4.12 The Effect of Monomer Molecular Weight on Grafting Reaction

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Abstract

In this paper, some condensed ethylene glycol acrylate monomers with different molecular weight being grafted to the PE film by means of pre-irradiation is reported. The effect of molecular weight of monomer on grafting reaction and the hydrophilicity of grafting sample have been discussed. The experimental results show: molar degrees of grafting decreased non-linearly with the increasement of molecular weight of monomer, the grafting reaction of polymer is greater effected by the swelling degree of PE film, the greater the swelling degree of grafting material, the higher the grating degree grafting is, the initial rate of grafting reaction decreased with the increasement of molecular weight of monomer.

Keywards:
pre-irradiation, grafting polymerization, biomedical material

Introduction

Currently many researchers have performed investigations on improving the biocompatibility of biomedical material. Improving the surface hydrophilicity of this kind of material is considered as one of the effective methods. Many reports about grafting hydrophilic monomer (for example methyl acrylic- β -hydroxyl ethylester, N -vinylpyrrolidone, acrylamide) are being published continuously,but in most of these grafting experiments,low molecular weight chemical as monomer was used[1-3], one disadvantage of such system is difficult to control the grafting chain structure. To make the grafting chains more regular and controlabe, it is a good way to graft polymers instead of low molecular weight monomer[4,5]. So it is most important to study the effect of molecular weight on grafting, so far, all about these havn't been reported. In our experiments we adopted the method of pre-irradiation to graft condensed ethylene glycol acrylate on PE film, and studied the effect of molecular weight on grafting reaction.

Experimental

Low density PE film ($50\times30\times0.08mm^3$, PE 579-50, Shanghai Plastic Film Factory) was used as substrate which was irradiated by EB at a dose rate of 667 Gy/s, dose of 50KGy in ambient condition. The grafting reaction was carried out in a test tube which contained monomer, condensed ethylene glycol acrylate (synthesized by our laboratory), cyclohexane-n-propynal mixture as grafting medium and the pre -irradiated PE film. The grafting reaction was achieved by storing the test tube at 90℃ for desired time under N_2 protection. The degrees of grafting and ratio of water absorption were defined as:

$$G = \frac{W_d - W_o}{W_o} \times 100$$

$$H = \frac{W_w - W_d}{W_o} \times 100$$

Where: G —— degree of grafting

H —— ratio of water absorption

W_d — net weight of grafted film

W_o — net weight of ungrated film

W_w — weight of grafted film and its absorbing water

Results and Discussion

1.| The process of grafting reaction

Fig.1 is the kinetic curve of grafting reaction in 90℃, monomer concentration is 20% and the solvent proportion of cyclohexane/n-propynal is 2/1. Fig.1 indicates that the degree of grafting was proportional to reaction time in the initial stage, the reaction rate is constant. The reaction rate is controlled by monomer diffusion in grafting reaction, in the case of the lower change ratio of monomer, the monomer concentration is nearly constant,so the diffusion rate and the reaction rate are constant. The reaction rate reduces with the reaction going on, and finally it tends to zero. Because the active centers which come from pre-irradiation are gradually consumed till they are exhausted. The degrees of grafting tend to saturate.

The relationship between the initial reaction rate of grafting and molecular weight of monomer is shown in Fig.2 (Fig.2 and following figures are the same reaction condition as Fig.1). It is clear from Fig.2 that the initial rate of grafting linear decreased with the increasement of molecular weight of monomer. Under the same reaction condition, the diffusion rate becomes less as the molecular weight of monomer is increasing, therefore the rate of grafting reaction controlled by monomer diffusion drops down.

2. The saturate degree of grafting and molecular weight of monomer

Fig.1 shows that the degrees of grafting are not increase in pace with the reaction time after it get to the maximum we call this maximum degree of grafting as saturate degree of grafting. Fig.3 is the relationship between the saturate degrees of grafting and molecular weight of monomer. The saturate degrees of grafting linear reduce with the growing of molecular weight of monomer. If divide degree of grafting by monomer molecular weight, we obtain:

$$G_m = \frac{G}{M} = \frac{W_d - W_o}{M \cdot W_o} = \frac{W_d - W_o}{M} \cdot \frac{1}{W_o}$$

where: M is molecular weight of monomer, W_d-W_o can be considered as the weight of material which have been grafted on PE sample, so $(W_d - W_o)/M$ is the mole number of monomer forming grafting sample. We call G_m the molar grafting degrees which means the mole number of grafting monomer of the unit weight sample. Fig.4 shows the ralationship between the saturable molar grafting degree and the molecular weight of monomer. It's different from Fig.3 that the influence of molecular weight on the saturate molar grafting degrees is greater in the case of lower monomer molecular weight, but with the monomer molecular weight increasing, the influence on the saturate molar grafting degrees becomes smaller.

3. Solvation

In grafting reaction system, solvent influences greatly the grafting reaction, it is connected with grafting-depth, grafting reaction rate and grafting degree. We use the mixture of cyclohexane/n-propynal as solvent. Fig.5 shows how the change of solvent influences the grafting degree, each grafting degree of the three systems reduces with the rising of the proportion of n-propynol. In addition, the change of grafting degrees tend to relax after one turn point of solvent proportion. The turn point goes in the direction of increasing of n -propynal constituent. n-propynal isn't good solvent of PE, but cyclohexane is. Therefore the reducing of n-propynal constituent leads the swell ability of PE to enhance and the monomer molecular to diffuse, so the degree of grafting rises. The higher the molecular weight of monomer, the more diffcult the diffusion is,so high molecular monomer is more sensitive to the swell ability and the turn point come to earlier (in the direction of increasing of the cyclohexane constituent)

4. Hydrophilicity of the sample

Ratio of water absorption can be considered as one of the expressions of hydrophilicity. The hydrophilicity of material becomes better as the ratio of water-absorption is increasing. Fig.6 shows the relationship between the ratio of water absorption and the grafting degree of sample.The ratio of water absorption is almost in proportion to the grafting degree. Each slope (k) of the line in Fig.6 is:

$$K = \frac{H}{G} = \frac{W_w - W_d}{W_d - W_b}$$

where K is the weight of water absorption of the unit weight, it's to be said absorption ratio. Fig.6 shows with the increasement of the molecular weight of grafting monomer, the absorption ability decrease because of the increasement of grafting monomer condensed ethylene glycol acrylate and the decreasement of proportion of the -OH whose hydrophilicity is the best.

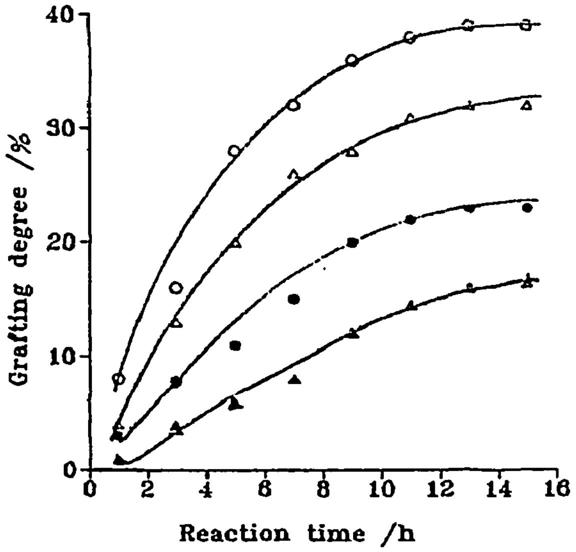

Fig.1 The kinetics curves of grafting reaction
- o acrylic acid
- △ ethylene glycol acrylate
- ● condensation diethylene glycol acrylate
- ▲ condensation triethylene glycol acrylate

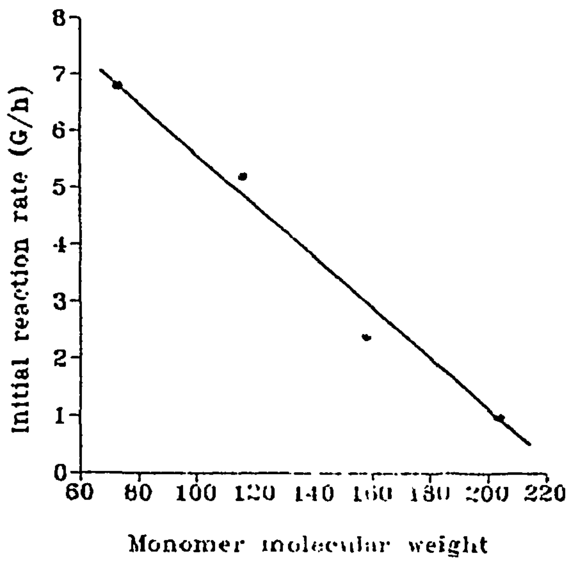

Fig.2 The relationship between molecular weight of momer and initial reaction rate

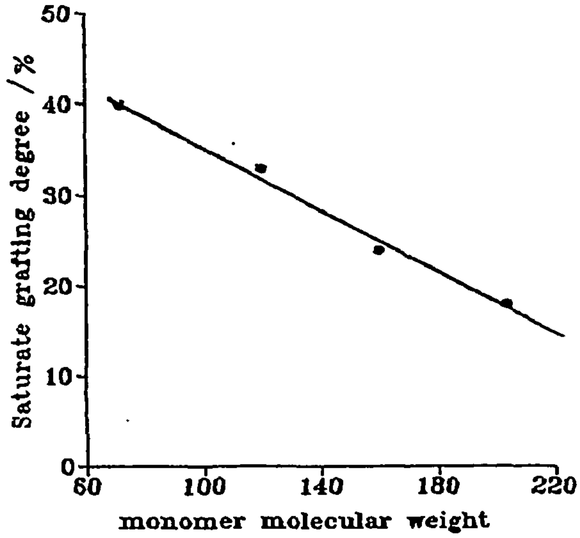

Fig.3 The influence of molecular weight of monomer on saturate degree of grafting

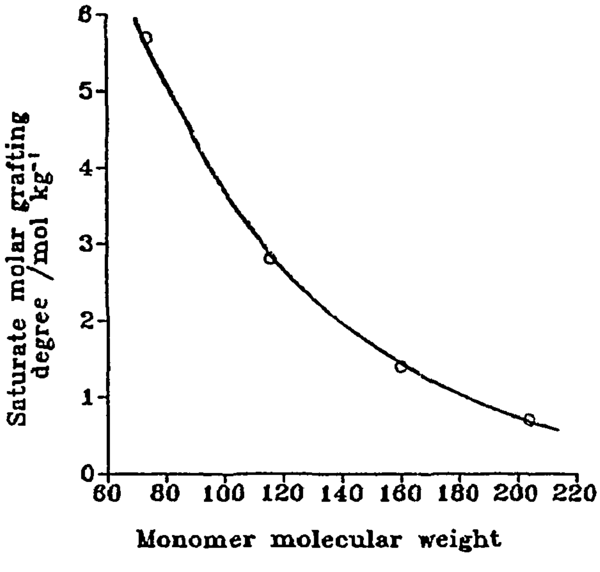

Fig.4 The influence of monomer molecular weight on the saturate molar grafting degree

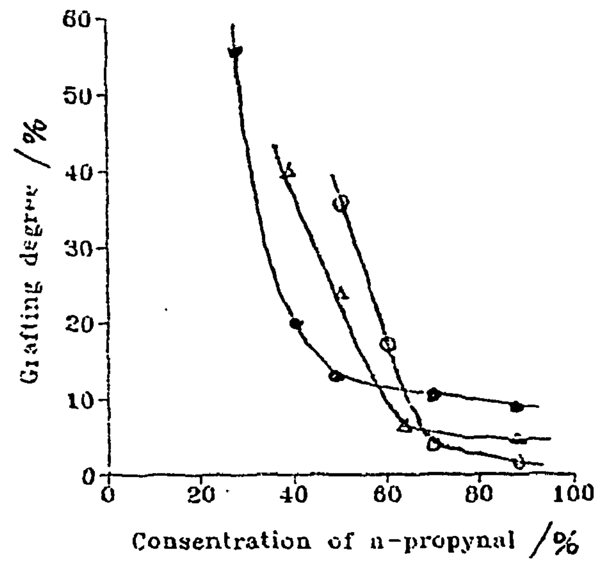

Fig.5 The influence of solvent on grafting degree

• -- acrylic acid,
△ -- ethylene glycol acrylate,
○ -- condensation diethylene acrylate.

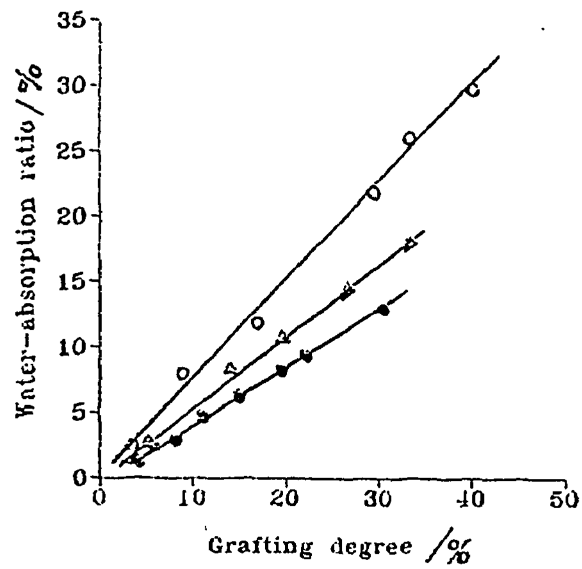

Fig.6 The relationship between the ratio of water absorption and grafting degree

○ -- acrylic acid,
△ -- ethylene glycol acrylate,
○ -- condensation diethylene glycol acrylate.

References

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