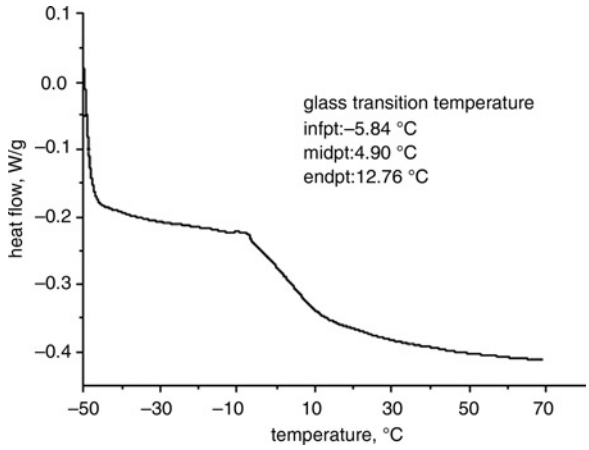


Figure 5 *DSC curve of film*

where m_1 is the mass fraction of the flexible monomer; m_2 is the mass fraction of the rigid monomer; t_{g1} is the glass transition temperature of the homopolymer of the flexible monomer; t_{g2} is the glass transition temperature of the homopolymer of the rigid monomer. The following equation can be obtained via differentiating (1)

$$\frac{dt_g}{dm_1} = \left(\frac{1}{t_{g2}} - \frac{1}{t_{g1}}\right) \bullet t_g^2 \tag{2}$$

In (2), t_{g2} is bigger than t_{g1}; so $1/t_{g2}$ is less than $1/t_{g1}$, and dt_g/dm_1 is negative, that is, the t_g of polymer decreased with the increase of the amount of the flexible monomer [12]. In the present study, the increase of the amount of SN-10 means that the amount of the flexible monomer in the mixed monomers is increased. In addition, the polyoxyethylene segment in the SN-10 acts as the internal plasticisation in the latex system, which also leads to the decrease of T_g of latex. Besides, in Fig. 5, it can be seen that the latex has only one glass transition temperature, which shows that the latex is a type of random copolymer and the consistency among the chain segment is fairly good [13].

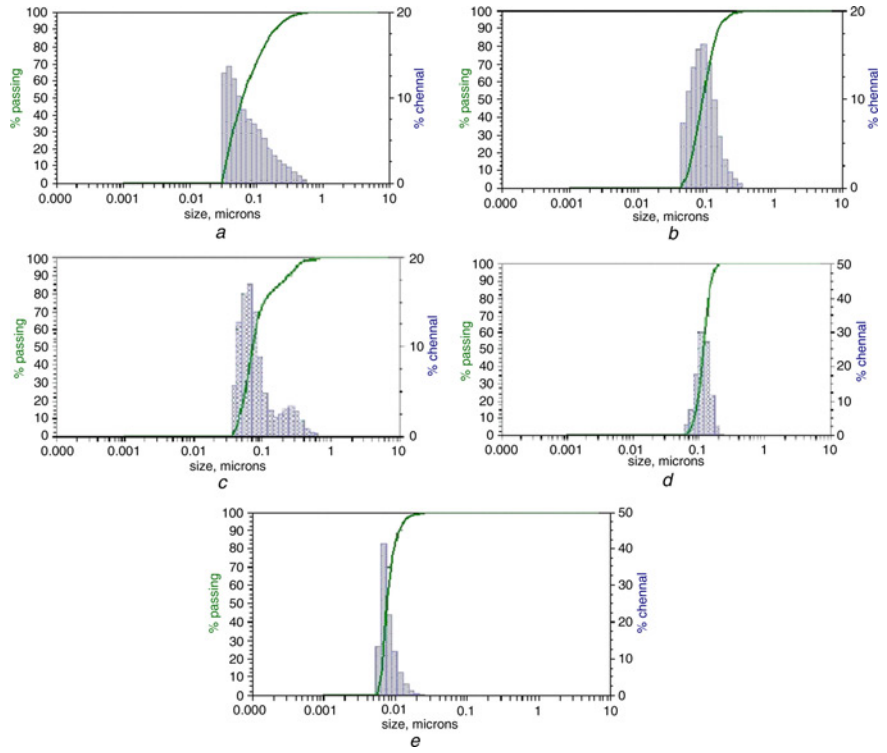


Figure 6 *Pictures of average particle size of latexes prepared with different amounts of SN-10*
a Dv = 0.0832 μm, m (SN-10) = 0.50 g
b Dv = 0.088 μm, m (SN-10) = 1.00 g
c Dv = 0.1070 μm, m (SN-10) = 1.50 g
d Dv = 0.1172 μm, m (SN-10) = 2.00 g
e Dv = 0.1218 μm, m (SN-10) = 2.50 g

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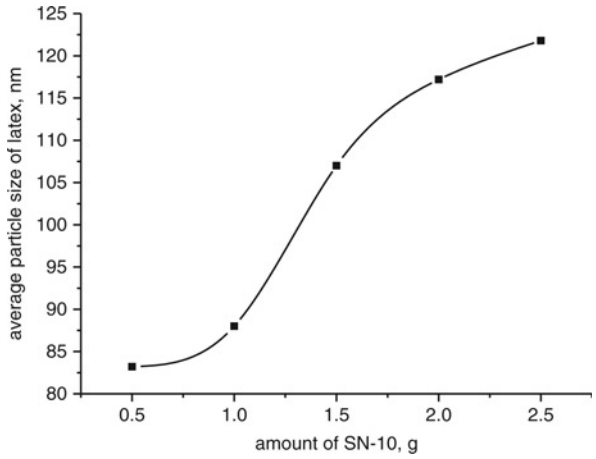


Figure 7 *Influence of amount of SN-10 on average particle size of latex*

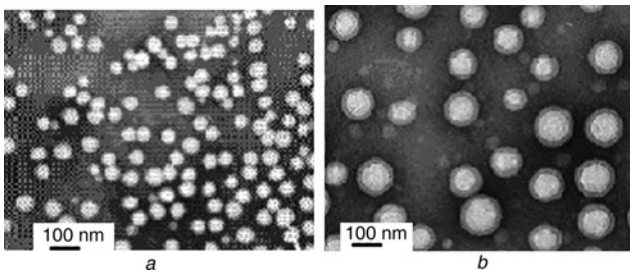


Figure 8 *TEM images of latexes*
a TEM of latex prepared with 0.50 g of SN-10
b TEM of latex prepared with 2.50 g of SN-10

3.4. Particle size of latex: The pictures of the average particle size of latexes prepared with different amounts of SN-10 are given in Fig. 6. The influence of the amount of SN-10 on the particle size of the latex is presented in Fig. 7. Fig. 7 shows that the particle size of latex is increased with the increase of the amount of SN-10. This can be explained by the fact that the nucleation mechanism of the latex prepared with SN-10 is different from the one of the latex prepared with conventional emulsifiers during the course of the emulsion polymerisation. The nucleation mechanism of the latex prepared with conventional emulsifiers is the micelle nucleation, that is, the emulsifiers are formed to micelles and the site of the emulsion polymerisation-reaction centre is formed after the part of the micelles obtain the free radicals which are decomposed from the initiator [14]. Usually, the bigger the amount of the conventional emulsifiers is, the more the number of the micelles is, and the bigger the probability of forming the reaction centre is. Therefore the number forming the particles of the emulsion is more and the particle size of the emulsion is smaller. However, the nucleation mechanism of the latex prepared with SN-10 is homogeneous nucleation, that is, a small amount of monomers dissolved in the water is copolymerised with SN-10 to precipitate the high molecular polymers, which is not dissolved in the water. They collide with the precipitated polymers around to form the reaction centre. They collide and grow up to form the particle of the emulsion. When the amount of SN-10 is increased, the smaller is the proportion of the micelles nucleation of the latex, and the bigger the proportion of homogeneous nucleation of the latex. Therefore the number of particles of the latex is fewer and the particle size of the latex is bigger. In addition, TEM images of the latexes prepared with 0.50 and 2.50 g of SN-10 are shown in Fig. 8. It can be seen that the particle size of the resultant latexes is accords well with the dynamic light scattering characterisation results. Furthermore, in Fig. 6*c*, it can be found that there are two peaks in the light scattering results, which may be ascribed to enhanced particle stabilisation by the presence of SN-10.

4. Conclusions: The PAL with submicro particle size was prepared via semi-continuous seeded emulsion polymerisation of BA and MMA in water phase initiated with KPS and emulsified with mixed surfactants of SDBS and ANPPE. The FTIR spectrum and DSC confirm the resultant latex. The contact angle of the film first is increased and then decreased with the increase of the amount of SN-10. The glass transition temperature of the film is decreased with the increase of the amount of SN-10. However, the particle size of the latex is increased with the increase of the amount of SN-10.

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