J. Rubb. Res., **21(4)**, 236-255

Synthesis of Polyisoprene via *Miniemulsion Polymerisation: Effect on Thermal Behaviour, Colloidal Properties and Stereochemistry*

J. CHOUYTAN[1], S. BERAHENG[1], E. KALKORNSURAPRANEE[1],
C.M. FELLOWS[2#] AND W. KAEWSAKUL[1#]

The synthesis of polyisoprene (isoprene rubber) in latex form was carried out by conventional emulsion polymerisation and by miniemulsion polymerisation using hexadecanol as a hydrophobe and the two methods compared. The influence of an emulsion system, monomer and surfactant concentration on conversion, particle size, gel content and coagulation were investigated. Molecular characteristics, thermal behaviour and stereochemistry were investigated by GPC, DSC, TGA and ^{1}H-NMR. With decreasing monomer concentration and increasing surfactant concentration, the number of stabilised droplets in the miniemulsion was found to increase. The greater number of loci for the polymerisation reaction thus obtained a lead to an increased conversion as well as a reduced gel content.

Keywords: Polyisoprene; free radical; polymerisation; emulsion; gel

Natural rubber (NR) has excellent elasticity since it consists almost entirely (98%) of *cis*-1,4-isoprene units giving rise to helical chains[1]; however, this gives it a lower modulus than polyisoprene with a greater proportion of *trans*-1,4 isomerism. NR latex based products such as rubber gloves and condoms require both high elasticity and a high modulus, and there is a continual need to improve modulus without sacrificing elasticity[2]. Addition to NRL of synthetic polyisoprene (IP) latex with a higher proportion of *trans* isomerism may be a good candidate for this purpose, as it is in the latex form and has a high compatibility with NR[3]. One problem with the use of IP latex is the relatively high gel content typically seen in products of emulsion polymerisation[4]. This gel can adversely affect the reactivity of the rubber, giving poorer vulcanisation[5,6].

Emulsion polymerisation is a well-known technique used in the commercial manufacture of many polymers. The kinetics of emulsion polymerisation differ greatly from bulk or suspension polymerisations because it depends on a complex interplay of chemical and physical processes, *i.e.* the nucleation, growth and stabilisation of polymer particles – which rely on the mechanisms of radical polymerisation in combination with various colloidal phenomena.

Miniemulsion polymerisation is one of a number of heterogeneous polymerisations similar to emulsion polymerisation. Rather than the relatively large monomer droplets being reservoirs of monomer for a polymerisation process occurring at other loci, in miniemulsion polymerisation monomer droplets are homogenised to a

---

[1] Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat Yai Campus, Songkhla 90110, Thailand.
[2] School of Science and Technology, University of New England, NSW 2351, Australia.
[#] Corresponding authors (e-mail: w.kaewsakul@utwente.nl; cfellows@une.edu.au)

smaller size range of 50 nm to 500 nm[7]. These droplets are the loci of polymerisation. Ostwald ripening[8] of these droplets, the thermodynamically-driven growth in droplet size seen in an emulsion on standing is avoided by incorporation of insoluble, nonpolar species of low molecular weight such as hexadecanol[9] or hexadecane[9,10] (a "hydrophobe"). Similar to conventional emulsion polymerisation, in miniemulsion polymerisation the monomer droplets are stabilised with surfactants, *e.g.* sodium dodecyl sulfate (SDS)[9,11,12,13], 2-acrylamido-2-methyl-1-propane sulfonic acid[14,15], and sodium dodecyl benzene sulfonate[14]. As the locus of polymerisation is the monomer droplets, the initiator may be either water-soluble, *e.g.* hydrogen peroxide[16] or potassium persulfate (KPS)[10,13,14,17] or water-insoluble, *e.g.* benzoyl peroxide (BPO)[10] or azobis-isobutyronitrile (AIBN)[9,13].

Recently much research has been carried out on the synthesis of isoprene rubber (IP) latices and their use for thin-film based rubber applications such as gloves and condoms. Apolinar *et al.* [18] synthesised polyisoprene using microemulsion polymerisation[19], a method which uses extremely high concentrations of surfactant to achieve stabilised small droplets initiated using a redox couple of *tert*-butyl hydroperoxide/ tetraethylenepentamine with SDS as stabiliser. The final conversion was low and low molecular weights were obtained, which was attributed to chain scission. Cheong *et al.* [20] performed emulsion polymerisation of polyisoprene with the use of both thermal and redox initiators. They found that polymerisations of isoprene using redox initiator at 25°C and *t*-dodecyl mercaptan as chain transfer agent gave a high yield and negligible gel fraction. Boonchoo *et al.* [21] synthesised polyisoprene–montmorillonite (Mt) nanocomposites *via* differential microemulsion polymerisation using AIBN as initiator, and studied the effect of monomer and surfactant concentration on particle size, yield and solid-content. Results showed that the conversion was influenced by the ratio of isoprene monomer to water and the Mt loading. The mechanical properties of Mt-modified isoprene rubber were improved when compared to unmodified NR.

The radical polymerisation of polyisoprene results in branched molecules typically containing more than 65 mol% of the 1,4-*trans* configuration[4], followed by 1,4-*cis* units and low percentages of 1,2 and 3,4 units[18,20]. A high fraction of 1,4-*cis* units can be achieved using coordination polymerisation[4,22] or anionic polymerisation[4,23], but such polymerisations are not suitable for application in dispersed aqueous systems.

A gel content of 10 – 80% is normally obtained, increasing with conversion and with temperature[24]. With excessive branching, polyisoprene prepared by radical polymerisation becomes an insoluble gel[20]. On the other hand, radical polymerisation is the easiest way to synthesise polyisoprene and is low–cost in terms of both chemicals and processing compared to anionic or coordination polymerisation.

The effect of monomer and surfactant concentration on the colloidal properties, thermal behaviour and stereochemistry in radical emulsion polymerisation have not been extensively studied. Thus in this work, we seek to overcome the restrictions of radical polymerisation using polymerisation conditions which should lead to a high content of 1,4-*trans* structure of polyisoprene and acceptable colloidal properties of the obtained latex. The effect of the emulsion system, monomer and surfactant concentration on the thermal behaviour, colloidal properties, kinetics and the stereochemistry of the product are assessed.

EXPERIMENTAL

Materials

Isoprene monomer, analytical reagent or AR grade, was supplied by Sigma-Aldrich, USA, Lot no. SHBG0593V. The inhibitor type 4-tert-butylcatechol in isoprene monomer was removed prior to its polymerisation using sodium hydroxide solution as a neutraliser (AR grade, RCL Labscan, Thailand, Lot no.12080277) with anhydrous sodium sulfate as a moisture absorber (AR grade, Ajax Finechem, Australia, Lot no. 0706021). Other chemicals were used including potassium persulfate (KPS) as initiator (Laboratory reagent or LR grade, Ajax Finechem, Australia, Lot no. AF407122); hexadecanol (HD) as a hydrophobe (AR grade, Sigma-Aldrich, Germany, Lot no. BCBK9378V); sodium dodecyl sulfate (SDS) as a primary surfactant (LR grade, Ajax Finechem, Australia, Lot no. 1306143459) and sodium bicarbonate or NaHCO3 as a buffer to control the pH of the emulsion (AR grade, Ajax Finechem, Australia, Lot no. 1502523935); and n-dodecyl mercaptan (*n*-DM) as a chain transfer agent to control the molecular weight distribution (LR grade, Aldrich, USA, Lot no. STBD9677V); they were used as received. Ethyl methyl ketone (MEK) (LR grade, Ajax Finechem, Australia, Lot no. 1512209984) was employed as coagulating agent; methanol (Commercial grade, Liquor Distiller Organization Excise Department, Ministry of Finance, Thailand, Lot no. 5C251115) was used for washing the coagulated polymer and toluene (AR grade, Fisher Scientific, UK, Lot no. 1524777) was employed as gel extraction reagent. Deionised water (DI) was prepared using a tri-column filter containing ion exchange resin: styrene cationic resin and quaternary ammonium anionic resin was used as an aqueous phase.

Synthesis of Polyisoprene

The reactor employed in this work was a 250 mL polytetrafluoroethylene tubular chamber with a 10 mm thick steel jacket equipped with a removable lid. The lid was equipped with a pressure gauge, as well as inlet and outlet valves and was rated to function at up to 350°C and 60 bar.

The recipes employed in this work are shown in *Table 1*. The procedure began with combining DI water, surfactant (SDS), hydrophobe (HD), buffer ($NaHCO_3$) and chain transfer agent (*n*-DM) in the reactor, then adding isoprene monomer (IP). Different procedures were adopted for preparing latices by conventional (CE) and miniemulsion (ME) techniques. For CE polymerisation, all ingredients with 40 wt% IP (CE 40 IP) were emulsified under stirring with a magnetic bar at 150 rpm for 1 h at 0 – 3°C to prevent evaporation of IP. For ME polymerisation, the same mixture of chemicals (ME 40 IP) was sonicated using an ultrasonic sonicator (Model 275TAE, Crest Ultrasonic, Malaysia) at a frequency of 60 Hz for 30 min to generate the small monomer droplets. The sonication was performed at low temperature (*ca.* 1 – 3°C) using a water/ice bath. 22.56 mL of 0.10 M KPS solution was then added as a single shot.

The resulting emulsions were placed in an oil bath at a temperature of 70°C under N_2 atmosphere and continuously stirred with a magnetic bar at 150 rpm. The polymerisation proceeded for 24 h prior to isolation of the products.

Characterisations and Property Determinations

Percentages of conversion, coagulation and gelation. The resulting latice from the

TABLE 1. RECIPES USED FOR CONVENTIONAL (CE) AND MINIEMULSION (ME) POLYMERISATION

Recipes	IP	SDS[a]		KPS[a]		$NaHCO_3$[a]		*n*-DM[a]		HD[a]		DI Water
	mass (g)	conc. (%wt)	mass (g)	conc. (%wt)	mass (g)	conc. (%wt)	mass (g)	conc. (%wt)	mass (g)	conc. (%wt)	mass (g)	mass (g)
ME 10 IP	10	7.50	0.81	1.50	0.15	1.50	0.15	0.50	0.05	0.50	0.05	88.78
ME 20 IP	20	7.50	1.62	1.50	0.30	1.50	0.30	0.50	0.10	0.50	0.10	77.57
ME 30 IP	30	7.50	2.43	1.50	0.46	1.50	0.46	0.50	0.15	0.50	0.15	66.35
ME 40 IP	40	7.50	3.24	1.50	0.61	1.50	0.61	0.50	0.20	0.50	0.20	55.14
ME 2.5 S	40	2.50	1.03	1.50	0.61	1.50	0.61	0.50	0.20	0.50	0.20	57.35
ME 5.0 S	40	5.00	2.11	1.50	0.61	1.50	0.61	0.50	0.20	0.50	0.20	56.27
ME 7.5 S	40	7.50	3.24	1.50	0.61	1.50	0.61	0.50	0.20	0.50	0.20	55.14
CE 40 IP	40	7.50	3.24	1.50	0.61	1.50	0.61	0.50	0.20	-	-	55.34

[a]Amount relative to monomer content

polymerisation process were vacuum filtered using a 300 mesh steel wire cloth. The residual rubber retained on the filter mesh was considered to be coagulum arising from the aggregation of rubber particles. This residual coagulum was dried and weighed (W_1). The extent of coagulation was determined using *Equation 1*, where W_M is the initial weight of monomer.

$$\text{Coagulation (\%)} = W_1/W_M \times 100 \qquad \ldots 1$$

The percentage conversion was determined by coagulation of the obtainable rubber latices. 10 g of latex sample from each batch was coagulated with MEK. The coagulum was washed with methanol and dried until it reached a constant weight (W_2). The conversion can be calculated in relation to the entire weight of monomer input as expressed in *Equation 2*, where W_L was the final weight obtained for each latex.

$$\text{Conversion (\%)} = W_2/W_M \times W_L / 10 \qquad \ldots 2$$

The gel content was determined by soxhlet extraction. Small pieces of the dried rubber sample were wrapped with soxhlet thimble paper and introduced into the soxhlet apparatus. Toluene was used as a solvent. The extraction was performed at boiling temperature of toluene for 24 h (~105°C in the soxhlet tube). The residue was dried to a constant weight (W_3) and the gel content was obtained according to *Equation 3*.

$$\text{Gel content (\%)} = W_3/W_2 \times 100 \qquad \ldots 3$$

Particle size. The particle size of rubber particles dispersed in the aqueous solution was measured by laser diffraction using a laser particle size analyser (Coulter LS230, Jinan Winner Particle Instrument Stock, China). Resolution of the instrument was from 40 nm to 2000 µm at a scattering angle of 90°. The light source was a tungsten-halogen lamp and a polarisation intensity differential scattering detector.

Chemical structure. The structure of polyisoprenes in deuterated chloroform or ($CDCl_3$ AR grade, ReAgent, UK) was measured by proton nuclear magnetic resonance (^{1}H-NMR) at a frequency of 400 MHz, 25°C, and a pH of 7 (Unity Innova 500, Varian, USA).

Molecular weight and molecular weight distribution. The dried rubber samples were dissolved in tetrahydrofuran (THF) (AR grade, RCL Labscan, Thailand) at a concentration of 1 mg/mL and then the molecular weight (MW) was determined using gel permeation chromatography (GPC, Shodex KF-806, Showa Denko, Japan) equipped with a column plus reflective index detector. THF was used as an eluent at a flow rate of 4.0 mL/min at 40°C. The number- and weight-average molar masses (M_n and M_w, respectively) were calibrated with six polystyrene standards possessing M_w of 2.90×10^3; 6.87×10^3; 1.98×10^4; 4.60×10^4; 1.11×10^5 and 2.55×10^5 g/mol. The MW of synthesised polyisoprene was calculated by means of universal calibration applying a Benoit factor of 0.67[25].

Thermal analysis. The glass transition temperature (T_g) of the samples was determined using a differential scanning calorimeter (DSC 2920, TA Instruments, USA). The sample (*ca.* 5 mg) was cooled down to -100°C with a cooling rate of 10°C/min. The sample was then heated from -100 to 50°C with a heating rate of 5°C/min under N_2.

Thermogravimetric analysis (TGA) of samples was carried out over the temperature range of 20 to 600°C with a heating rate of 10°C/min under a nitrogen atmosphere (HI-Res TGA 2950, TA Instruments, USA).

RESULTS AND DISCUSSION

Effects of Polymerisation Technique on Properties of IP Latex

As isoprene has a low boiling point at 34°C, it is necessary to use a high-pressure reactor for reactions at 70°C to prevent loss of volatile monomer. Pressure rises within the chamber due to evaporation of isoprene monomer at 70°C giving elevated pressure within the closed system. As the reaction proceeds, pressure decreases as polymerisation of isoprene gives a reduced pressure of vapour in equilibrium with the liquid isoprene (*Figure 1*).

The rate of increase in the internal pressure of the ME reaction shown is higher than for CE, but the ultimate pressure obtained is lower. This is attributed to the greater number concentration of particles for ME, $N_C = 1.4 \times 10^{18}$ L^{-1} as compared to CE with $N_C = 6.4 \times 10^{17}$ L^{-1}. The ME system has more loci of polymerisation compared to CE system, leading to a faster rate of polymerisation (R_p), which is directly related to the particle number (N_p) according to *Equation 4*[20].

$$Rp = k_p [M]\, n(N_p / N_A) \qquad ...4$$

Where k_p is the rate coefficient of the propagation process, [M] is monomer concentration, n is the average number of the radicals per particle and N_A is Avogadro's constant. As the propagation reaction is exothermic, this leads to a higher rate of temperature increase and hence pressure increase.

Since the half-life of KPS at 70°C in water is about 5 h, beyond 5 h both systems have a slow reaction rate because of the exhaustion

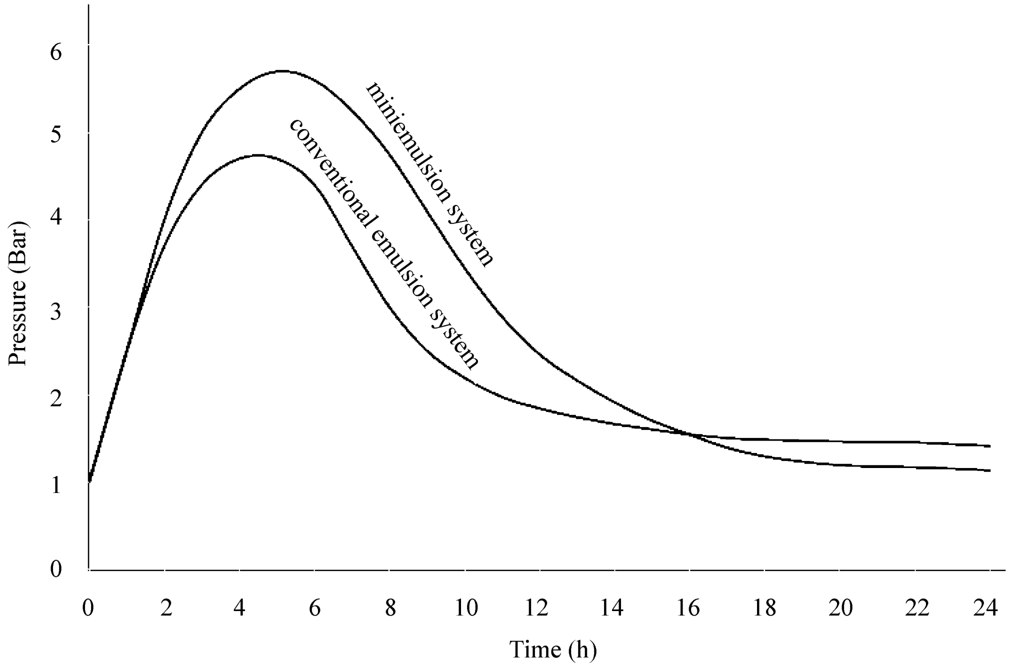

Figure 1. Effect of emulsion polymerisation systems on the internal pressure of reactor as a function of time at a constant temperature of 70°C. The monomer concentration for both system was 40 wt%.

of the initiator. The conventional reaction is slower overall because of the smaller number of polymerisation loci, so does not get as close to completion as the miniemulsion reaction which retains more loci for the reaction. This outcome is consistent with what is normally expected at high conversions (*Table 2*).

Apart from the higher conversion of products obtained by ME technique, the size of the particles dispersed in latex is smaller (*Table 2*). This is the expected result for miniemulsion polymerisation, due to the action of the hydrophobe in controlling particle size distributions by preventing Ostwald ripening[26]. This phenomena results in an increase in overall average particle size with time[27] and the effect of the hydrophobe can be seen both in terms of influence of monomer content (*Figure 2a*) and surfactant content (*Figure 2b*). However, greater coagulation was observed for the ME experiments due to the higher N_C. The ME latices also had higher gel content compared to the CE latex. This is also a consequence of the larger number of loci of polymerisation: as the reaction is faster, particles will experience more time with a high polymer: monomer ratio at a relatively high radical flux, which will encourage grafting and crosslinking reactions.

Considering the molar mass distributions obtained from the two polymerisation methods (*Figure 3*), the polymer synthesised from CE has a lower MW and Đ and less of a shoulder at high MW region. The lack of a shoulder can be attributed to the reduction in grafting reactions. Grafting is expected to be less at lower conversions and hence lower polymer: monomer ratios[20], while the larger cross-sectional area of the particles formed

TABLE 2. TECHNICAL PROPERTIES OF POLYISOPRENE OBTAINED IN THIS STUDY

Recipes	Conversion (%)	Gelation (%)	Coagulation (%)	Particle diameter (nm)	Particle dispersity %	T_g (°C)	T_d (°C)	Molecular weight (g/mol)		
								M_n	M_w	Đ
CE 40 IP	62.8	19.2	1.8	94	0.34	N/A	N/A	1.07×10^4	2.85×10^4	2.68
ME 10 IP	94.9	29.6	0.1	74	0.18	-59	364	1.49×10^4	4.93×10^4	3.31
ME 20 IP	91.1	25.8	0.6	79	0.24	-61	359	1.10×10^4	4.39×10^4	3.99
ME 30 IP	92.2	25.5	0.9	79	0.22	-60	355	8.67×10^3	3.94×10^4	4.54
ME 40 IP	78.5	23.4	3.3	78	0.21	-63	356	9.29×10^3	3.68×10^4	3.96
ME 2.5 S	61.5	22.3	4.2	100	0.26	-65	352	1.16×10^4	3.51×10^4	3.03
ME 5.0 S	65.2	22.3	3.8	91	0.17	-65	353	7.79×10^3	3.54×10^4	4.54
ME 7.5 S	78.5	23.4	3.3	78	0.21	-63	356	9.29×10^4	3.68×10^4	3.96

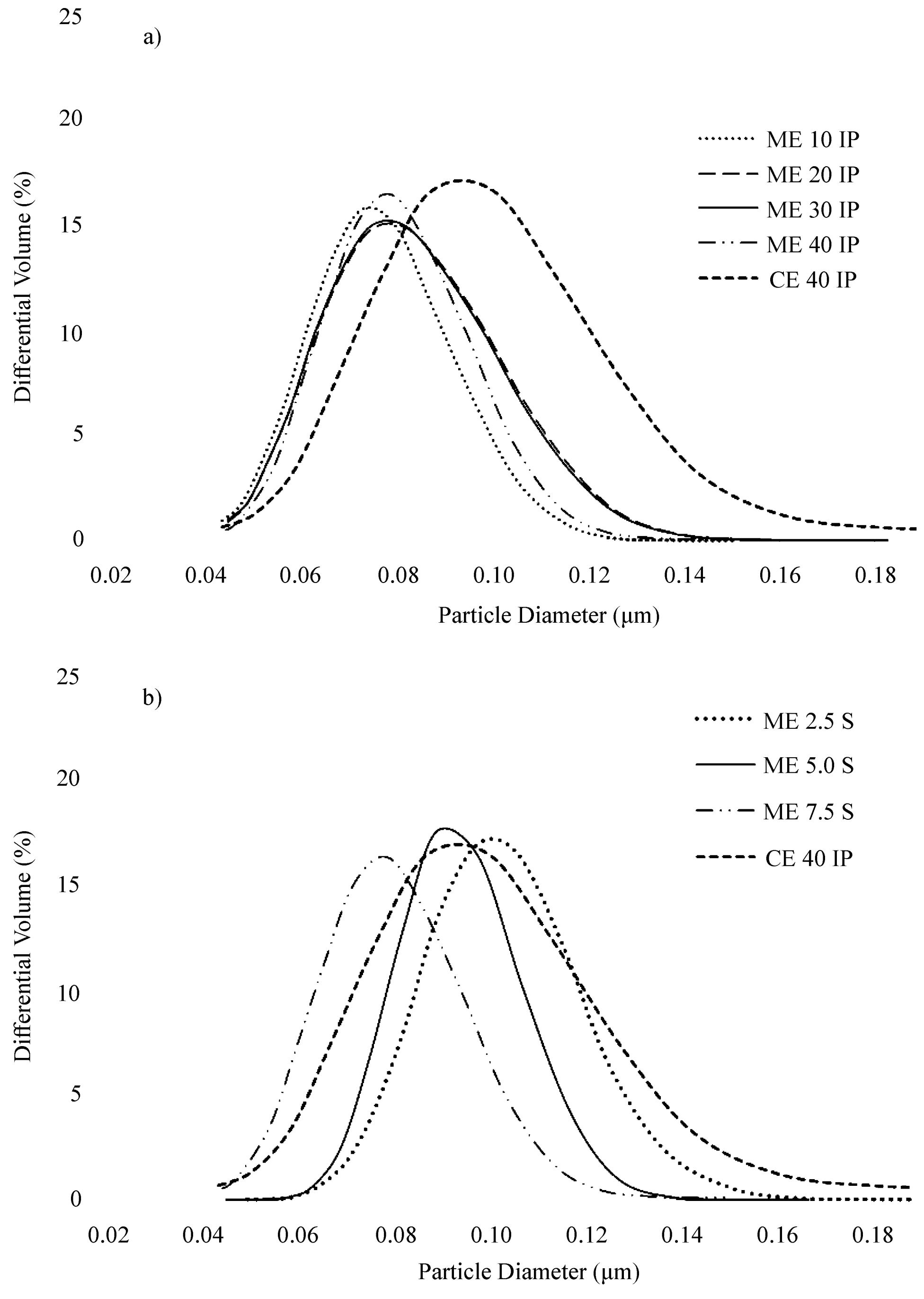

Figure 2. Particle size distribution of the synthesised polyisoprene prepared with varied monomer concentrations (a) and surfactant concentrations (b).

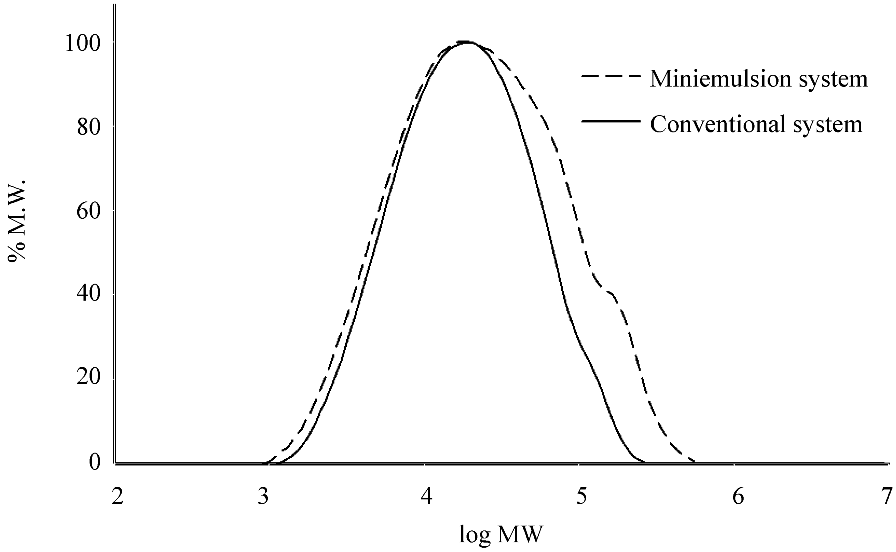

Figure 3. Molecular weight distribution of polyisoprenes synthesised with miniemulsion and conventional emulsion technique using a fixed monomer concentration at 40 wt%.

in CE in comparison to ME should lead to a greater entry rate of radicals into the CE particles, other things being equal, and hence more rapid termination of growing polymer radicals on average.

The chemical structure of the synthesised latices was confirmed using proton NMR[20,28] (*Figure 4*). This spectrum is consistent with previous spectra obtained for polyisoprene. The proportion of *cis*-1,4 was higher than typically reported for polymerisation of isoprene, 28 – 29% compared to a literature range of 8 – 23 mol%[20,29]. Conversely, the intensities of 1,2 and 3,4 units are less than the previously reported data which gave values of 5 – 7 % for each of these units[24] (*Table 3*). The only difference which may be significant between the structure of the CE and ME latices was a reduction in the apparent amount of 3,4 addition in CE relative to ME, which is counter-intuitive as this is the functionality that is most likely to react at high conversions (as it gives a pendant double bond with a stabilising methyl substituent at one end).

Effects of Varying Monomer Concentration

The results of experiments carried out with different monomer concentrations are shown in *Figure 5* and *Table 2*. The conversion remained similar in ME experiments when monomer content is increased from 10 – 30 wt%, *i.e.* 95 to 92 wt%. However, a substantial drop is seen at a monomer content of 40 wt%, giving a yield as low as 79 wt%. This is likely to be due to the competition between miniemulsion and bulk polymerisation in droplets as the potential instability at the higher concentration of monomer will give fewer loci of polymerisation, resulting in a slower reaction rate and thus reduced percent yield. This is consistent with the increased amount of coagulum obtained at 40 wt% monomer.

An average particle size in the range of 74 – 79 nm was found for all ME experiments carried out with 7.5 wt% SDS. It is not surprising that the particle size and dispersity are independent of monomer

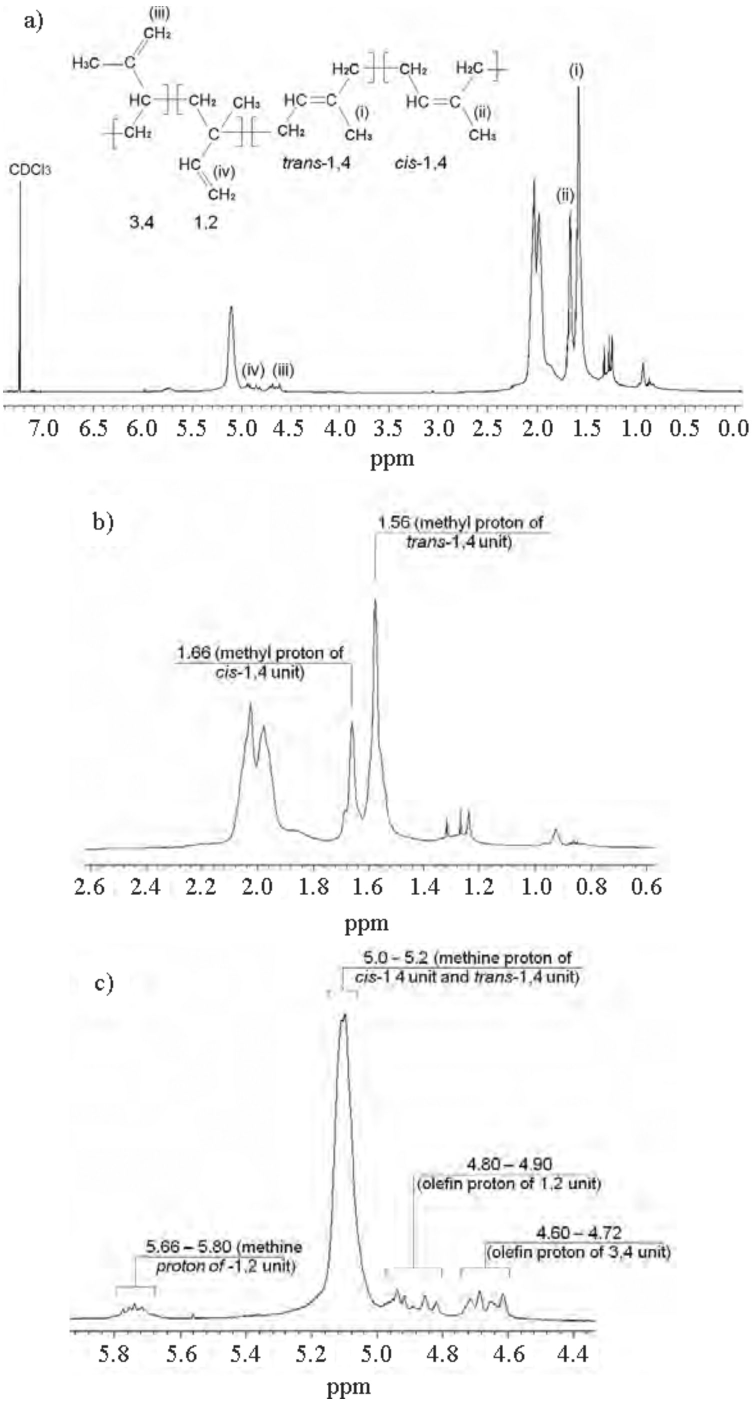

Figure 4. 1HNMR spectrum of polyisoprene prepared with miniemulsion technique using 40 wt% monomer: the entire spectrum (a); the peaks assigned for cis-*1,4 and* trans-*1,4 unit (b); and the peaks assigned for 1,2 and 3,4-unit (c).*

TABLE 3. EFFECT OF EMULSION POLYMERISATION SYSTEM, MONOMER CONCENTRATION AND SURFACTANT CONTENT ON STEREOCHEMISTRY OF THE SYNTHESISED POLYISOPRENE

Recipes	*Trans*-1,4 (%)	*Cis*-1,4 (%)	3,4-addition (%)	1,2-addition (%)
Commercial IP	3.6	93.5	3.0	n/a
CE 40 IP	63.7	29.3	3.2	3.8
ME 10 IP	63.6	28.4	4.1	3.9
ME 20 IP	63.6	28.4	4.2	3.9
ME 30 IP	63.4	28.4	4.3	3.9
ME 40 IP	63.2	28.6	4.3	4.0
ME 2.5 S	63.3	27.6	4.4	4.7
ME 5.0 S	63.1	28.0	4.8	4.1
ME 7.5 S	63.2	28.6	4.3	4.0

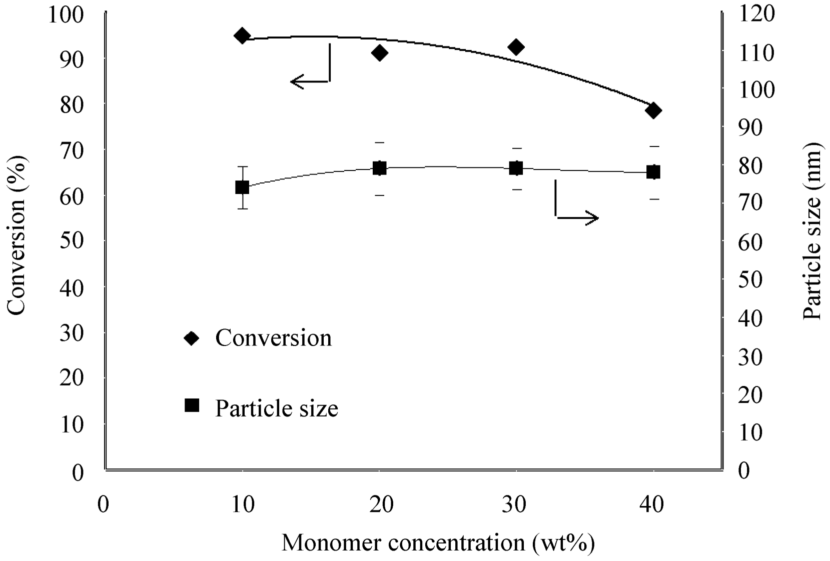

Figure 5. Effect of monomer concentration on the conversion and particle size of the obtainable polyisoprene.

concentration (*Figure 2a*), as the monomer: hydrophobe ratio and monomer: surfactant ratios remain constant and these will be the main determinants of particle size in a well-stabilised miniemulsion.

The particle number concentration N_C can be determined by calculation of the solid mass per volume, which results in variable values subject to the monomer concentrations as follows: 10 wt% = 4.9×10^{18} L^{-1}; 20 wt% = 7.8×10^{17} L^{-1}; 30 wt% = 1.2×10^{18} L^{-1}; and 40 wt% = 1.4×10^{18} L^{-1}. It can be seen that the particle number concentration decreases with increasing monomer concentration up to 20 wt%, and then slightly increases with further increasing monomer content, in good agreement with the decreasing conversion obtained.

A difference in the MW distributions with monomer concentration is the increasing shoulder seen at high molar mass (*Figure 6a*). *Figure 7* shows the mechanism of chain transfer in polyisoprene. The effect of this chain transfer on MW will be most significant at the end of a radical polymerisation when almost all monomer has been consumed. In the present study, chain transfer is likely to influence the dispersity of the product by creating more branched polymers into the system, as monomer adds to the new radical site which is located along the polymer backbone (*Figure 8*). It can clearly be seen that 10 wt% IP latex gives the most complete polymerisation (~95 %); it has the most significant shoulder in the molar mass distribution and a broad MW distribution, in agreement with the mechanisms of gel formation.

Glass transition temperature (T_g) slightly increases with decreasing monomer content (*Figure 9a*), consistent with the higher molar mass observed at lower monomer contents. However, extrapolating these results to infinite molar mass according to the Flory-Fox Equation (*Equation 5*)[30]:

$$T_g = T_{g,\infty} - K/(M_n M_w)^{1/2} \qquad \ldots 5$$

gives a $T_{g,\infty}$ of -54°C, significantly above the literature value of -60°C[18,31]. This suggests crosslinking plays an important role in raising the T_g of these particles. This value is also significantly above the T_g of NR, which is approximately -70°C[32]. This is because the obtained polyisoprenes have a relatively high percentage of *trans*-1,4-polyisoprene in their structure (*Table 3*). The *trans* structure is normally associated with close packing of adjacent molecules and therefore gives a more glassy material compared to one which has a predominantly *cis* structure.

The samples with the higher molar masses and higher degrees of crosslinking are correlated with higher decomposition temperatures in thermal analysis (*Figure 10a*), which is reasonable.

Effects of Varying Surfactant Concentration

In order to understand the role of surfactants in this system, the amount was varied from 2.5 – 7.5 wt% relative to monomer content or 1.0 – 3.0 wt% relative to the entire emulsion (*Figure 11* and *Table 2*). It can clearly be seen that with increasing surfactant levels, the product conversion increases from 62 – 79 wt%, and the average size of rubber particles decreases from 100 to 78 nm (*Figure 2b*). Variation of surfactant content thus has a more significant impact on latex properties than variation of monomer content. Particle numbers are 2.5% surfactant, 5.2×10^{17} L^{-1}, 5.0% surfactant, 7.3×10^{17} L^{-1}; 7.5% surfactant, 1.4×10^{18} L^{-1}. Increasing the amount of surfactant leads to higher particle number concentration as a consequence of a reduced amount of coagulation. The smaller particles lead to a more complete conversion due to the large number of polymerisation loci, again giving rise to a more extended period of time at a high polymer: monomer

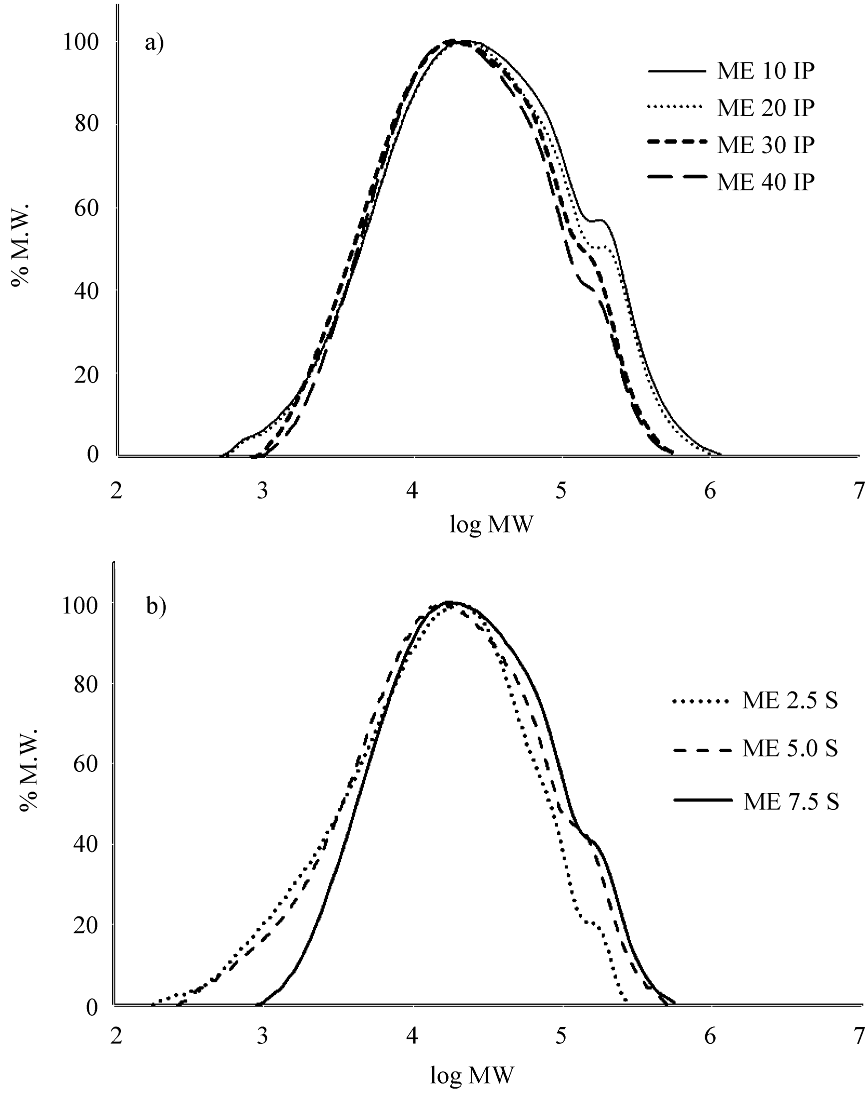

Figure 6. Molecular weight distribution of the synthesised polyisoprene prepared with different monomer concentrations (a) and surfactant concentrations (b).

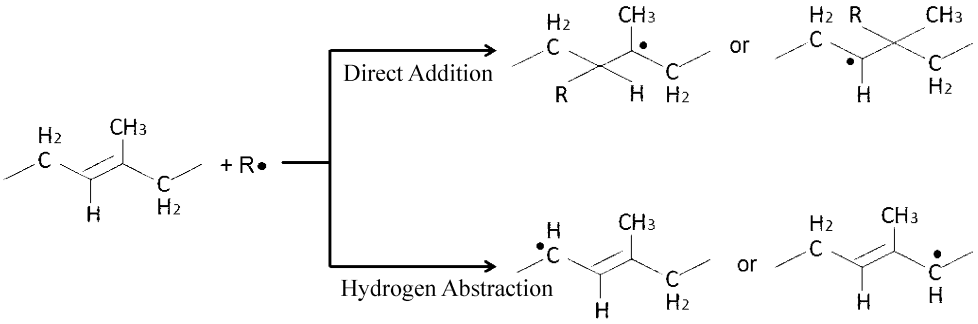

Figure 7. Chain transfer mechanism during polymerisation of polyisoprene.

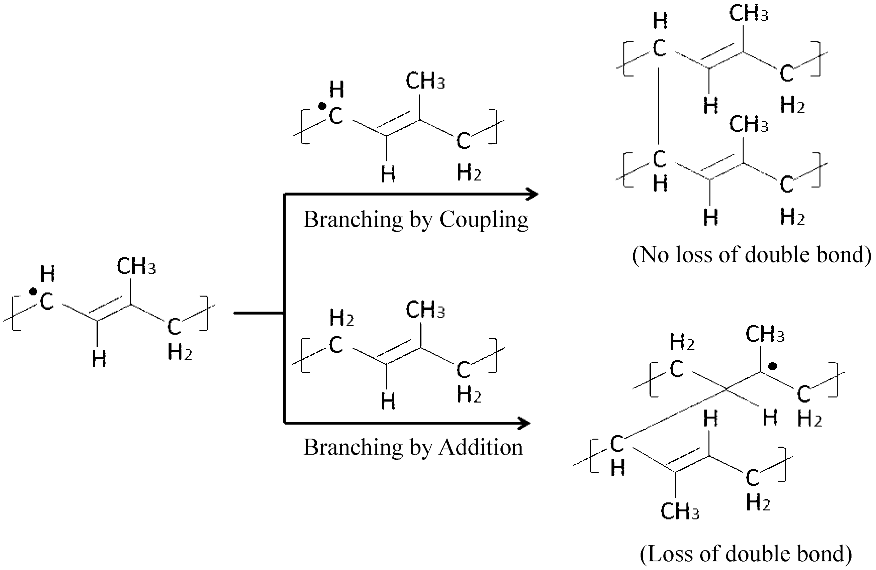

Figure 8. Branching and crosslinking mechanisms during polymerisation of polyisoprene.

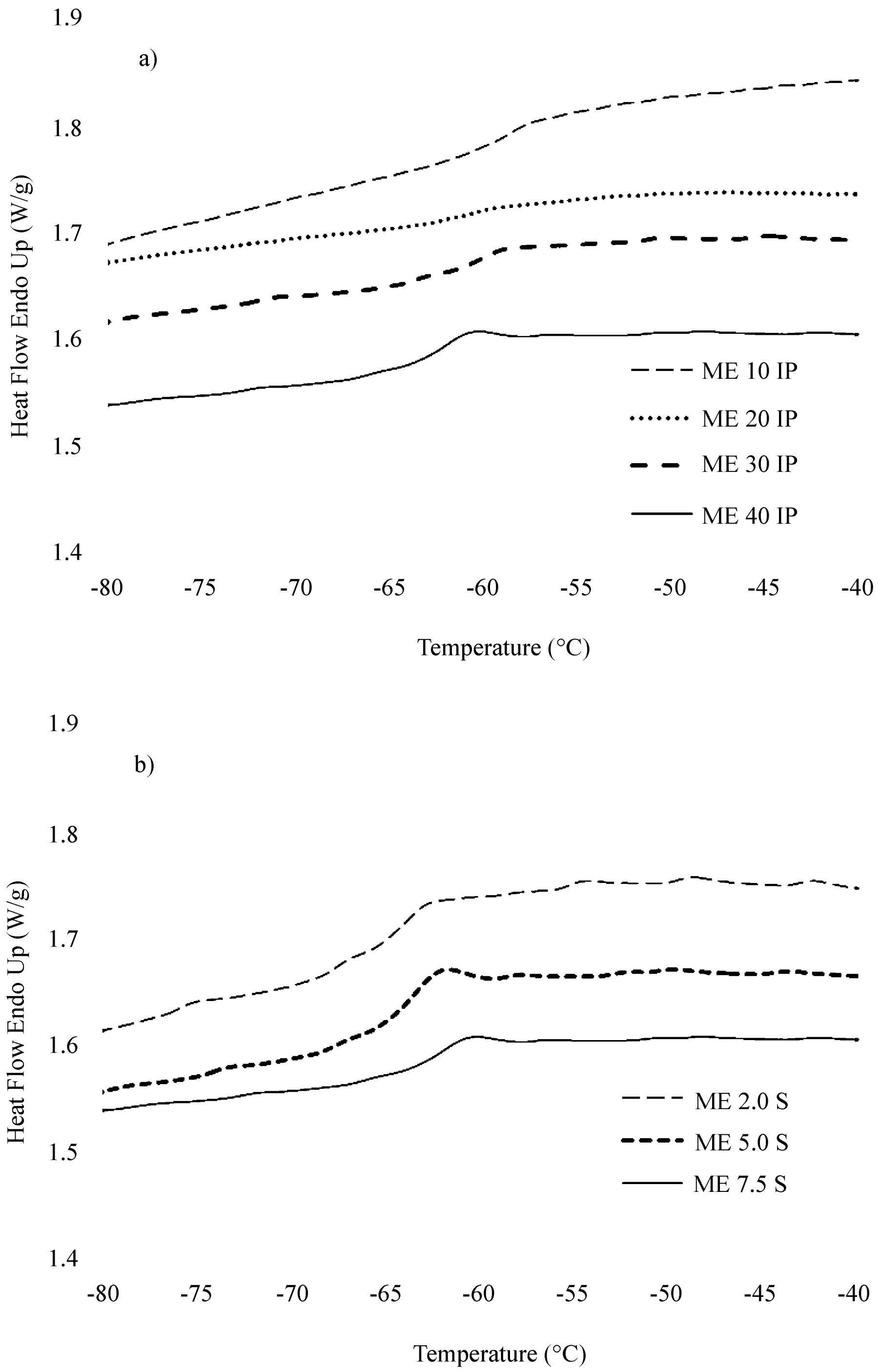

Figure 9. DSC thermograms of the synthesised polyisoprene prepared with different monomer concentrations (a) and surfactant concentrations (b).

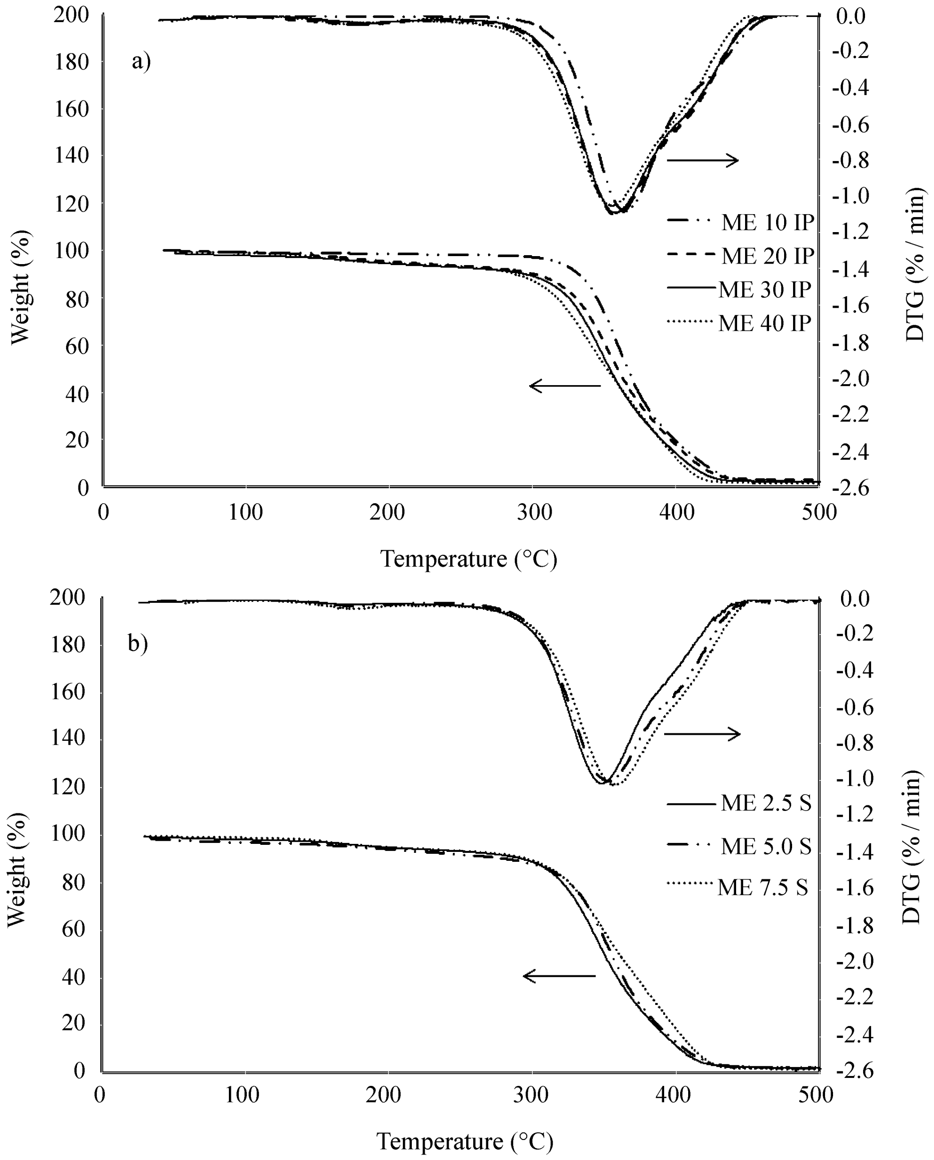

Figure 10. TGA and DTG thermograms of polyisoprene synthesised with varied monomer concentrations (a) and surfactant concentrations (b).

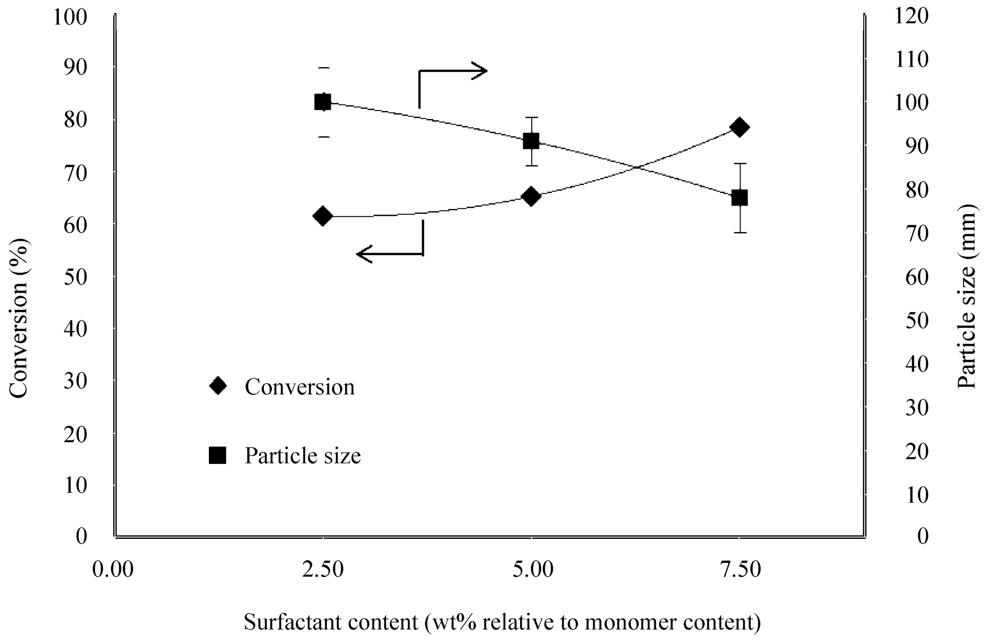

Figure 11. Influence of surfactant content on conversion and particle size of the resulting polyisoprene.

ratio where crosslinking and grafting reactions can take place.

All three curves show small shoulders due to branching in the high MW region, with larger extents of branching again corresponding to higher conversions (*Figure 6b*). The batches containing lower surfactant contents (2.5 and 5.0 wt% relative to monomer content) show broader curves deviating particularly in the region of low MW: it appears that adding a smaller amount of emulsifier leads to a greater proportion of short chains of polyisoprene.

A slight increase in T_g was found with increasing surfactant loading (*Figure 9b*). This is again consistent with the higher molar mass found at higher surfactant loadings, and the higher molar masses are again correlated with higher decomposition temperatures in thermal analysis (*Figure 10b*).

CONCLUSIONS

The miniemulsion technique gives a smaller size of rubber particles, hence a larger number of loci for polymerisation, leading to high conversion and concomitant higher amounts of gel and coagulum. This extent of gelation is not significantly greater than conventional polymerisation, and the coagulation can be minimised by control of the monomer and surfactant concentration. The proportion of *cis*-polyisoprene was greater than commonly reported for isoprene polymerisation, which may be attributable to the relatively high temperature at which the polymerisation was carried out, as the *cis*-isoprene fraction has been reported to increase with temperature. Intriguingly an increased amount of 3,4-addition was seen in the miniemulsion polymerisation compared to the conventional polymerisation. With increasing monomer concentration from 10

– 30 wt%, the conversion slightly decreases, but dramatically drops at 40 wt% of monomer. This was consistent with the number of stable droplets maintained in the miniemulsion, with the fall in conversion being accompanied by a drop in particle number and increase in coagulum consistent with some loss of stabilisation and polymerisation in large droplets. Surfactant had a significant effect on polymer particle size, with a higher surfactant: monomer ratio giving smaller particles. All results were consistent with an increase in grafting and crosslinking reactions at high conversions, giving an increasing gel fraction and shoulders in the molar mass distributions at high molar masses. The better understanding derived from this work will be useful in further improvements in synthesis of polyisoprene lattices with the aim of reducing the gel content.

ACKNOWLEDGEMENTS

The authors would like to acknowledge financial supports from the Natural Rubber Innovation Research Institute, Prince of Songkla University: PSU (Grant No. SCI581227S) and the Thailand Education Hub for ASEAN Countries (TEH-AC) scholarship for PhD study, the Graduate School, PSU (Grant No. TEH2557-001). The award from the PSU Graduate School on a program Overseas Thesis Research (Grant No. OTR2559-007), is also highly appreciated for supporting Jadsadaporn Chouytan to undertake a research exchange at the University of New England, Australia. Discussion within the team of Rubber Product Development Group, Faculty of Science, PSU, was always beneficial for this work.

Date of receipt: May 2018
Date of acceptance: October 2018

REFERENCES

1. SAKDAPANICH, J. (2010) Natural Rubber Technology. Bangkok: Technobiz Publisher.
2. BLACKLEY, D.C. (1997) Polymer Latices, Science and Technology. **Vol 3**: Applications of Latices", 2nd edition, London: Chapman and Hall.
3. SHORT, J.N., THORNTON, V. AND KRAUS, G. (1957) Effect of *Cis-Trans* Ratio on the Physical Properties of 1,4 Polybutadienes. *Rubb. Chem. Technol.*, **30 (4)**, 1118 – 1141.
4. BLACKLEY, D.C. (1983) Synthetic Rubbers: Their Chemistry and Technology. London: Applied Science Publishers.
5. TONG, Z. AND DENG, Y. (2007) Synthesis of Polystyrene Encapsulated Nanosaponite Composite Latex via Miniemulsion Polymerization. *Polym.*, **48**, 4337 – 4343.
6. NAKASON, C., KAESAMAN, A. AND SUPASANTHITIKUL, P. (2004) The Grafting of Maleic Anhydride onto Natural Rubber. *Polym. Test.*, **23**, 35 – 41.
7. RUGGERONE, R. (2009) Highly Filled Polymer Nanocomposite Films Derived from Novel Nanostructured Latexes, Thesis number 4581, École Polytechnique Federale De Lausanne, Switzerland.
8. THRELFALL, T. (2003) Structural and Thermodynamic Explanations of Ostwald's Rule. *Organic Proc. Res. Dev.*, **7(6)**, 1017 – 1027.

9. LELU, S., NOVAT, C., GRAILLAT, C., GUYOT, A. AND BOURGEAT-LAMI, E. (2003) Encapsulation of an Organic Phthalocyanine Blue Pigment into Polystyrene Latex Particles Using a Miniemulsion Polymerization Process. *Polym. Int.*, **52**, 542 – 547.

10. WANG, C., CHU, F., GRAILLAT, C., GUYOT, A., GAUTHIER, C. AND CHAPEL, J.P. (2005) Hybrid Polymer Latexes: Acrylics–Polyurethane from Miniemulsion Polymerization: Properties of Hybrid Latexes versus Blends. *Polym.*, **46**, 1113 – 1124.

11. TSAVALAS, J.G., GOOCH, J.W. AND SCHORK, F.J. (2000) Water-Based Crosslinkable Coatings via Miniemulsion Polymerization of Acrylic Monomers in the Presence of Unsaturated Polyester Resin. *J. Appl. Polym. Sci.*, **75**, 916 – 927.

12. LUO, Y. AND ZHOU, X. (2004) Nanoencapsulation of A Hydrophobic Compound by A Miniemulsion Polymerization Process. *Polym. Chem.*, **42**, 2145 – 2154.

13. TIARKS, F., LANDFESTER, K. AND ANTONIETTI, M. (2001) Preparation of Polymeric Nanocapsules by Miniemulsion Polymerization. *Langmuir*, **17**, 908 – 918.

14. KIM, Y.K., CHOI, Y.S., WANG, K.H. AND CHUNG, I.J. (2002) Synthesis of Exfoliated PS/Na-MMT Nanocomposites via Emulsion Polymerization. *Chem. Mater.*, **14**, 4990 – 4995.

15. CHOI, Y.S., CHOI, M.H., WANG, K.H., KIM, S.O., KIM, Y.K. AND CHUNG, I.J. (2001) Synthesis of Exfoliated PMMA/Na-MMT Nanocomposites via Soap-Free Emulsion Polymerization. *Macromol.*, **34**, 8978 – 8985.

16. LI, M., DANIELS, E.S., DIMONIE, V., SUDOL, E.D. AND EL-AASSER, M.S. (2005) Preparation of Polyurethane/Acrylic Hybrid Nanoparticles via a Miniemulsion Polymerization Process. *Macromol.*, **38**, 4183 – 4192.

17. CHERN, C.S. (2006) Emulsion Polymerization Mechanisms and Kinetics. *Prog. Polym. Sci.*, ***31***, 443 – 486.

18. APOLINAR, Y., RAMOS, L.F., SAADE, H., LEON, R.D. AND LOPEZ, R.G. (2010) Polyisoprene Nanoparticles Prepared by Polymerization in Microemulsion, Nanomaterials. *J. Nanomater.*, **2010**, 1 – 6.

19. FULL, A. P., KALER, E. W., ARELLANO, J. AND PUIG, J. E., (1996) Microemulsion Polymerization of Styrene: Effects of Salt And Structure. *Macromol.***, 29**, 2764 – 75.

20. CHEONG, I.W., FELLOWS, C.M. AND GILBERT, R.G. (2004) Synthesis and Cross-Linking of Polyisoprene Latexes. *Polym.*, **45**, 769 – 781.

21. BOONCHU, P., REMPEL, G.L. AND PRASASSARAKICH, P. (2014) Synthesis of Polyisoprene–Montmorillonite Nanocomposites via Differential Microemulsion Polymerization and Application of PIP–Mt in Natural Rubber, *Appl. Clay Sci.*, **88**, 186 – 193.

22. ZAIKOV, G.E. (2006) New Topic in Polymer Research Handbook, New York: Nova Science Publisher.

23. RODRIGUEZ, V.I., MINARI, R.J., ESTENOZ, D.A., GUGLIOTTA, L.M. AND MEIRA, G.R. (2012) Emulsion Polymerization of Isoprene: Mathematical Model for Long-Chain Branching. *J. Appl. Polym. Sci.*, 1038 – 1046.

24. SIMIONESCU, C.I. AND PERCEC, V. (1980) Thermal Cis-Trans Isomerization of Cis-Transoidal Polyphenyl Acetylene. *J. Polym. Sci.*, **18**, 147 – 155.

25. BUNEL, J.P. (1982) Data Handing in G.P.C. for Routine Operations. *Polym.*, **23**, 137 – 141.

26. LORENZ, R. AND VOORHEES, P. W. (2002). Growth and Coarsening: Ostwald Ripening in Material Processing. New York: Springer, 117 – 118.

27. ARIYAPRAKAI, S. AND WU, J., I. (2013) Stability of Orange Oil-in-Water Emulsion Prepared by Multilayer Membranes, *J. KMUTT R&D*, **2**, 171 – 183.

28. GERMACK S. D, AND WOOLEY, K., L. (2007) Isoprene Polymerization via Reversible Addition Fragmentation Chain Transfer Polymerization, *J. Polym. Sci.*, **45**, 4100 – 4108.

29. MATSUMOTO, A., MATSUMURA, T. AND AOKI, S. (1996) Stereospecific Polymerization of Dialkyl Muconates through Free Radical Polymerization: Isotropic Polymerization and Topochemical Polymerization. *Macromol.*, **29**, 423 – 432.

30. KOW, C., MORTON, M., FETTERS, L.J. AND HADJICHRISTIDIS, N. (1982) Glass Transition Behavior of Polyisoprene: The Influence of Molecular Weight, Terminal Hydroxy Groups, Microstructure, and Chain Branching. *Rubb. Chem. Technol.*, **55**, 245 – 252.

31. WIDMAIER, J.M. AND MEYER, G.C. (1981) Glass Transition Temperature of Anionic Polyisoprene. *Macromol.*, **14**, 450 – 452.

32. TRELOAR, L. (2005) The Physics of Rubber Elasticity Handbook. Oxford: Clarendon Press.