Grafting of styrene onto poly(butyl acrylate) in emulsion

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The effect of time, temperature, the concentration of initiator and emulsifier, and the ratio of starting polymer to monomer on the degree of conversion (*MC*) of styrene and the grafting efficiency (*GE*) of polystyrene has been investigated. The reaction was initiated with potassium persulphate. It has been found that the degree of conversion of styrene and the grafting efficiency change in opposite directions when plotted as functions of the reaction parameters studied. The graft copolymerization is assisted by short reaction times and weight ratios of poly(butyl acrylate) to styrene greater than unity. The results obtained suggest that higher grafting efficiencies are obtained when the concentration of emulsifier is below its c.m.c. (critical micellar concentration) value. When using two different anionic emulsifiers it has been observed that the effect of initiator concentration on the degree of conversion of styrene and the grafting efficiency is complicated. Both the quantities studied (*MC* and *GE*) exhibit extrema in the range of initiator concentration studied ($3.7\text{–}33.3 \times 10^{-5}$ mol dm^{-3} of H_2O). No meaningful effect of temperature in the range 60°–90°C or that of dodecyl mercaptan (molecular weight regulator) used in an amount 0–0.4% in relation to poly(butyl acrylate) and styrene has been observed on the *MC* and *GE* values.

Keywords Styrene; poly(butyl acrylate); grafting; emulsion; critical micellar concentration

INTRODUCTION

Grafting of vinyl monomers onto acrylic rubbers in emulsion is a widely used industrial process for the preparation of the ASA-type polymers[1]. Rubber containing mainly butyl acrylate units is preferred for these polymers. However, these processes are described in the patents[1-7], and the graft products so obtained are used as impact modifiers and processing aids for vinyl polymers (mainly the polychlorovinyls). The structure of the ABS-type modifiers for poly(vinyl chloride), obtained by grafting of a mixture of styrene and acrylonitrile onto polybutadiene in emulsion, was studied by electron microscopy[8]. It has been found that the most important effect on the structure of the latex particles formed is that of the emulsifier concentration (at concentrations higher than c.m.c., the homogeneous SAN particles are formed), then the effect of the polymer to monomer ratio, and the kind of initiator used (particularly its solubility in water).

In spite of this, our present knowledge concerning the mechanism of grafting of vinyl monomers onto acrylic rubbers in emulsion and some other aspects of this reaction is limited.

EXPERIMENTAL

Materials

Styrene and n-butyl acrylate were purified by distillation under reduced pressure. Potassium persulphate was of analytical purity. n-Dodecyl mercaptan, the molecular weight regulator, obtained from Riedel de Haen (W. Germany), was used without further purification.

Anionic surfactants (emulsifiers). S1, a product of Pollena, Wrocław (Poland), was a mixture of sodium alkylbenzenesulphonates of the general formula $R^1C_6H_4SO_3Na$ ($R^1 = C_{10}-C_{14}$) and sodium alkyl sulphates R^2OSO_3Na ($R^2 = C_{16}-C_{18}$) in a weight ratio 3:2. The critical micellar concentration of the S1 in aqueous solution was determined by the conductometric method to be 0.45% at 20°C. The second emulsifier used was S2, sodium laurate; its c.m.c. determined as above was 0.6% at 20°C in aqueous solution.

Procedures

Emulsion polymerization of n-butyl acrylate. The reaction was carried out in a round-bottomed flask equipped with a reflux condenser and a stirrer. To 1 l of water containing 6 g of the S1 or S2 emulsifier, 200 g of butyl acrylate containing 0.1 g of n-dodecyl mercaptan was added. The mixture was stirred for 20 min at ambient temperature, then 0.1 g of potassium persulphate dissolved in 10 cm^3 of water was introduced. The temperature was raised to 75°C and maintained at this level for 7 h under nitrogen blanket. The yield of poly(butyl acrylate) was 99%.

Graft polymerization. To an emulsion of styrene containing an emulsifier and n-dodecyl mercaptan, polybutyl acrylate latex was added and the emulsion was stirred for 20 min at ambient temperature, then potassium persulphate dissolved in a small volume of water was added. The weight ratio of the aqueous to organic phase

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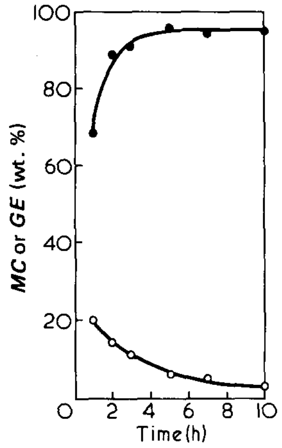

Figure 1 Monomer conversion, *MC* (curve ●) and grafting efficiency, *GE* (curve ○) vs. reaction time. Reaction conditions: temperature = 75°C; c_{S1} = 0.6 wt% in H_2O; c_i = 18.5 x 10^{-5} mol dm^{-3} of H_2O; c_{RSH} = 0.025 wt% per P + M; P/M (by weight) = 50/50

was 5:1. The emulsion was heated to the desired reaction temperature. The latex was coagulated with an aqueous aluminium chloride solution, rinsed with water until no chlorides could be detected, and dried to constant weight in vacuum at 50°C.

Characterization of polymers

Determination of the content of poly(butyl acrylate) (PBA) in the graft product. 0.5 g of the polymer was dissolved in 50 cm^3 of acetone, to which 10 cm^3 of ~1 N methanolic NaOH solution was added. The sample was hydrolysed under reflux. After cooling, the mixture was titrated with 0.4 M HCl in a 1:1 v/v ethylene glycol–isopropanol solution in the presence of cresol red. Simultaneously, a blank determination was performed.

Separation of ungrafted polystyrene. The basic idea of the separation method was to crosslink the graft product. It was assumed that only ungrafted poly(butyl acrylate) and the graft copolymer, poly(butyl acrylate-*g*-styrene) can be crosslinked. According to ref. 9, under the crosslinking conditions used, polystyrene should not be crosslinked; one can expect only some degree of degradation to occur.

5 g of the grafting product was dissolved in 80 cm^3 of acetone, then 0.15 g of dicumyl peroxide (3 wt% to polymer) was added. The acetone solution was cast to give a polymer foil which then was pressed for 1 h at 150°C under a pressure of 10 kg cm^{-2}. The crosslinked foil 0.1 cm thick was cut into pieces of 0.5 x 0.5 cm and extracted with dioxane at ambient temperature for 72 h. The polymer was precipitated from a dioxane solution with methanol, filtered and dried. The polymer was obtained as a white powder which was then hydrolysed as described above to determine the content of PBA. The PBA content in this fraction averaged 1.7 wt%. This fraction was assumed to be a 'free' ungrafted polystyrene.

The monomer conversion (*MC*) was calculated:

$$MC = \frac{\text{total amount of styrene in the graft product}}{\text{initial amount of styrene}} \qquad (1)$$

The grafting efficiency (*GE*) of polystyrene was calculated (PS = polystyrene).

$$GE = \frac{\text{amount of PS in the product} - \text{ungrafted PS}}{\text{amount of PS in the graft product}} \qquad (2)$$

RESULTS AND DISCUSSION

Grafting of styrene onto poly(butyl acrylate) in the presence of the S1 emulsifier

The effect of temperature, initiator and emulsifier concentration, and polymer to monomer ratio on the monomer conversion and the efficiency of grafting for polystyrene has been investigated.

In *Figure 1* the relationship between *MC* and *GE*, as functions of the reaction time at 75°C are shown. The conversion of styrene rapidly increases in the initial stage of the reaction (first 2 h), then slowly attains a value of 95% after the next 5 h. Further extension of the reaction time to 10 h has no marked effect on *MC*. The grafting efficiency decreases with increasing time of reaction from ~20% after 1 h to ~3–4% after 10 h. This suggests that the probability of reactions leading to the formation of the graft copolymer decreases with increasing time of the reaction when compared with the probability of styrene homopolymerization.

The results shown in *Figure 2* indicate that the reaction temperature in the range 60°–90°C has a weak effect on both styrene conversion and its grafting efficiency. The styrene conversion increases in the temperature range given above from 80 to 90%, and its grafting efficiency from 4 to 8%.

In *Figure 3* the relationship between styrene conversion and its *GE versus* the initiator (potassium persulphate) concentration is presented. It can be seen that here, too, an increase in styrene conversion is accompanied by a decrease in grafting efficiency, and *vice versa*. Within the concentration range studied one can observe a maximum and a minimum both for *MC* and *GE* values. At the initiator concentration 25.9 x 10^{-5} mol dm^{-2} of water the minimum in styrene conversion was 55%, but the grafting efficiency is high (57%). As a high value of *MC*, i.e., > 90%, the grafting efficiency of polystyrene is very low, of the order of a few per cent. A number of studies on emulsion polymerization of styrene indicate that the rate of polymerization and, thus, the monomer conversion under specified conditions is proportional to the square root of initiator concentration, c_i[10]. The accurate interpretation of the presented data is rather difficult at present,

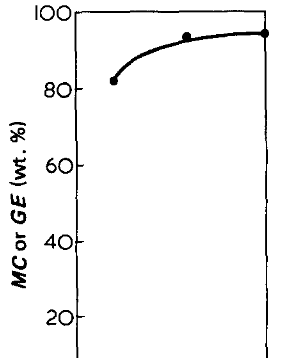

Figure 2 Monomer conversion, *MC* (curve ●) and grafting efficiency, *GE* (curve ○) vs. reaction temperature. Reaction conditions: time = 7 h; c_{S1} = 0.6 wt% in H_2O; c_i = 18.5 x 10^{-5} mol dm^{-3} of H_2O; c_{RSH} 0.025 wt% per P + M; P/M (by weight) = 50/50

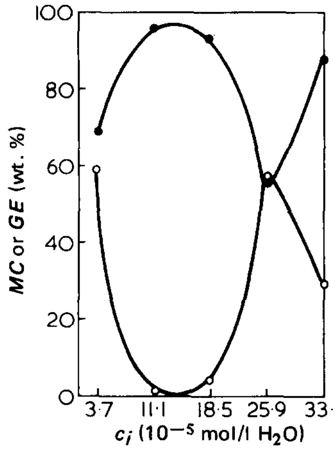

Figure 3 Monomer conversion, *MC* (curve ●) and grafting efficiency, *GE* (curve ○) vs. initiator concentration. Reaction conditions: time = 7 h; c_{S1} = 0.6 wt% in H_2O; c_{RSH} = 0.025 wt% per P + M; P/M (by weight) = 50/50; temperature = 75°C

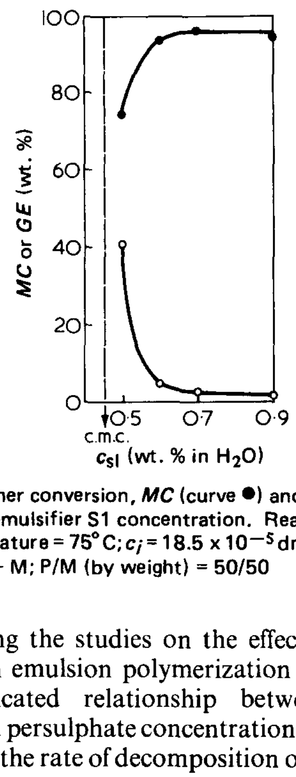

Figure 4 Monomer conversion, *MC* (curve ●) and grafting efficiency, *GE* (curve ○) vs. emulsifier S1 concentration. Reaction conditions: time = 7 h; temperature = 75°C; c_i = 18.5 x 10^{-5} dm^{-3} of H_2O; c_{RSH} = 0.025 wt% per P + M; P/M (by weight) = 50/50

although during the studies on the effect of potassium persulphate on emulsion polymerization of butadiene a rather complicated relationship between butadiene conversion and persulphate concentration was found[10]. It is possible that the rate of decomposition of persulphate is affected by the presence of the S1 emulsifier and some of the impurities contained in it[10]. The relationship observed may be also a result of competition between monomer and polymer for the primary radicals and competition between mutual and primary radical termination for both polystyrene and poly(butyl acrylate) radicals.

The relationship between the emulsifier concentration, c_{S1}, *versus MC* and *GE*, is shown in *Figure 4*. The emulsifier present in the poly(butyl acrylate) latex and thus introduced into the reaction system was also accounted for. The critical micellar concentration (c.m.c.) of the S1 is 0.45 wt% in aqueous solution at 20°C. As the concentration of the emulsifier increases from 0.5 to 0.6 wt%, the conversion of styrene increases from 75 to 95%. A further increase in emulsifier concentration (>0.6 wt%) has no effect on styrene conversion (*Figure 4*). The grafting efficiency decreases rapidly from 40% for an emulsifier concentration of 0.5 wt% to 3–4% for an emulsifier concentration of 0.6 wt% and more.

The observed relationship can be explained in the following way: at emulsifier concentrations greater than c.m.c., the probability of styrene homopolymerization increases according to the micellar mechanism. Below this value, both the processes of graft copolymerization and styrene homopolymerization proceed probably in parallel inside the poly(butyl acrylate) particles swollen with styrene. This problem is currently being studied by electron microscopy. In the case of emulsifier concentrations higher than c.m.c. the presence of homogeneous polystyrene particles containing no poly(butyl acrylate) in the latex is possible, as was observed similarly in the case of the grafted types of ABS[8].

Figure 5 illustrates the relationship between *MC* and *GE*, *versus* the weight ratio of polymer to monomer, P/M. An increase in poly(butyl acrylate) content in the reaction system has no effect on the monomer conversion which in the range of polymer to monomer ratios studied was high (95%). An increase in the polymer fraction and, thus, in the number of poly(butyl acrylate) particles acting as sites of graft copolymerization, brings about an increase in the grafting efficiency up to 30% at a weight ratio of polymer to monomer of 70/30 (*Figure 5*).

We have also investigated the effect of concentration of molecular weight regulator (n-dodecyl mercaptan) in the range of its concentrations from 0 to 0.04 wt% in relation to the weight of polymer and monomer together. No effect of this additive, either on the monomer conversion or grafting efficiency, was observed. The monomer conversion was in the range 89–94%, and the grafting efficiency was 0 to 4%. It can be concluded that, in agreement with current views on emulsion polymerization, the effect of this additive is limited only to decreasing the molecular weight of polymers[10].

Grafting of styrene onto poly(butyl acrylate) in the presence of the S2 emulsifier

In order to confirm the complicated relationships obtained between the monomer conversion and the grafting efficiency in particular and the concentration of the initiator (*Figure 3*), we carried out further studies by using another type of anionic-type emulsifier—sodium laurate—whose c.m.c. value was determined to be 0.6 wt%. It was supposed that the emulsifier used in our earlier studies, i.e., the S1, being a technical product

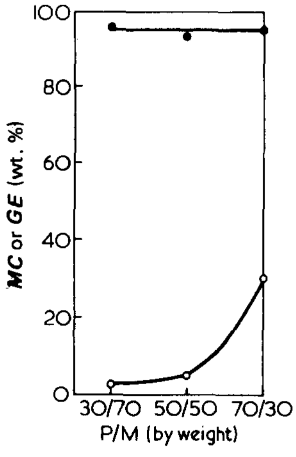

Figure 5 Monomer conversion, *MC* (curve ●) and grafting efficiency *GE* (curve ○) vs. polymer/monomer P/M ratio. Reaction conditions: time = 7 h; temperature = 75°C; c_i = 18.5 x 10^{-5} mol dm^{-3} of H_2O c_{RSH} = 0.025 wt% per P + M; c_{S1} = 0.6 wt% in H_2O

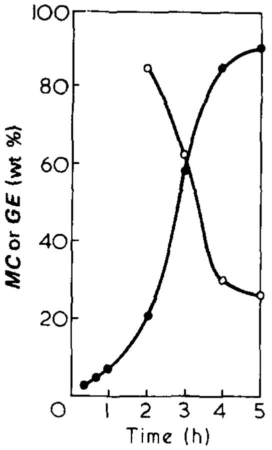

Figure 6 Monomer conversion, *MC* (curve ●) and grafting efficiency, *GE* (curve ○) vs. reaction time. Reaction conditions: temperature = 75°C; c_{S2} = 0.6 wt% in H_2O; c_i = 18.5 × 10^{-5} mol dm^{-3} of H_2O; c_{RSH} = 0.025 wt% per P + M; P/M (by weight) = 50/50

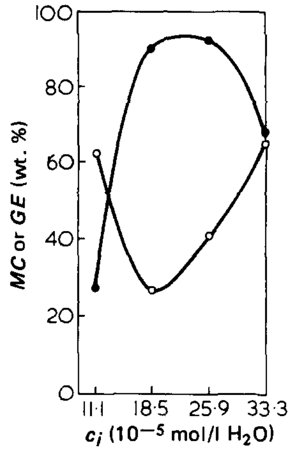

Figure 7 Monomer conversion, *MC* (curve ●) and grafting efficiency, *GE* (curve ○) vs. initiator concentration. Reaction conditions: time = 5 h; temperature = 75°C; c_{S2} = 0.6 wt% in H_2O; c_{RSH} = 0.025 wt% per P + M; P/M (by weight) = 50/50

probably containing various impurities, could be the cause of such complicated relationships as those described above (*Figure 3*). Therefore, we obtained a sample of poly(butyl acrylate) latex in the presence of sodium laurate and potassium persulphate. This product was subsequently used as a support polymer for grafting of styrene onto it in the presence of sodium laurate and potassium persulphate. The reaction procedure and other determinations were similar to those described in the Experimental section. The S2 concentration was equal to its c.m.c. and was 0.6 wt% in water.

In *Figure 6* the effect of the time of reaction on the monomer conversion and the grafting efficiency is shown. A rapid increase in styrene conversion in the presence of the S2 was observed to occur after a slightly longer reaction time (2–4 h) than in the case of the S1 emulsifier at the same temperature (75°C) (*Figure 1*). The grafting efficiency (*Figure 6*) decreases with increasing styrene conversion and reaction time. After 5 h at 75°C in the presence of the S2 the monomer conversion was 90% and the grafting efficiency was 26%; thus it was higher than after the same reaction time in the presence of the S1 emulsifier. This may result from the concentration of the S2 emulsifier used, which was equal to its c.m.c.

In *Figure 7* the relationship between potassium persulphate concentration and the monomer conversion as well as grafting efficiency in the presence of the S2 emulsifier is presented. The results obtained are similar to those described above (*Figure 3*). A maximum in monomer conversion and the corresponding minimum in grafting efficiency were found at a slightly higher concentration of potassium persulphate ($c_i = 18.5$–25.9×10^{-5} mol dm^{-3} of water) than for the S1 emulsifier ($c_i = 11.1$–18.5×10^{-5} mol dm^{-3} of water) (*Figure 3*). The lowest grafting efficiency in the presence of the S2 (sodium laurate) is still greater than that observed in the case of S1; it is 26 and 1–4% respectively. This may be caused by the concentration of the S2 used, which equals its c.m.c.

CONCLUSIONS

Generally, the changes in the monomer conversion proceed in the opposite direction to the changes in the grafting efficiency resulting from the variation of reaction parameters. Such relationships can be expected in the case of two competitive reactions in which the monomer is consumed, i.e., homopolymerization and graft copolymerization. Our results seem to suggest that the particles of a support polymer are the sites where both these reactions take place. Together with a higher extent of reaction, the availability of the support polymer in relation to the monomer probably decreases, manifested by a decrease in the grafting efficiency. The emulsifier concentration also has a marked effect on the grafting efficiency. At emulsifier concentrations higher than the c.m.c., the grafting efficiency rapidly decreases, suggesting that under such conditions the probability of the monomer homopolymerization is greater according to the micellar mechanism. This question is currently being studied by electron microscopy.

The results obtained for monomer conversion and grafting efficiency as functions of initiator concentration (potassium persulphate) cannot be explained unequivocally at present. It is possible that the relationships obtained are the characteristic features of the graft copolymerization in emulsion. One can state that formation of the graft copolymer poly(butyl acrylate-*g*-styrene) is assisted by short reaction times and polymer to monomer weight ratios greater than unity.

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