

# Graft polymerization of acrylamide onto poly(hydroxybutyrate-co-hydroxyvalerate) films

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Graft polymerization of acrylamide onto poly(hydroxybutyrate-co-hydroxyvalerate) (P(HB-co-HV)) film using benzoyl peroxide was studied, and the morphology and properties of grafted film were investigated. The effect of various polymerization conditions such as reaction time, monomer and initiator concentration on the graft% was studied. Graft% was increased initially with the increase of reaction time, monomer and initiator concentration, and levelled off above a certain level. Grafted films with different graft% and film thickness showed different internal structures. To elucidate the morphology of grafted film, characterization methods such as Fourier transform infra-red and X-ray photoelectron spectroscopy and dimensional change analysis were used. It was observed that grafting of polyacrylamide occurred well inside the film, not just being limited to the film surface. Swelling phenomena of grafted film in various solvent mixtures were also investigated in order to test the applicability of the grafted polymers to a permselectivity. © 1997 Elsevier Science Ltd.

(Keywords: P(HB-co-HV); graft polymerization; polyacrylamide)

## INTRODUCTION

Even though polymeric materials have been widely used for their desirable properties such as flexibility, strength, resistance to organic materials, impact resistance, etc., property modifications of polymers using various methods have been extensively studied to further improve the inherent properties<sup>1-19</sup>. Out of these, graft polymerization is a well-known method for the modification of chemical and physical structure to tailor properties for a specific application. This polymerization is of particular interest to achieve specifically designed polymer properties by connecting the different types of polymers having the desired properties in the same polymer chain.

Many polymers, i.e. poly(ethylene terephthalate), polyethylene, polyamide, etc., have been used as a substrate for graft polymerization, and their properties such as strength, colour absorption, adhesion, hydrophilicity and antistatic properties, have been improved<sup>1-19</sup>. The typical method of graft polymerization is a radical polymerization of various monomers initiated by chemical initiators<sup>1-9</sup>, plasma<sup>9-14</sup>, electromagnetic and gamma radiation<sup>15-19</sup>. Out of these methods, chemical initiators have been extensively used for graft polymerization.

Conventional polymeric materials require an extended period of time to be naturally degraded, causing environmental pollution when being discarded.

In order to facilitate the natural degradation process, biodegradable polymers have been widely studied to alleviate the environmental problems<sup>20-22</sup>. Even since the Poly(hydroxyalkanoates) (PHAs), being biodegradable polymers, were first obtained by Lemoign in 1925<sup>20</sup>, various studies on these polymers have been reported to understand their properties such as structure and morphology<sup>23,24</sup>, crystallization behaviour<sup>25,26</sup>, thermal properties<sup>27</sup>, etc. Even though PHAs show excellent biodegradability, their applicability has been severely limited due to their inherent physical properties such as brittleness, thermal instability. Various methods, especially blending with the conventional polymers, have been investigated to improve the properties and processibility of those biodegradable polymers<sup>28-30</sup>.

In this study, graft polymerization of acrylamide onto poly(hydroxybutyrate-co-hydroxyvalerate) (P(HB-co-HV)) film using benzoyl peroxide (Bz<sub>2</sub>O<sub>2</sub>) as an initiator was carried out to modify the physical properties of base polymer and extend its limited applicability. Although graft polymerization onto P(HB-co-HV) is rather difficult due to its high crystallinity and nonactive chemical structure, graft polymerization of acrylamide onto P(HB-co-HV) film was successively achieved in this study. The effect of various parameters, such as initial thickness of base films, reaction time, monomer and initiator concentration of graft%, were also investigated. The morphology of grafted film was examined with various methods. The surface and bulk structure of grafted film was studied with Fourier transform infra-red (FTi.r.) spectroscopy using attenuated total reflectance

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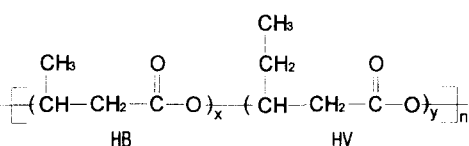


Figure 1 Chemical structure of P(HB-co-HV) copolymer

(ATR) method, and X.p.s. As a preliminary study on the permselectivity of the grafted film, the swelling behaviour was also tested in various solvent mixtures.

## EXPERIMENTS

### Materials

The P(HB-co-HV) copolymer used in this study was provided by ICI<sup>®</sup>. The chemical structure of P(HB-co-HV) is shown in Figure 1. In order to make the base film, the P(HB-co-HV) powder was initially dissolved, using an autoclave, in chloroform to make about 2% (w/v) solution at 80°C for 2 h. The film was then obtained by casting the polymer solution onto the glass plate, followed by drying at the atmospheric condition. The film was further dried in vacuum overnight at 60°C to completely remove the residual solvent. P(HB-co-HV) films of 7.5, 25 and 45  $\mu\text{m}$  thickness were cut to circular discs of 6 cm diameter.

Acrylamide monomer was twice purified by the recrystallization method using acetone and chloroform. Distilled water was used as a solvent for the graft polymerization. All other reagents were used as received.

### Polymerization procedure

The grafting reaction was carried out in a 500 ml polymerization vessel. P(HB-co-HV) film was placed in the vessel containing monomer and benzoyl peroxide ( $\text{Bz}_2\text{O}_2$ ). Prior to the reaction, the polymerization vessel was extensively purged by dry nitrogen gas. Then the vessel was placed into the water bath adjusted to the reaction temperature, i.e. 70°C. The reaction was carried out under  $\text{N}_2$  atmosphere. The film was taken from the polymerization vessel after a specified reaction time, and precipitated into the methanol. There was an extensive homopolymerization in addition to the graft polymerization. Residual homopolymer and unreacted monomer were then removed from grafted film by washing the film in boiling water for 3 h. The washing water was changed at least three times to completely remove the homopolymer residues from the reacted film. This washing procedure gave similar results to those obtained by Soxhlet extracting method done for several hours. Even though there may be a small amount of homopolymer remaining in the film after the washing process due to the physical entanglement, the amount of homopolymer is expected to be small compared with the grafted polymers. It is to be noted that the grafted polyacrylamide chains may loosen the film structure by being swollen in the washing solvent, i.e. water, to facilitate the removal of the physically entangled homopolymers. The film was then dried in vacuum for 12 h. Graft% was calculated from the added weight, i.e.

$$\text{Graft \%} = \frac{W - W_0}{W_0}$$

where  $W_0$  and  $W$  are weights of P(HB-co-HV) base film and grafted film, respectively.

### Fourier transform infra-red spectroscopy

The i.r. spectra were obtained with a Nicolet model 520 FT i.r. spectrometer. The spectra of the film surface were obtained with ATR equipment using germanium crystal. The penetration depth into the film during ATR measurement is about 5–25  $\mu\text{m}$  for the i.r. radiation in mid-i.r. range. The relative composition of P(HB-co-HV) to polyacrylamide was obtained from the absorbance ratio of carbonyl stretching peaks of amide to ester functional groups.

### X-ray photoelectron spectroscopy

The nitrogen content within the top 50  $\text{\AA}$  layer of the grafted film was obtained with S-Probe X.p.s. Prior to measurement, the sample was stored under dry conditions to remove the moisture effect.

### Dimensional change

Dimensional change upon graft polymerization was measured by obtaining the thickness and diameter of grafted film measured with Elcometer<sup>®</sup> and calipers, respectively. The mean value of nine measurements for the different part of the same film was used for the film thickness.

### Degree of swelling

For swelling experiments, water/acetone, water/methanol, acetic acid/methanol and acetic acid/*n*-butanol mixture systems were used. The grafted films having different graft% were immersed in various solvent mixtures of different volume composition at 25°C for 1 h to achieve equilibrium state. The size of these grafted films was measured under the same conditions. The swelling ratio was defined as the volume of swollen film ( $V$ ) relative to its original volume ( $V_0$ ).

## RESULTS AND DISCUSSION

### Graft polymerization

The base polymer P(HB-co-HV) is soluble in such organic solvents as chloroform and dimethyl formamide. However, the grafted chain (polyacrylamide) is not soluble to the above solvents. Since water is a good solvent for polyacrylamide and acrylamide monomers, graft polymerization was done in water. It is to be noted that the base polymer maintained the physical shape during the entire course of graft polymerization resulting in heterogeneous polymerization system.

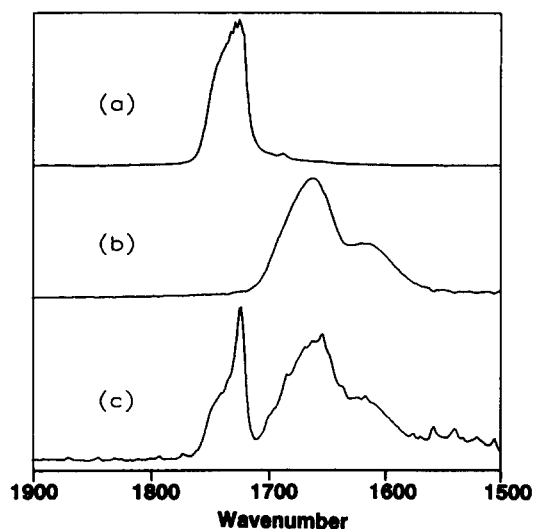
The formation of an appreciable quantity of radicals in polymer chains, which can initiate the grafting reaction, may not be easily achieved due to the heterogeneous reaction system having base polymer film with a high degree of crystallinity. High crystallinity and large amount of the interphase between the crystalline and amorphous region may retard the diffusion of monomers and initiator in the bulk of the polymer film.

In order to investigate the effect of swelling the substrate with solvent and inclusion of monomer and initiator on graft% prior to polymerization, the substrate was treated by various methods before graft polymerization. In the case of poly(ethylene terephthalate) which consists of two parts, semirigid aromatic and flexible

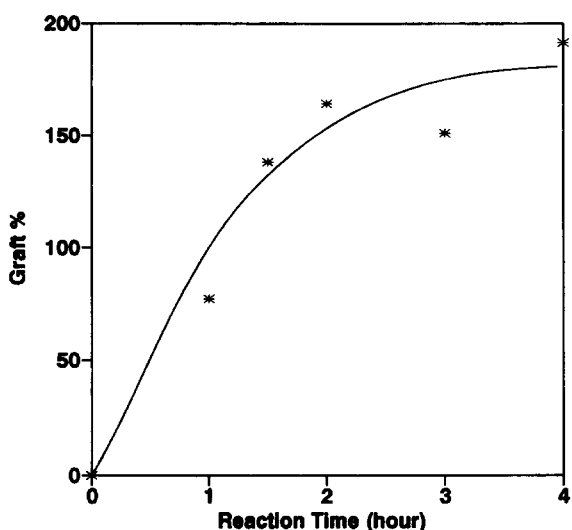
**Table 1** Effect of monomer and initiator inclusion on graft polymerization<sup>a</sup>

| Reagent                   | Time (h) | Graft% |
|---------------------------|----------|--------|
| (a) Untreated             | 0        | 171    |
| (b) Monomer and initiator | 24       | 205    |
| (c) Solvent (swelling)    | 24       | 149    |

<sup>a</sup> reaction conditions: monomer concentration, 7.5 (w/v)%; initiator concentration, 1.8 (w/v)%; reaction time, 2 h; reaction temperature, 70°C; film thickness, 15  $\mu\text{m}$



**Figure 2** FTIR spectra. (a) P(HB-co-HV) copolymer. (b) Polyacrylamide. (c) Grafted film



**Figure 3** Graft% as a function of reaction time (film thickness, 45  $\mu\text{m}$ ). Initiator concentration, 0.45 (w/v)%; monomer concentration, 7.5 (w/v)%; temperature, 70°C

aliphatic segments, the solubility parameter ( $\delta$ ) of the aromatic part ( $-\text{CO}-\text{C}_6\text{H}_4-$ ) is about 9.8, and that of the flexible aliphatic ester ( $-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-$ ) is about 12.1<sup>31</sup>. Since P(HB-co-HV) is aliphatic polyester, its solubility parameter is expected to be close to 12.1. Since the solubility parameter of dimethyl sulfoxide (DMSO) is known to be 12.9 which is close to that of aliphatic ester group, the base film was initially treated with DMSO containing monomer and initiator at room temperature for 24 h prior to graft polymerization. The favourable interaction between this solvent and base

polymer was expected to provide the necessary chemical energy to disrupt intermolecular cohesive forces between polymer chains and permit chain mobility.

Table 1 shows the results of these treatments of graft%. The film treated with monomer and initiator prior to the graft polymerization yielded a slightly higher value of graft% (b). This results may be due to the swelling of the base film with the DMSO resulting in the inclusion of monomer and initiator into the film, which may increase the chance of growing chains to contact monomers. However, for the film treated with DMSO only, a decreased graft% was obtained (c). Even though the exact reason for this decreased graft% is not clear at this stage, this may be caused by the chain transfer from the active growing chain to DMSO. Since the pretreatment of the base film with the DMSO containing monomer and initiator did not increase graft% significantly, all graft polymerizations were done without pretreatment.

Figure 2 shows the carbonyl stretching region of the i.r. spectra of grafted film (c), polyacrylamide homopolymer (b) and P(HB-co-HV) copolymer before graft polymerization (a). The absorption frequency of carbonyl stretching vibrating of the amide group is well separated from that of the ester group. It is clear from the spectrum of grafted film that grafted film showing two separate peaks of ester, and amide groups consists of P(HB-co-HV) copolymer and polyacrylamide. These results demonstrate that graft polymerization of acrylamide onto P(HB-co-HV) film was successively achieved.

The extent of grafting is surprisingly high in view of the fact that the monomer does not penetrate the base film to any appreciable extent. It is to be noted that the pretreatment of the film with monomer and initiator prior to the graft polymerization showed only a minor effect on the grafting, as shown in Table 1. The initial grafting is thus expected to occur at the film surface. Once there are polyacrylamide chains grafted at the surface, they will loosen the structure of the base film by being swollen in the reaction medium, i.e. water, which is a very good solvent to polyacrylamide to facilitate the diffusion of monomers and initiators in the bulk of the base film.

Since the grafted film was not soluble in any common solvents, there were limited methods available to use to get the information on the graft site. It is speculated that the methine protons of P(HB-co-HV), which are the most acidic protons, may be abstracted to generate the radicals initiating the graft polymerization. Unfortunately, the difference of the CH stretching regions of the i.r. spectra between the grafted and control film was too small to decisively point out the graft site. More studies are required to confirm the graft site and to explain the mechanism of the grafting chemistry.

Graft% was measured as a function of reaction time, and the results are shown in Figure 3. Graft% increased rapidly during the earlier reaction period and levelled off after about 2 h. Even though there is a slight increase of graft% after 2 h of reaction time, most of the reaction seems to occur within that period. Therefore all the grafting reactions were terminated after 2 h.

Figure 4 shows the relationship between graft% and initiator concentration. Obviously, graft% increased initially with the increase of initiator concentration and levelled off. Increased graft% was due to the increased chance of the hydrogen abstract from the backbone and

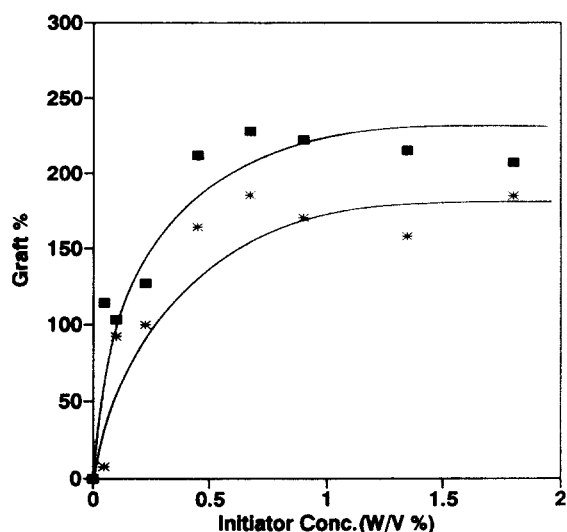


Figure 4 Graft% as a function of initiator concentration (film thickness: ■, 25 μm; \*, 45 μm). Monomer concentration, 7.5 (w/v)%; temperature, 70°C; reaction time; 2 h

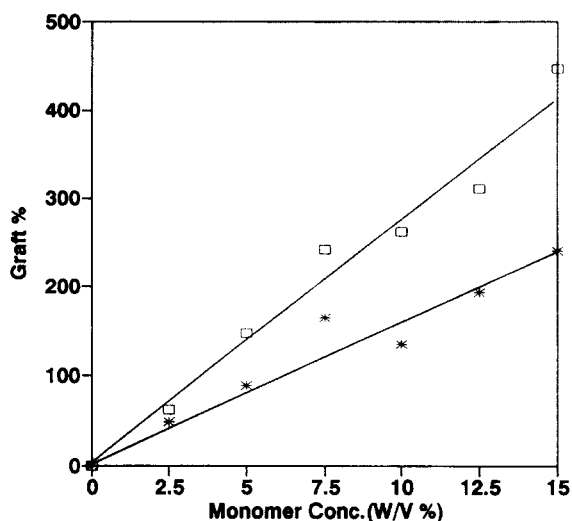


Figure 5 Graft% as a function of monomer concentration (film thickness: □, 7.5 μm; \*, 45 μm). Initiator concentration, 0.45 (w/v)%; temperature, 70°C; reaction time 2 h

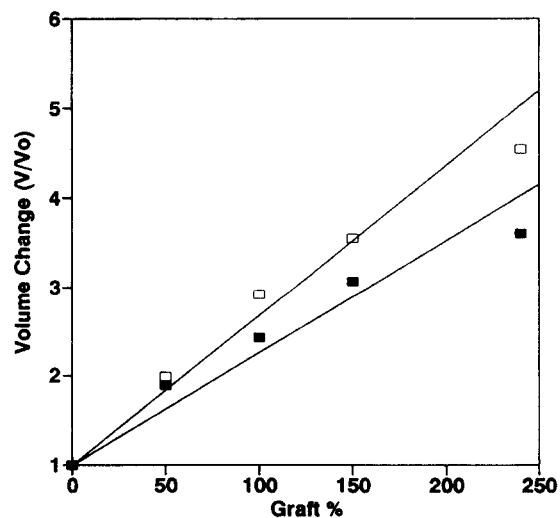


Figure 6 Dimensional change as a function of graft% (film thickness: □, 7.5 μm; ■, 25 μm)

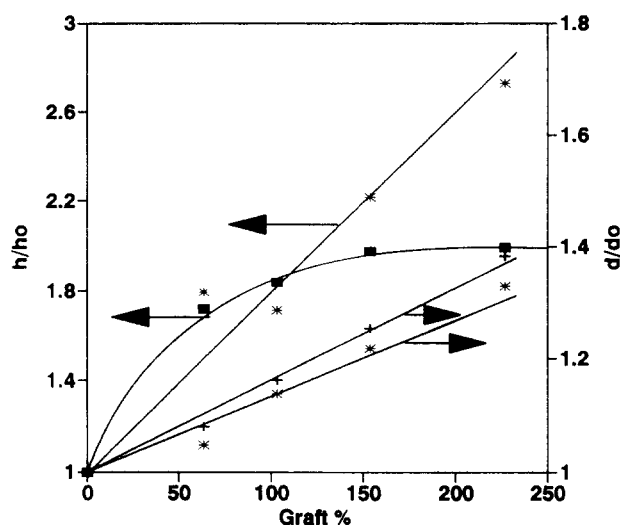


Figure 7 Thickness and diameter change as a function of graft% (film thickness: ■, +, 25 μm; \*, 45 μm). Original film diameter; 6 cm

the chain transfer reaction of polyacrylamide homopolymer to P(HB-co-HV) film. Since the recombination of primary radicals and termination reaction of growing grafted chains can be enhanced at higher initiator concentration, the increase of initiator concentration usually results in the decreased graft%<sup>1-4</sup>. However, levelling off at graft% in Figure 4 may be due to the increased viscosity in the polymerization system resulting in retarded mobility of growing chains. Film thickness also seems to affect the degree of graft%. Thin film showed a consistently higher graft%.

The effect of monomer concentration on graft% is shown in Figure 5. Graft% was almost linearly proportional to monomer concentration. This indicates that increasing monomer concentration seems to increase the monomer concentration inside the film and the chance of growing chains to react with the monomers. There is a noticeable difference between the two sets of data, i.e. graft% of thin (7.5 μm) and thick (45 μm) films. For the given monomer concentration, graft% of the thin film was higher than that of the thick film. These results are consistent with the previous data (Figure 4).

If grafting frequency is higher on the film surface, or if diffusion rate of initiator and monomer into the bulk is not fast enough, the film surface may contain a larger number of grafted chains. Since the diffusion rate of monomer and initiator into the bulk of the film is expected to be independent of the film thickness, saturation of grafted chains within the thin film will be faster, resulting in a higher graft%. The data in Figures 4 and 5 indicate that the graft% is somewhat affected by the specific surface area of the film. This point will be discussed further with X.p.s. data.

#### Dimensional change and graft process

Dimensional change of grafted film as a function of graft% is shown in Figure 6. With the increase of graft%, it was observed that dimensional change increased almost linearly. However, dimensional change of grafted film having different film thicknesses seems to follow different paths. Figure 7 shows thickness and diameter change as a function of graft%. In the case of thin film, thickness increased rapidly at low graft% and levelled off. This indicates that initial volume change was mainly

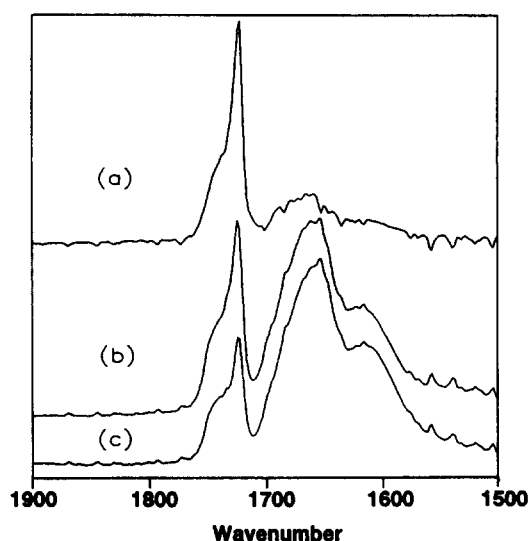


Figure 8 ATR spectrum of the grafted film (graft%: (a) 37.5%, (b) 147%, (c) 266.8%)

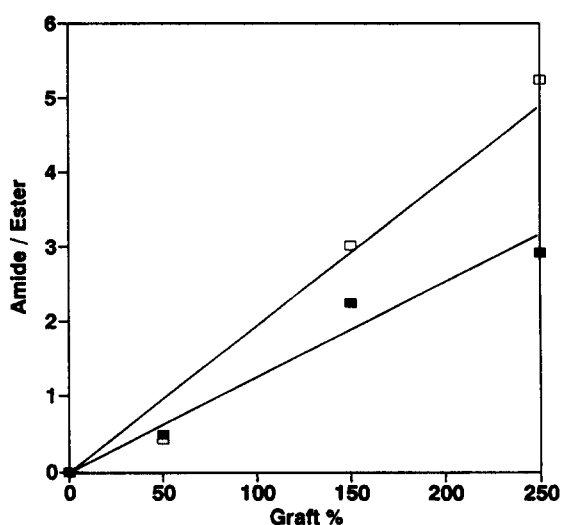


Figure 9 Relative intensity of carbonyl stretching peak of amide group to ester group as a function of graft% (film thickness: □, 7.5  $\mu\text{m}$ ; ■, 25  $\mu\text{m}$ )

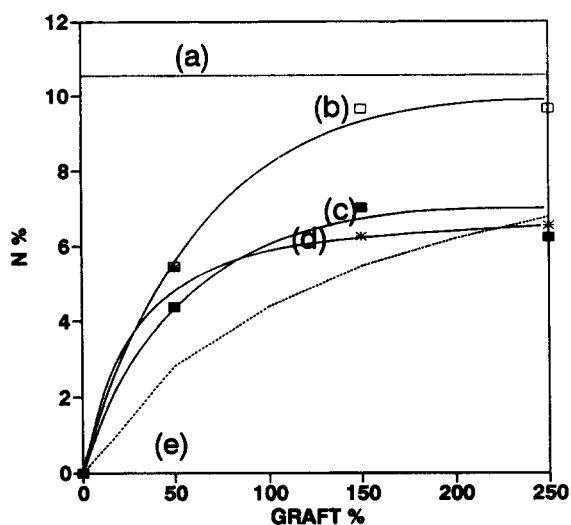


Figure 10 Nitrogen content of film surface as a function of graft%: (a) pure polyacrylamide; (b) 7.5  $\mu\text{m}$  film; (c) 25  $\mu\text{m}$  film; (d) 45  $\mu\text{m}$  film; (e) calculated based on the homogeneous mixture of two polymers

due to the thickness change for the thin film. Dimensional change of the thick film showed a different tendency. Thickness and diameter increased almost linearly with graft% for the graft% range studied. These results indicate that, for the thin film, the grafting frequency is increased rapidly at lower graft%. The saturation of grafted chain within the thin film is faster. Thus, most of the thickness change is obtained at lower graft%. However, for thick film, the grafting frequency is increased continuously with graft%, which could be the reason for the continuous increase of film thickness.

#### Bulk phase structure

The graft polymerization of the acrylamide chain can be further studied with the FTi.r.-ATR method. Figure 8 shows three ATR spectra of grafted films having different graft%. These spectra show two distinct carbonyl stretching peaks, i.e. one at  $1720\text{ cm}^{-1}$  corresponding to the ester groups of the base film and another at  $1670\text{ cm}^{-1}$  corresponding to the amide groups of the grafted acrylamide chains. The intensity ratio between these two peaks are shown in Figure 9 as a function of graft% calculated from the added weight. The correlation between the two sets of data are reasonably good within the experimental error. Even though the exact distribution of the grafted chain along the thickness direction cannot be assessed from these results, due to the relatively high penetration depth of the i.r. radiation, it is clear that the ratio between the two peaks of the thin film is always higher than that of the thick film. This seems to indicate that for the thin film the intensity ratio is more affected by the acrylamide chain preferentially residing at the surface.

#### Surface phase structure

The concentration of grafted chains at the top surface (within a top layer of about  $75\text{ \AA}$  thickness) was obtained with X.p.s. experiments. Since only the acrylamide chains have nitrogen atoms, the relative amount of grafted chains can be obtained from the nitrogen signals of the X.p.s. measurements. Figure 10 shows nitrogen content as a function of graft% for different film thicknesses. The lower dot line represents calculated nitrogen content assuming the homogeneous mixture of two polymers for the given graft%, and the upper dot line shows that of the polyacrylamide homopolymer. Polyacrylamide concentration at the film surface increased rapidly, and levelled off at high graft%. With graft% higher than 150%, the polyacrylamide concentration of the thin film is almost comparable with that of pure polyacrylamide. This result indicates that the top surface of the thin film is covered almost completely with polyacrylamide chains. However, the nitrogen content of the thick film appears to be similar with that value calculated based on the homogeneous mixture. For the thick film, penetration of the grafted chain into the bulk of the film continued to occur at this graft% level. These results are consistent with those in Figure 7.

Judging from the results mentioned above, it can be concluded that the morphology of the grafted film seems to be affected by the specific surface area of the base film. Although grafted film contained a higher polyacrylamide concentration at the film surface at low graft%, grafting was not limited to the film surface. The bulk of the film appears to be mixed with polyacrylamide chains, even

though the exact distribution of polyacrylamide is dependent on the film thickness.

#### Degree of swelling

Generally, polyesters are hydrophobic materials. However, grafted film has a hydrophilic property, due to the grafted polyacrylamide chains which are soluble in water. Since two polymers, i.e. P(HB-co-HV) copolymer and polyacrylamide, are soluble in very different solvent systems, it was speculated that permselectivity for various solvent mixtures may be achieved. Initial results regarding the permselectivity of the grafted film was not desirable, due to the large pore size of the grafted film observed with scanning electron micrographs. If the grafted film is crosslinked with a proper crosslinking agent or if the non-porous solid film is obtained by controlling the degree of graft%, permselectivity for certain solvent mixtures may be improved. In this work, the volume phase transition phenomenon of the grafted film was studied in various solvent mixtures as a

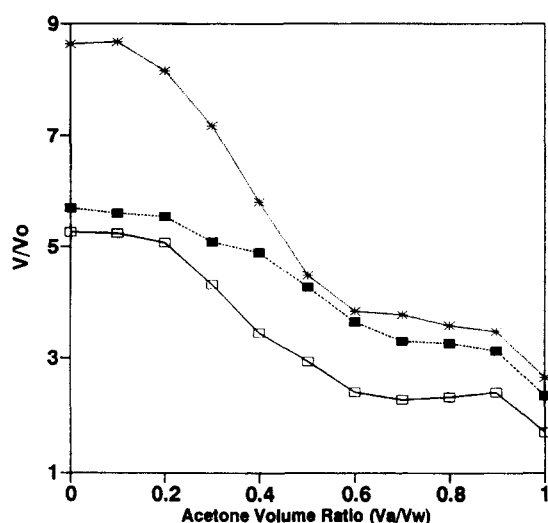


Figure 11 Swelling ratio as a function of composition in a water-acetone solvent system (graft%: 250%; film thickness: □, 7.5 μm; ■, 25 μm; \*, 45 μm)

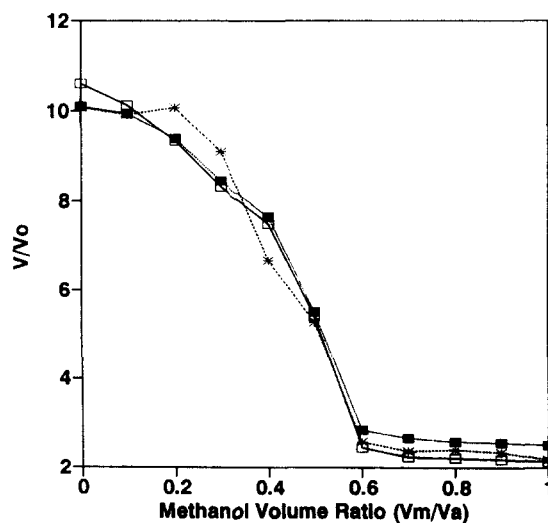


Figure 12 Swelling ratio as a function of composition in an acetic acid-methanol solvent system (graft%: 250%, film thickness: □, 7.5 μm; ■, 25 μm; \*, 45 μm)

preliminary study on the structure of the grafted film in the mixed solvent environments.

There are several types of intermolecular forces inducing swelling and volume phase transition, i.e. van der Waals, hydrogen-bond and ionic forces<sup>32</sup>. Swelling behaviour is also affected by temperature and degree of crosslink in a polymer network. In this study, various solvent mixtures were used at room temperature. Degree of swelling of the grafted film generally increased with graft% for the solvent system studied. However, the swelling behaviour of the grafted film was very sensitive to film thickness, and composition of solvent mixture.

Figure 11 shows the degree of swelling as a function of solvent composition in a water-acetone solvent system. Similar results were obtained with a water-methanol solvent system. If water is used in the solvent mixture, a higher swelling ratio was obtained with the thicker film for all solvent compositions. Since the thicker film contains a large amount of grafted acrylamide chains for the given graft%, the higher swelling ratio seems to be mainly affected by the acrylamide chains.

Figure 12 represents the degree of swelling as a function of solvent composition in an acetic acid-methanol solvent system. Using acetic acid as a good solvent, swelling behaviour showed a very different tendency from the previous results. Contrary to the previous results, swelling ratio is not dependent on the film thickness. Also, the volume phase transition is clearly observed at about 50/50 mixture and the swelling ratio is larger than the previous results. This behaviour may be due to the strong interaction between the amide groups of the grafted chain and the acid groups in acetic acid. Acetic acid can penetrate into the film easily, and swell the film evenly. In addition, acetic acid swells pure P(HB-co-HV) film about 12%. The clear volume transition behaviour appears to be related to the internal structure change. The exact structural variations and the applicability of this behaviour to permselectivity need to be investigated further. A similar tendency was observed in the acid-*n*-butanol solvent mixture.

#### CONCLUSIONS

The polyacrylamide was successfully grafted onto the P(HB-co-HV) copolymer film, in spite of its high crystallinity and nonactive chemical structure.

The applicability of biodegradable polymer, P(HB-co-HV), appears to be extended by the graft polymerization. The effect of various polymerization conditions, such as monomer concentration and reaction time, on graft polymerization were also studied. In general, increasing the initiator concentration above a certain level decreases the graft%, due to the increased probability of the termination reaction, through the combination of the growing active chains. However, the decreased graft% was not observed at the initiator concentration examined in this study. This behaviour seems to be due to the heterogeneous nature of the reaction, which may retard the mobility of the grafted chain.

The bulk of grafted film appears to be mixed with polyacrylamide chains, even though the exact distribution of grafted chains along the thickness direction may be dependent on the film thickness. The saturation of polyacrylamide chains appears to be faster with thin film than with thick film and film surface has a higher polyacrylamide concentration. For the thick film (45 μm),

the bulk of the film may not be saturated at the highest graft% (250%) studied here. These results indicate that the exact distribution of the grafted chain is affected by the specific surface area of the base film.

Swelling behaviour was also studied in various mixed solvent systems. For the given graft%, thick film showed a higher swelling ratio if water is used as a good solvent. In the case of the solvent system containing acetic acid as a good solvent, the swelling ratio was not affected by the film thickness. This is due to the very strong interaction between the amide group in the grafted chain and the acid group in acetic acid. The clear volume transition behaviour was also observed. The swelling ratio is drastically changed at certain volume ratios (for example, 60% of methanol mixed with 40% acetic acid). This abrupt volume decrease is expected to be related to the internal structural variation. Further study on the morphology of the grafted film in the mixed solvent environment is needed, in order to test the applicability of this type of volume transition behaviour to a permselectivity.

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