Chain transfer grafting of butyl acrylate onto poly(vinyl chloride) in emulsion

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In this paper, the chain transfer method was adopted to study the graft copolymerization of butyl acrylate onto poly(vinyl chloride) (PVC) in emulsion. This approach to the synthesis of graft copolymers was first suggested by Flory, and was experimentally demonstrated by Hayes, Blumczynski and Mayo. The work reported here shows that for the chain transfer method, the grafting efficiency does not increase, as Flory's chain transfer theory predicted, but decreases with increasing copolymerization temperature. An explanation of these observations is proposed. In addition, *FT*i.r. was used to study the resultant graft copolymer and the parent homopolymers in order to investigate the structural changes in PVC consequent on grafting. Thermogravimetry results showed that the thermal stability of the graft copolymer is better than those of PVC and PVC/poly(butyl acrylate) blend.

(Keywords: chain transfer; grafting; butyl acrylate)

Introduction

Unlike an unsaturated polymer, poly(vinyl chloride) (PVC) is difficult to graft using direct radical initiation since there are essentially no reactive groups. Therefore, many PVC graft copolymers have been produced by means of either irradiation grafting[1,2], cationic grafting[3,4], anionic grafting[5,6], or by first introducing active groups such as thiols and peroxides into the PVC substrate to make it reactive[7,8]. An alternative approach, chain transfer grafting, is a relatively convenient and effective method. The mechanism of this grafting method involves conventional initiation of the grafting monomer to give a propagating chain which is terminated by abstraction of hydrogen or chlorine from the PVC backbone. The polymer radical so formed initiates the growth of a grafted branch. The procedure gives rise to grafted polymer and homopolymer. This mode of synthesis was first suggested by Flory[9], who concluded that chain transfer grafting would be favoured by an increase in temperature because the activation energy for chain transfer is greater than that for propagation; it has been generally accepted ever since that grafting efficiency (*GE*) is increased with increasing polymerization temperature. This view was supported by the experimental results of Hayes[10], Blumczynski[11] and Mayo[12] on chain transfer grafting of vinyl acetate, methyl methacrylate and styrene onto PVC. In the grafting system of butyl acrylate (BA) and PVC, however, we observe that the *GE* does not increase but decreases with increase in polymerization temperature.

Experimental

All graft copolymerization was carried out in a four-necked flask under nitrogen protection. The procedure adopted was to mix PVC latex with BA at room temperature for various periods of time in order to prepare PVC latex particles swollen by BA. The polymerization was initiated by introducing the appropriate amount of a solution of the initiator ($K_2S_2O_8 + NaHSO_3$) in distilled water to this stirred and heated mixture. (The molar ratio $K_2S_2O_8/NaHSO_3 = 0.55/1$; all the wt% values of initiator concentration are for $K_2S_2O_8$ to BA monomer.) The graft copolymerization was continued at a predetermined temperature. The resultant polymer was coagulated by cooling the latex in a freezer and then recovered by filtration and washed with distilled water. Finally, the resultant polymer was dried in a vacuum oven at 50–60°C for 20 h. The consumption of BA in all cases was in the range of 97–100%.

The determination of *GE* requires some means of separating the poly(butyl acrylate) (PBA) homopolymer from the PVC/PBA graft copolymer. This was achieved by extraction with cyclohexane, which removes the PBA and leaves the graft copolymer and the PVC which is not grafted. In this experiment, a weighed amount of the sample was sealed in a special paper bag, placed in a Soxhlet thimble and extracted with cyclohexane for 24 h. The undissolved polymer was dried, weighed and again extracted with cyclohexane for 24 h. This process was repeated until no further weight loss was observed. There was no evidence for the presence of PVC residues in the extracted materials as judged by i.r. analysis, indicating that none of the graft copolymer or unbranched PVC had been dissolved. When a 50:50 blend of PVC and PBA was extracted by this procedure, nearly 100% of the PBA was removed.

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The *GE* was determined by dividing the amount of PBA which was grafted onto PVC by the total amount of PBA present before extraction. It can be calculated by the following equation:

$$\frac{\text{original mass of sample before extraction} - \text{mass of PVC contained} - \text{mass of PBA extracted}}{\text{original mass of sample before extraction} - \text{mass of PVC contained}}$$

Results and discussion

Graft copolymerization. (1) Effect of pre-swelling PVC latex with BA on grafting efficiency. *Figure 1* shows that *GE* increased with increasing pre-swelling time. This was expected because since the emulsion reaction system is heterogeneous, pre-swelling PVC with the monomer raises the probability of contact between the initially formed PBA and the backbone PVC and hence increases the probability of grafting BA onto PVC. Consequently, with an increase in pre-swelling time, *GE* increases initially, but approaches a limiting value (very insignificant increase after 12 h). This probably results from equilibrium swelling.

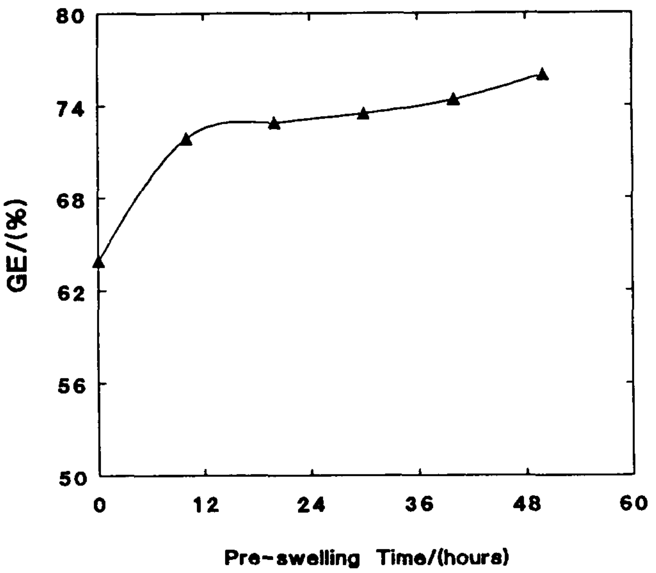

Figure 1 Effect of pre-swelling time on grafting efficiency. BA/PVC = 40/60; initiator concentration, 0.2%; reaction conditions, 50°C, 5 h

(2) The effect of BA/PVC ratio on grafting efficiency. From *Figure 2* it can be seen that *GE* increases as the BA/PVC ratio is increased. This is in agreement with the result of Hayes' investigation of grafting of vinyl acetate onto PVC in an emulsion system[10]. There is no good explanation for this. It may be attributed to the improved miscibility of the grafted PVC and growing PBA chain with increase in the grafting of BA onto PVC.

(3) The effect of copolymerization temperature on grafting efficiency. Flory[9] concluded, on the basis of theoretical considerations, that a higher copolymerization temperature would give rise to higher *GE* and Hayes' work with vinyl acetate/PVC provided support for this prediction. But it is very interesting to note that for this BA/PVC system *GE* decreased with an increase in polymerization temperature (*Figure 3*).

Normally, the chain transfer constant tends to increase with temperature because activation energy for chain transfer is higher than that for chain propagation. However, in some reaction systems, the activation energy for the propagation and transfer are comparable, then the temperature has very little and may even have a negative effect. This negative effect may be attributed to polarity mismatch at higher temperature, as some earlier workers suggested[13].

Apart from polymerization temperature, the initiator concentration used in the BA/PVC reaction system is found to have a very interesting effect on *GE*. The results recorded in *Table 1* shows that *GE* is unaffected initially when the initiator concentration is low, in the range 0.025–0.05% (concentrations lower than 0.025% cannot be used because the monomer cannot be fully converted), but at concentrations 0.05–1.5% it decreases dramatically. Furthermore, we observe that in this reaction system, PBA homopolymer is the main product in the initial period of polymerization (30–60 min) and its molecular weight is very low.

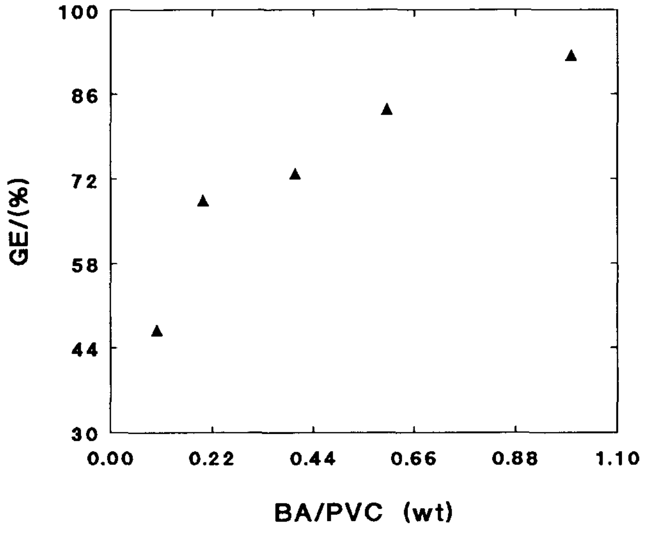

Figure 2 Effect of BA/PVC ratio on grafting efficiency. Initiator concentration, 0.2 wt%; pre-swelling time, 20 h; reaction conditions, 50°C, 5 h

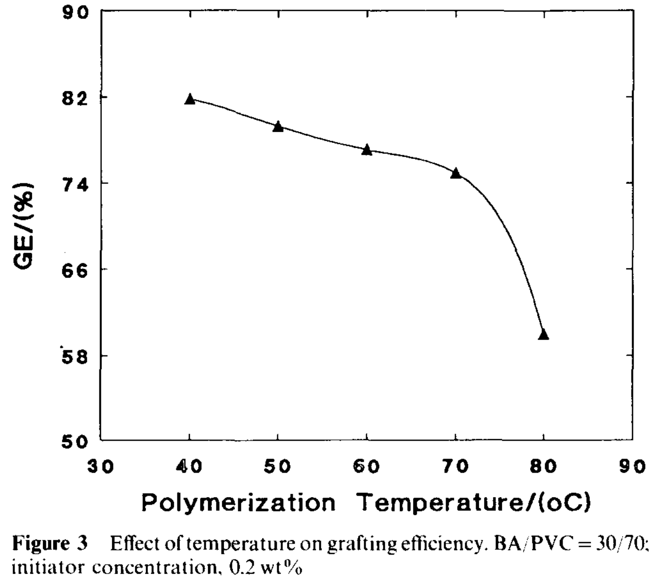

Figure 3 Effect of temperature on grafting efficiency. BA/PVC = 30/70; initiator concentration, 0.2 wt%

Table 1 Effect of radical concentration on grafting efficiency

Parts initiator/ 100 parts monomer (w/w)	Grafting efficiency (%)
0.025	70.0
0.050	70.2
0.100	61.0
0.200	58.5
0.400	54.0
0.600	49.6
0.800	39.8
1.000	37.7
1.500	23.0

BA/PVC = 25/75. Reaction condition, 50°C, 5 h

This evidence seems to suggest that the chain transfer reaction may hardly take place when the growing active chains are short and/or that the grafting process is auto-catalytic. Although, from the chemistry point of view, the significant dependence of radical reactivity on chain length occurs only for very short chains, with long chains their reactivities should be independent of chain length; some very interesting experimental evidence shows that there is some relationship between the length of growing active chains and chain transfer reaction. Barbosa *et al.*[14] have worked on the synthesis of poly(ethylene-*co*-vinyl acetate-*g*-styrene) (EVA-*g*-polystyrene), using EVA modified by mercapto-acetic acid as chain transfer agent, and their results also show that *GE* is very low initially when the number average molecular weight (M_n) of polystyrene is low. More interesting is that with increasing reaction time, both *GE* and M_n of the graft polystyrene branch increase rapidly, while the M_n of polystyrene homopolymer increases initially and very quickly approaches a limiting value of around 10×10^3, which does not increase any further after 24 h of reaction time, although there is still some 45% of monomer to convert. These results indicate that the length of growing active chains appears to be important to chain transfer reaction, which is directly associated with *GE*. The reason why the length of growing active chains (reflected by the molecular weight of the homopolymer) has a significant effect on *GE* is unknown and needs to be studied further. It might be associated with the relative mobility change of the growing active chains, monomers and backbone polymers which contain chain transfer groups, as the length of growing active chains increases, which might affect the competition of chain transfer and chain propagation.

FT*i.r. spectroscopy study.* A Fourier transform infrared spectrometer was used to study the structural changes in PVC after grafting in order to determine how the chain transfer grafting reaction took place. The i.r. spectra of the resultant graft copolymer and its parent homopolymers, PBA and PVC, are shown in *Figures 4–8*.

Figure 4 is the spectrum of pure PVC; the absorption peak at 1250 cm^{-1} shows the absorption band of the C–H group and the peak at 1420 cm^{-1} indicates the characteristic band of the CH_2 group. Between 600 and 700 cm^{-1}, peaks appear at 618 and 688 cm^{-1}, which characterize the absorption band of the C–Cl group in the PVC molecule.

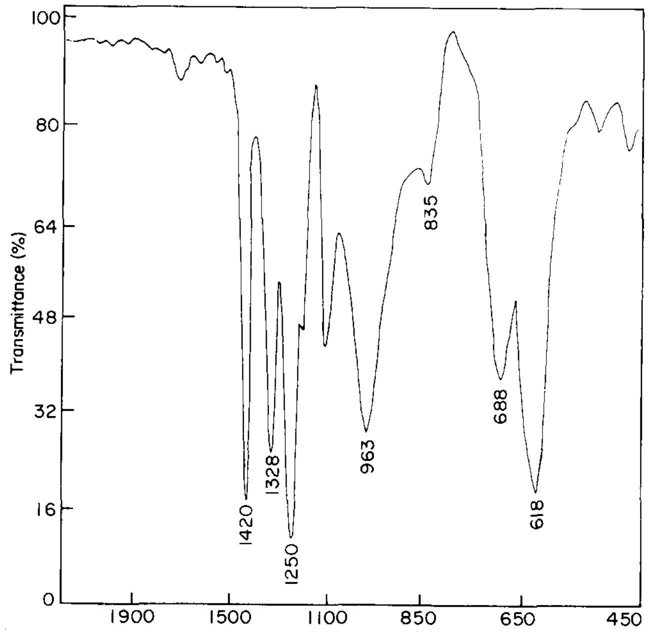

Figure 4 *FT*i.r. spectrum of PVC

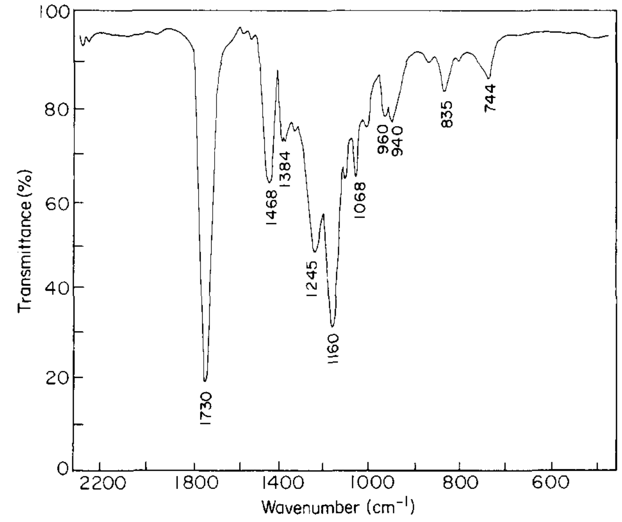

Figure 5 *FT*i.r. spectrum of PBA

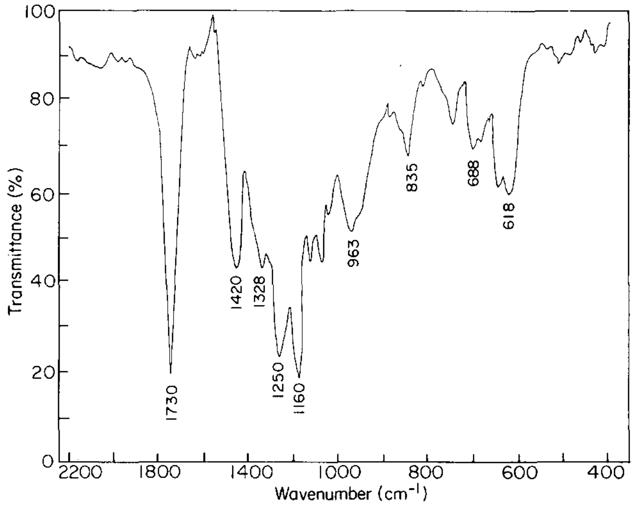

Figure 6 *FT*i.r. spectrum of the graft copolymer

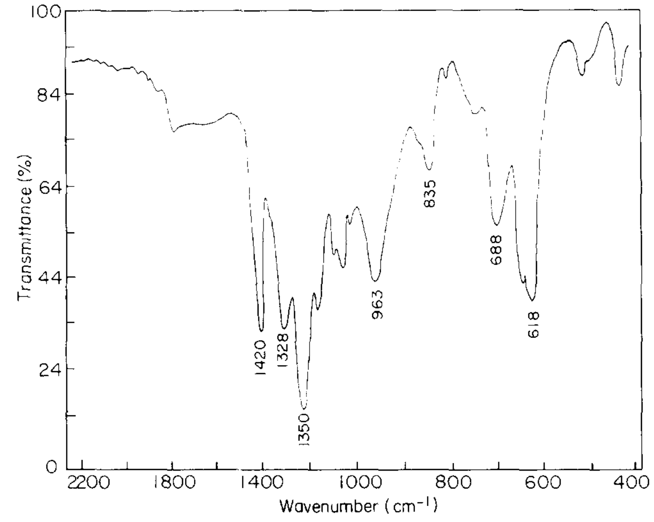

Figure 7 Subtraction spectrum: the graft polymer – PBA

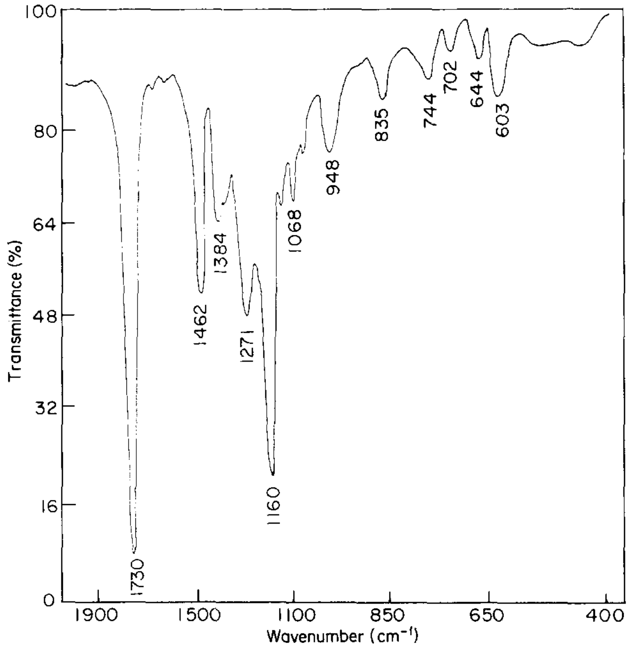

Figure 8 *FT*i.r. spectrum of the PBA homopolymer produced in graft copolymerization

The i.r. spectrum of the graft copolymer is given in *Figure 6* and shows characteristic absorption of both PVC and PBA (*Figure 5*), which has very strong absorption of the carbonyl group at 1730 cm^{-1}.

By comparing *Figure 7*, the i.r. spectrum of the graft copolymer minus the i.r. spectrum of PBA homopolymer, and *Figure 4*, the i.r. spectrum of PVC, it can be seen that they are almost identical, except for some intensity change after grafting; the absorption peak at 1420 cm^{-1}, which characterizes the CH_2 group, has decreased in intensity relative to the CH group absorption peak at 1250 cm^{-1}. This suggests that the chain transfer reaction takes place by removing a methylene hydrogen atom from the PVC molecule, which produces additional CH groups by reducing CH_2 groups.

Compared with *Figure 5*, which is the spectrum of the normal PBA, the i.r. spectrum of the PBA homopolymer (*Figure 8*) produced in the grafting process shows that new weak absorption bands appear at 603, 644 and 702 cm^{-1}, which indicates the possible introduction of low concentrations of C–Cl groups in the PBA homopolymer. This finding is consistent with the hypothesis that the chain transfer reaction also removes a chlorine atom from the PVC, resulting in PBA homopolymer with terminal chlorine atoms.

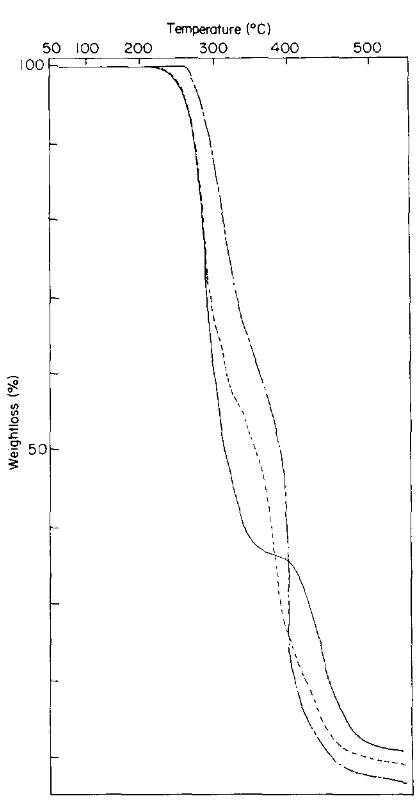

Figure 9 Results of thermogravimetric analysis (in N_2): ——, PVC; – – –, PVC/PBA (80/20) blend; – · – ·, resultant graft copolymer

The *FT*i.r. study therefore implies that chain transfer occurs via both hydrogen abstraction from methylene, and chlorine abstraction.

Thermogravimetric study. Thermogravimetry was used to study the thermal stability of PVC, a blend of PVC and PBA and the graft copolymer of PVC and PBA (the composition ratio of the blend and the graft copolymer is the same, PVC/PBA = 80/20). From the results (*Figure 9*) it can be seen that the thermal stability of the graft copolymer is significantly improved compared to that of PVC, whereas blending results in almost no improvement in the stability of PVC. This can be understood from the *FT*i.r. analysis results: in the chain transfer reaction some chlorine groups of PVC have been taken away, hence reducing the major groups; this results in degradation of PVC, starting with the loss of hydrogen chloride and replacement of chlorine by PBA grafts, leading to interruption of the so-called unzipping and self-catalytic process involved in HCl elimination.

Conclusion

This work demonstrates that the generally accepted view of the effect of temperature on chain transfer grafting needs to be modified, in as much as the increase or decrease in efficiency will be a complicated function of the nature of the substrate polymer, the grafting monomer and the details of the reaction protocol adopted.

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