J. Rubb. Res., **4(1)**, 28–37

Miniemulsion Polymersation of a Bifunctional Macromonomer

H. MOHD. GHAZALY[*,***], E. S. DANIELS[*], A. KLEIN[*,**], AND M. S. EL-AASSER[*,**,#]

Evaluation of the miniemulsion polymerisation of a hydrophobic bifunctional macromonomer was undertaken. The rate of polymerisation of the macromonomer was faster when the reaction was carried out using a water-soluble initiator, potassium persulphate, KPS, than when an oil-soluble initiator, 2,2'-azobis(isobutyronitrile), AIBN, was used. Unsaturation peaks were no longer observable in the ^1H NMR spectrum of the reacted macromonomer when the gel content was ~50%. In both cases, depending on the reaction time, crosslinked products were obtained. For the KPS-initiated homopolymerisation, 50% – 60% gel content was already obtained by the first hour of reaction, while similar gel development in the macromonomer was only observed after 6 h – 12 h of polymerisation when AIBN was used. The polymerised macromonomer (using AIBN as initiator) exhibited a distinct physical change when water was removed, only when the gel content was ~50%, which corresponded to a substantial loss of unsaturation peaks in the ^1H NMR spectrum. The gel content remained low (< 10%) earlier in the polymerisation despite the steady increase in the reaction of the double bonds of the macromonomer.

Key words: miniemulsion polymerisation; hydrophobic; bifunctional macromonomer; potassium persulphate; 2,2'-azobis(isobutyronitrile); polymerised macromonomer

A telechelic ethylene-butylene copolymer with terminal acrylate reactive end groups, referred to as bifunctional macromonomer (Mac), was synthesized[1]. The macromonomer was prepared by reacting a hydroxyl-terminated ethylene-butylene copolymer (also known as the diol) with an excess of acrylic acid. The macromonomer had a number-average molecular weight ($\overline{M}_n$) of 3480 g/mol with a polydispersity index of 1.2 and a functionality of ~2.

Miniemulsion polymerisation is a process used to prepare latexes where the polymerisation takes place in monomer droplets[2]. Application of such a technique to prepare latex from the synthesized Mac was thought to be the most appropriate polymerisation method since Mac is highly water-insoluble. An oil-soluble initiator would be most suitable for this purpose;[3,4] however, the use of water-soluble initiator is also of interest. Interesting results

[*] Emulsion Polymers Institute, Lehigh University, 111 Research Drive, Bethlehem, Pennsylvania 18015, USA
[**] Department of Chemical Engineering,
[***] Rubber Research Institute of Malaysia, Malaysian Rubber Board, P. O. Box 10150, 50908 Kuala Lumpur, Malaysia
[#] Corresponding author

have been reported for some other macromonomer systems involving both types of initiators[5]. Macromonomers are felt to be slower reacting because of the 'polymer effect'. Since macromonomers are relatively of higher molecular weight species compared to smaller monomer molecules, the polymerisation reaction is thought to be slower because it is greatly influenced by diffusion[6]. It is generally hypothesized that although the rate of propagation in macromonomers is not favoured, the termination rate is hindered, and the overall polymerisation rates for the macromonomers (on a molar basis) can be comparable to, or may even be higher than, smaller molecules[7,8].

EXPERIMENTAL, RESULTS AND DISCUSSION

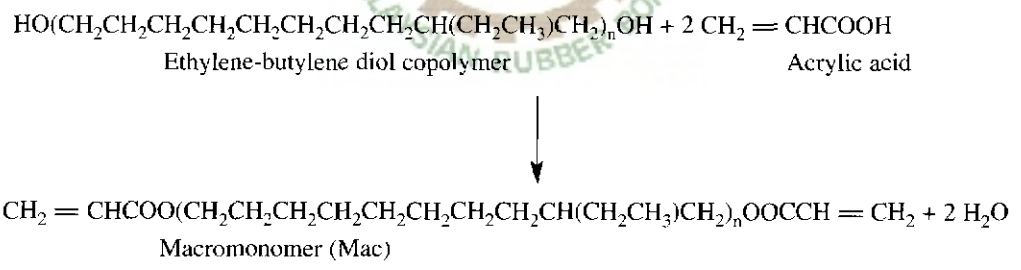
The chemical structure of Mac is given in *Scheme 1*. The number of repeat units (n) of the ethylene-butylene groups is ~21. A miniemulsion technique was employed for the preparation of the Mac homopolymer latex because of the highly hydrophobic nature of the macromonomer, which limits its transport in the aqueous media during polymerisation. With the miniemulsion approach, the polymerisation will occur at the site where the Mac monomer is present. The preparation of the Mac miniemulsion requires the presence of a costabilizer; in this case hexadecane (Aldrich) was used. The general recipe that was employed to prepare the miniemulsion is given in *Table 1*.

The oil phase, which is comprised of Mac dissolved in toluene (VWR Scientific), hexadecane, and AIBN (for the experiments where oil-soluble initiator was used; DuPont)

TABLE 1. RECIPE USED FOR THE PREPARATION OF THE MAC MINIEMULSION

Ingredient	Amount/g
Mac	0.4
Hexadecane	0.1449
Toluene	1.6
AIBN[a]	0.01
KPS[b]	0.04
Sodium lauryl sulphate	0.046
Deionized water	8.0

[a]AIBN – 2,2 Azobis (isobutyronitrile), ~ 30 mM based on the total oil phase
[b]KPS – Potassium persulphate, ~ 18 mM, based on the water phase



Scheme 1

was stirred for 30 min. This mixture was always kept chilled (~4°C) in an ice bath. The water phase was also prepared by dissolving the sodium lauryl sulphate (SLS) (J.T. Baker) in deionized (DI) water and stirring with a magnetic stirrer for 15 min. The water phase was then added into the oil phase to form a crude emulsion. Stirring by means of a magnetic bar was continued for an additional 30 min. The miniemulsion was then formed by sonification of the crude emulsion for 3 min using a Branson Sonifier (Model 450) by pulsing the mixture at a power output of 7 and a duty cycle of 50%. For the preparation of the miniemulsion containing KPS (water-soluble initiator; Aldrich), an aqueous solution of KPS was added after the miniemulsion was prepared. The Mac miniemulsions were then placed in a series of bottles, which were then purged with nitrogen and sealed. These bottles were then tumbled end-over-end in a bottle polymeriser unit at 70°C for various lengths of reaction time (1, 3, 6, 12 and 24 h). Stable (*i.e.* coagulum-free) Mac homopolymer latexes were obtained in all experiments.

Determination of Latex Particle Size and Size Distribution Using Transmission Electron Microscopy

Transmission electron micrographs of the poly(Mac) (PMac) homopolymer latexes prepared using both water- and oil-soluble initiator are shown in *Figure 1*. The latex particles were negatively-stained with 2% uranyl acetate solution[9]. A cold stage Transmission Electron Microscopy (TEM) attachment was employed for the imaging. At least 1000 particles were counted for the particle size analyses. Average particle sizes (both number-average, D_n, and weight-average, D_w) and their respective polydispersity indices (PDI= D_w/D_n) are given in *Table 2*. The average particle diameter of PMac prepared with the oil-soluble initiator was significantly lower, and the polydispersity index higher, compared to PMac that was synthesized with the water-soluble initiator. Analysis of the TEM micrographs shown in *Figure 1* indicates that there were a greater number of smaller particles present (with a few larger particles) in the latex prepared with AIBN compared to the latex prepared with KPS where the particles possessed more consistent diameters. *Figure 1* shows portions of the TEM micrographs for each of the latexes prepared. They show accurate representations of the distribution of particles for each of these systems.

^{1}H NMR Analyses

Films were prepared from both series of latexes by evaporating off the water from the PMac latexes at room temperature, followed by drying the film in a vacuum oven at room temperature until attaining constant weight. Opaque films were obtained in both cases. Upon handling the films, it became obvious that they exhibited different properties as a

TABLE 2. AVERAGE PARTICLE SIZES AND POLYDISPERSITY INDICES OF PMAC PREPARED USING WATER AND OIL-SOLUBLE INITIATORS

Particle size analysis	PMac, KPS	PMac, AIBN
D_n (nm)	117.0	60.0
D_w (nm)	170.0	110.0
D_v (nm)	153.0	81.0
PDI	1.5	1.9

D_n – number average diameter
D_w – weight average diameter
D_v – volume average diameter

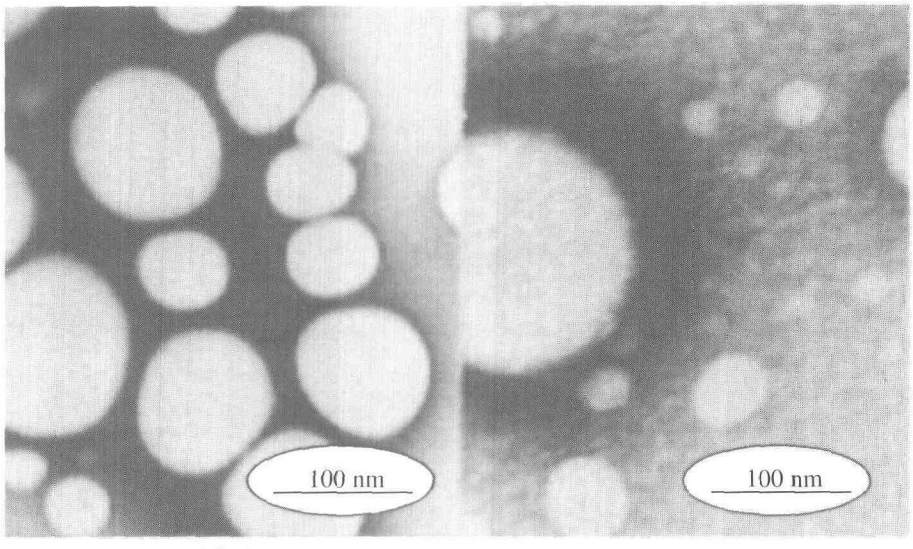


Figure 1. Transmission electron micrographs of PMac homopolymer latexes prepared using water- and oil-soluble initiators.

function of their synthesis time, particularly for PMac prepared using AIBN. Films from PMac prepared with KPS were very crumbly, but had a waxy, rubbery feel from the first hour of polymerisation onward, while films from PMac prepared with AIBN only exhibited similar properties after a polymerisation time of 12 h. PMac (prepared with AIBN) films had a toffee-like consistency and appearance before the twelfth hour of polymerisation. All 'films' were then dissolved in deuterated chloroform and subjected to ^{1}H NMR analyses. The ^{1}H NMR spectra of the PMac prepared using the water- and oil-soluble initiators are shown in *Figures 2* and *3*, respectively. In addition, *Figure 4* shows the NMR spectrum of the soluble fraction of PMac prepared from both initiators that was reacted for 24 h. Included in all the plots is the spectrum of the unreacted Mac in deuterated chloroform as a control. Double bonds (CH_2 = CH) of the unreacted Mac can be observed as three clusters of peaks located between 5.5 p.p.m. and 6.5 p.p.m.

The spectra shown in *Figure 2* indicate that no double bonds were observable from the first hour of polymerisation onward, suggesting that a substantial number of double bonds have reacted by this time. It is obvious that peaks attributed to the presence of double bond can be observed for the PMac prepared with AIBN for those latexes that were formed before 12 h of polymerisation. The loss of a substantial amount of unsaturation was presumably through polymerisation and crosslinking reactions. Changes in the physical appearance and feel of the polymer were also noted for the PMac prepared with AIBN and obtained at different reaction times. At the point where substantial loss of unsaturation was observed from the NMR analysis, PMac prepared with AIBN also showed physical

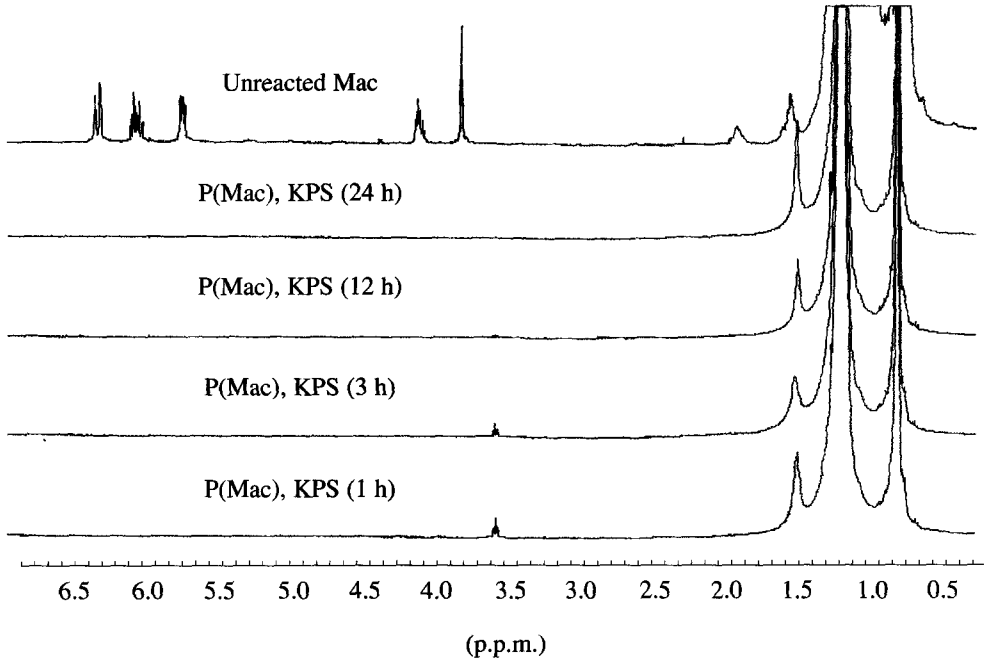


Figure 2. ^1H NMR spectra of PMac prepared with KPS at 70°C. The spectra have been scaled to the highest y-peak.

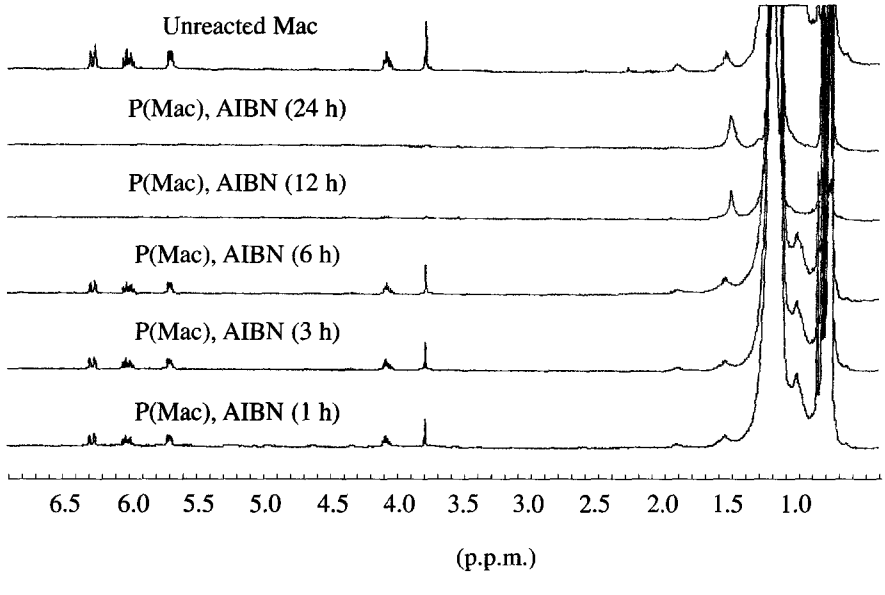


Figure 3. ^1H NMR spectra of PMac prepared using AIBN at 70°C. The spectra have been scaled to the highest y-peak.

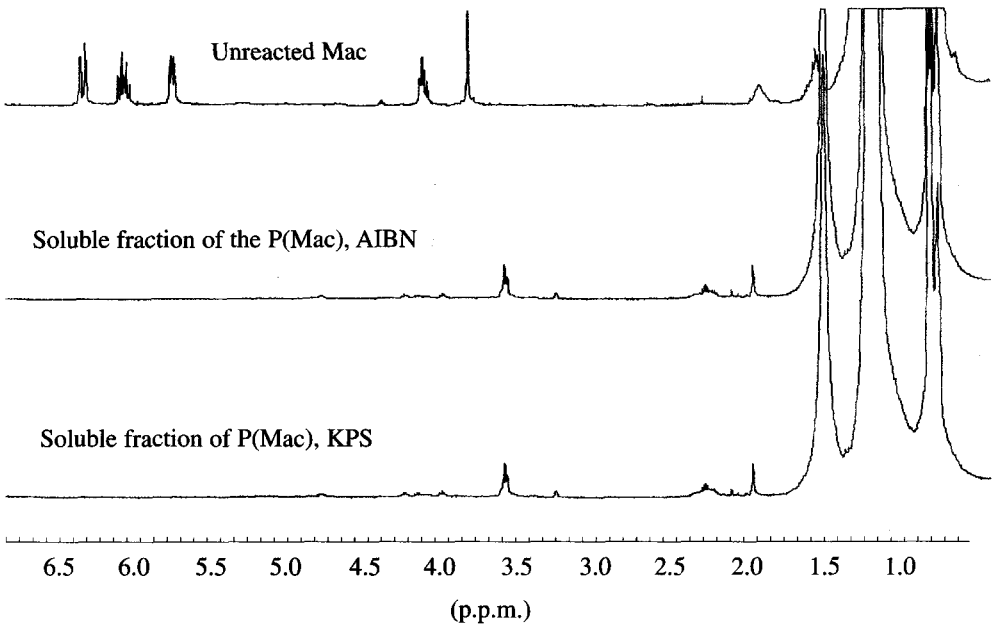


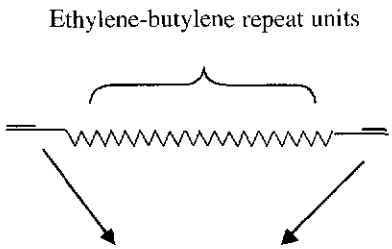
Figure 4. ^1H NMR spectra of the soluble fractions of PMac films obtained from latexes which have been reacted for 24 h. The spectra have been scaled to the highest y-peak.

changes, *i.e.* from a toffee-like consistency to a crumbly-leathery material. This would suggest that when a substantial amount of crosslinking was achieved for the Mac, a significant change in the properties of the product can be observed. Films obtained from PMac prepared from KPS from the first hour of polymerisation onward and those prepared from AIBN from the twelfth hour of polymerisation were not soluble in toluene, chloroform, or THF. In contrast, the unreacted Mac is soluble in all these solvents. After 24 h of reaction, the double bond peaks were no longer observed in the ^1H NMR spectra of the soluble fractions obtained from both samples of PMac.

From the ^1H NMR analyses, it could be inferred that the polymerisation of the Mac miniemulsion initiated with KPS was faster than the polymerisation of the miniemulsion of Mac utilising AIBN. Macromonomers are generally thought to be non-reactive because of the polymeric nature of the chain; however, many hydrophobic macromonomers have been shown to be polymerisable[10–12]. The polymerisation of Mac in the presence of KPS initiator poses several questions as to the mechanism and the nature of the KPS radicals that entered the Mac miniemulsion droplets. Droplet nucleation is hypothesized to occur instead of micellar or homogeneous nucleation because of the low water solubility of the Mac. Several workers[5,13] who have investigated the behaviour of macromonomers have shown that it was possible to observe greater or equal reactivity of a macromonomer (compared to a smaller monomer molecule). For example, Asami *et al.*[14] carried out homopolymerisations of vinylbenzyl-terminated polystyrene and

polyisoprene initiated by AIBN in benzene solution at 60°C. They concluded that the rates and degree of polymerisation are similar to those expected for styrene under similar reaction conditions. Ito *et al.*[5] showed that hydrophilic poly(ethylene oxide) (PEO) with alkyl groups present in the molecule, such as (ω-end groups, *p*-vinyl benzyl, or methacrylol groups, rapidly polymerised in water using a water-soluble initiator, 4,4`-azobis (4-cyanovaleric acid), compared to the situation when initiation was carried out using the oil-soluble AIBN in benzene.

The reactive groups present in Mac are located at the ends of the macromonomer chain and these groups are more hydrophilic compared to the ethylene-butylene repeat units. The presence of the aqueous phase in the miniemulsions may have induced the Mac chains to undergo an orientation such that the hydrophilic reactive end groups face the aqueous phase and the ethylene-butylene portion of PMac becomes oriented away from the water phase; the Mac chain structure is schematically shown in *Scheme 2*. The orientation of the chains may cause the polymerisation to become rapid once initiation begins. However, when initiation begins in the oil phase, geminate recombination and the termination rate of initiator fragments may be more dominant so that the polymerisation was delayed as reflected by the slower rate of polymerisation of the Mac miniemulsion when AIBN was used. In both cases, however, polymerisation with substantial loss of double bonds was obtained when sufficient reaction time was allowed. It is also possible that some residual inhibitor is present in the Mac droplets (originating from the synthesis of the Mac) which may have interacted with the AIBN radicals causing the delay in polymerisation (crosslinking) reactions in the case of AIBN-initiated system compared to the KPS-initiated system because the AIBN radicals are generated inside the droplets while the KPS radicals are usually generated in the aqueous phase.



Scheme 2

Determination of Gel Content of PMac

The dried films of PMac prepared using KPS initiator were all crumbly and leathery to the touch. For the products obtained from the reaction of Mac in the presence of AIBN as the initiator, only samples of PMac reacted for more than 12 h were crumbly and leathery. Pieces of these films were swollen in pre-weighed filter paper boats, which were then immersed in toluene in sealed bottles for 96 h at room temperature. The solvent was changed once during the swelling and extraction period. The amount of solvent used was approximately 1000 times more than the amount of the sample. The extraction bottle and its contents were intermittently agitated by gentle swirling. After the period allowed for the swelling and the extraction, the filter paper boats were gently lifted out of the extraction bottles. The amounts of gel retained in the filter paper boats were then determined. The development of the gel with polymerisation time is shown in *Figure 5* for PMac prepared using KPS and in *Figure 6* for PMac prepared with AIBN. Also included in *Figure 6* is the

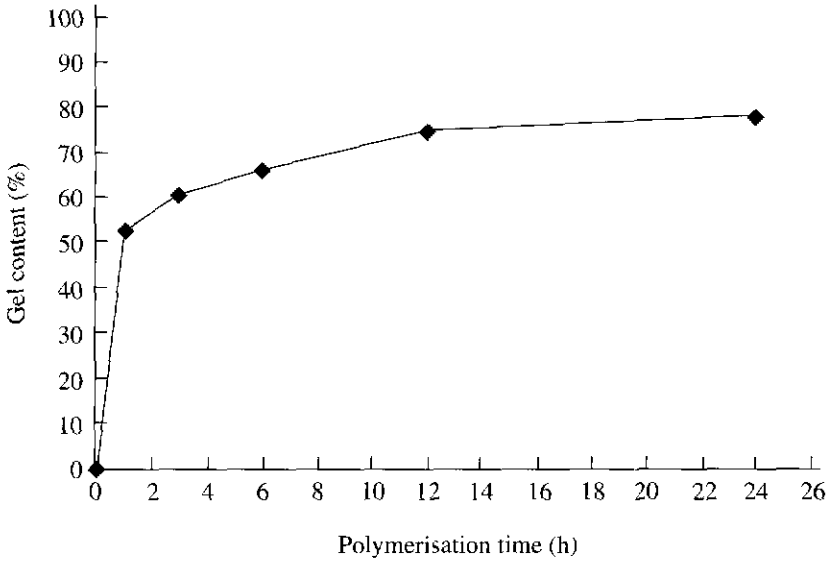


Figure 5. Development of gel content as a function of polymersation time for P(Mac) prepared using KPS.

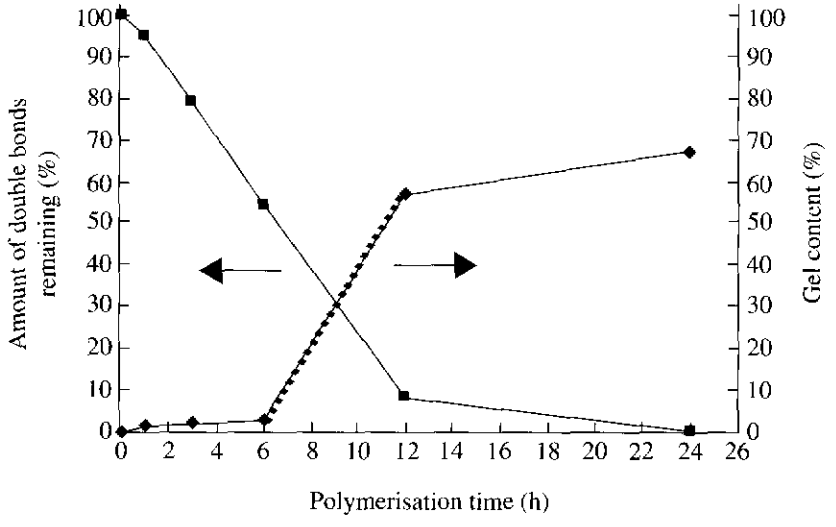


Figure 6. Development of gel content and amount of double bonds remaining as a function of polymerisation time for P(Mac) prepared using AIBN.

percentage of the remaining double bonds in the sample, derived from ^{1}H NMR analyses. The degree of unsaturation can be calculated by taking the ratio of the double bond peaks which occur between 5.5 p.p.m. – 6.5 p.p.m. and the methyl (CH_3) peak at ~0.9 p.p.m. in the NMR spectrum.

The development of gel in the PMac initiated with AIBN was particularly interesting. Before the twelfth hour of polymerisation the amount of gel in the latex was low (*Figure 6*) despite a steady decrease in the amount of unreacted double bonds. The data shows a distinct low gel content up to 6 h of polymerisation. A significant amount of gel was recorded after the twelfth hour of reaction. The increase in gel content is obvious after six hours of reaction, but the profile for the gel development between the sixth and the twelfth hour of polymerisation, as indicated by the dashed line, is not precisely known. After 12 h of polymerisation (approaching 24 h of polymerisation), the amount of gel was in the range from 60% to 70% which was similar to the gel content that was obtained for PMac prepared using KPS (*Figure 5*). In both cases, since the ultimate gel content was 70%, a fraction of 30% which did not contribute to the gel is therefore presumed to have been extracted into the solvent phase. It is also to be noted that the determination of the gel content may not be the most accurate procedure employed. This is because the smaller crosslinked particles may be able to pass through the filter paper pore into the extraction medium, or that the pores could be clogged by the smaller microgels, thus giving rise to incorrect determinations. The gel content values for the films being examined may therefore be higher or lower than the values reported here. Ideally, the gel determination should be performed directly on the latex particles.

The ^{1}H NMR spectra obtained for the soluble fractions in *d*-chloroform are given in *Scheme 2*. Unsaturation peaks cannot be observed for the soluble fractions in both cases. *Figure 5* shows that the gel content of PMac prepared using KPS varies by about 20%: *i.e.* 50% – 70% from the first hour of polymerisation to the final 24 h of reaction. Unsaturation was no longer easily observed on the sample of PMac prepared using KPS, even for the first hour of reaction (*Figure 2*). It can be concluded that when the gel content in the PMac is more than 50% – 60%, the double bonds can no longer be observed readily by ^{1}H NMR analysis; hence, the presence of very small amount of reactive groups is not easily detectable by this method especially in the presence of crosslinked structures.

The initiator concentration employed was 0.5 wt% of KPS (~18 mM) based on the water phase and 0.5 wt% of AIBN (~30 mM) based on the oil phase. The rates of radical flux for these systems are determined as follows. The rates of decomposition of the initiators are taken by multiplying the dissociation constants k_d, and the initiator concentrations, respectively. The k_d value for KPS[15] is calculated using 5.188×10^{16} exp (–33 500/1.987 (T_r + 273.15) sec^{-1}, and for AIBN[16] it is 2.6141×10^{14} exp (29 500/1.987 (T_r + 273.15) sec^{-1}. The radical flux at the beginning of the polymerisation for the KPS-initiated system is ~7.0×10^{-8} mole L^{-1} sec^{-1} and for AIBN is ~5.0×10^{-8} mole L^{-1} sec^{-1}. The radical flux for both systems appear to be similar; however, there was a significant difference in the rate of crosslinking reaction for the macromonomer crosslinker when the oil-soluble initiator was used compared with the water-soluble initiator.

CONCLUSIONS

A hydrophobic bifunctional macromonomer was polymerised *via* a miniemulsion poly-

merisation process. In the presence of a water-soluble initiator, the macromonomer polymerises at a much more rapid rate compared to the polymerisation of the Mac when an oil-soluble initiator was used. There may have been a higher incidence of geminate recombination of the oil-soluble initiator fragments as they were formed in the oil phase, which delayed the polymerisation reaction in the AIBN-initiated polymerisation of the Mac. Since the macromonomer Mac has bifunctional reactive groups, the miniemulsion polymerisation reactions resulted in a crosslinked structure. The resulting latex film obtained at the end of the polymerisation reaction remained insoluble in solvents such as toluene, chloroform and THF when dried.

Date of receipt: October 2000
Date of acceptance: February 2001

REFERENCES

1. H. MOHD. GHAZALY, DANIELS, E.S., DIMONIE, V. L., KLEIN, A. AND EL-AASSER, M. S. (2000) *J. appl. Polym. Sci.*, **77**, 1362.

2. SUDOL, E. D. AND EL-AASSER, M. S. (1997) Miniemulsion Polymerization. *Emulsion Polymerization and Emulsion Polymers (Lovell, P. A. and El-Aasser, M. S. eds.,)* Ch. 20, p. 699. England: John Wiley and Sons.

3. UGELSTAD, J., EL-AASSER, M. S. AND VANDERHOFF, J. W. (1973) *J. Polym. Sci., Polym. Lett.*, **11**, 503.

4. UGELSTAD, J., HANSEN, F. K. AND LANGE, S. (1974) *Makromol. Chem.*, **175**, 507.

5. ITO, K. (1998) *Prog. Polym. Sci.*, **23**, 581.

6. FRIIS, N. AND HAMIELEC, A. E. (1977) *Polym. Prod. Techn., Pt. 1: Polymer Reaction Eng.*, Ch. 5. Hamilton Ontario: McMaster University.

7. CAPEK, I., RIZA, M. AND AKASHI, M. (1992) *Makromol. Chem.*, **193**, 2843.

8. TSUKAHARA, Y., TSUTSUMI, K., YAMASHITA, Y. AND SHIMADA, S. (1990) *Macromol.*, **23**, 5201.

9. SHAFFER, O. L., EL-AASSER, M. S. AND VANDERHOFF, J. W. (1983) *Proc. Annual EMSA Meeting*, **41**, 30.

10. ASAMI, R. (1982) *IUPAC 28th Symp. on Macromol., Preprint*, Amherst, p. 71.

11. NIWA, M., HAYASHI, T. AND AKAHORI, M. (1986) *J. Macromol. Sci. – Chem.*, **A23**, 433.

12. NIWA, M., HAYASHI, T. AND AKAHORI, M. (1986) *J. Macromol. Sci. – Chem.*, **A24**, 433.

13. ITO, K., TANAKA, K., TANAKA, H., IMAI, G., KAWAGUCHI, S. AND ITSUMO, S. (1991) *Macromol.*, **24**, 2348.

14. ASAMI, R., TAKAKI, M. AND HANAHATA, H. (1983) Macromol., **16**, 628.

15. GNANOU, Y. AND LUTZ, P. (1989) *Makrol. Chem*, **190**, 577.

16. KOLTHOFF, I. M. AND MILLER, I. K. (1951) *J. Am. Chem. Soc.*, **73**, 3055.