

THE EFFECT OF MONOMER MOLECULAR WEIGHT OF ACRYLATE ON RADIATION GRAFTING OF POLYETHENE

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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 that molar degree of grafting decreased non-linearly with the increment 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 degree of grafting is, the initial rate of grafting reaction decreased with the increment of molecular weight of monomer.

KEYWORDS Pre-irradiation, Grafting polymerization, Biomedical material, Polyethene, Acrylate

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 controllable, 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 haven't been reported. In this paper, we adopted the method of pre-irradiation to graft condensed ethylene glycol acrylate on polyethene (PE) film, and studied the effect of molecular weight on grafting reaction.

1 Experimental

Low density PE film($50 \times 30 \times 0.08 \text{ mm}^3$, PE 579-50, Shanghai Plastic Film Factory)

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was used as substrate which was irradiated by EB at a dose rate of 667 Gy/s, dose of 50 kGy 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 N₂ protection. The degrees of grafting and ratio of water absorption were defined as:

$$G = \frac{W_d - W_0}{W_0} \times 100\%$$

$$H = \frac{W_w - W_d}{W_0} \times 100\%$$

where, G—degree of grafting. H—ratio of water absorption. w_d—net weight of grafted film, w₀—net weight of ungrafted film, w_w—weight of grafted film and its absorbing water.

2 Results and Discussion

1.1 The process of grafting reaction

Fig. 1 is the kinetic curve of grafting reaction in 90℃, monomer concentration 20% and the solvent proportion of cyclohexane/n-propynal 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

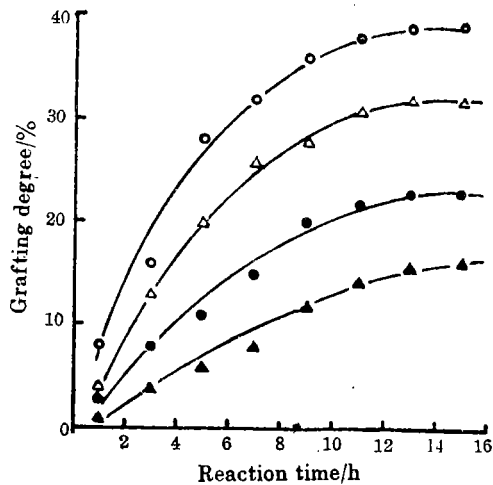


Fig 1. The kinetics curves of grafting reaction
 (○) acrylic acid (△) ethylene glycol acrylate
 (●) condensation diethylene glycol acrylate
 (▲) condensation triethylene glycol acrylate

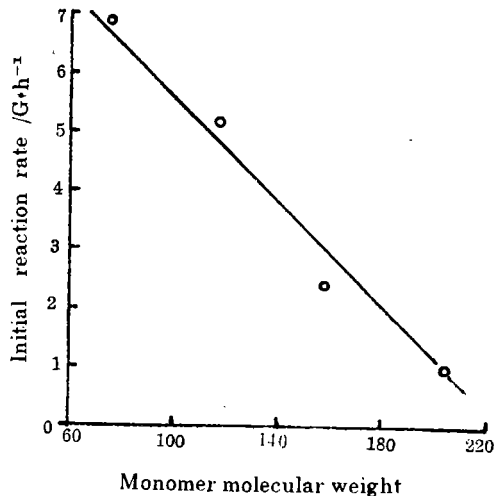


Fig 2. The relationship between molecular weight of monomer and initial reaction rate

condition as Fig.1). It is clear from Fig.2 that the initial rate of grafting linear decreased with the increment 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.

1.2 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:

$$G_m = \frac{G}{M} = \frac{w_d - w_0}{Mw_0} = \frac{w_d - w_0}{M} \cdot \frac{1}{w_0}$$

where: M is molecular weight of monomer, $w_d - w_0$ can be considered as the weight of material which have been grafted on PE sample, so $(w_d - w_0)/M$ 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 relationship between the saturable molar grafting degrees and the molecular weight of monomer. It's different from Fig.3 that the influence of molecular weight on the saturate molar grafting degree 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.

1.3 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*-propynal. In addition, the change of grafting degrees tend to relax after one turn point of solvent proportion. The turn point goes

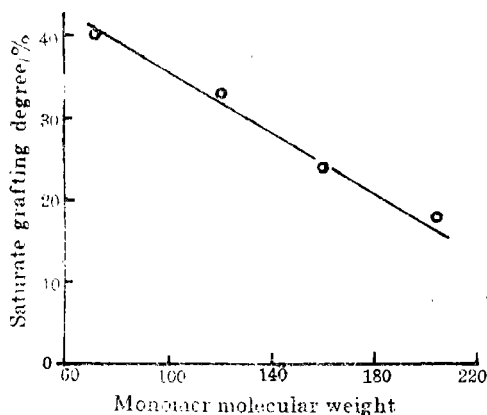


Fig 3. The influence of molecular weight of monomer on saturate degree of grafting

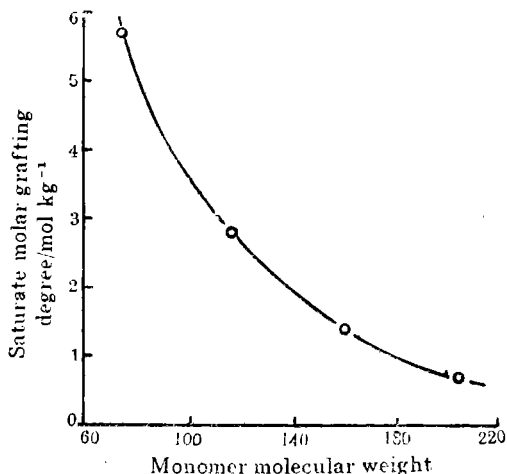


Fig 4. The influence of monomer molecular weight on the saturate molar grafting degree

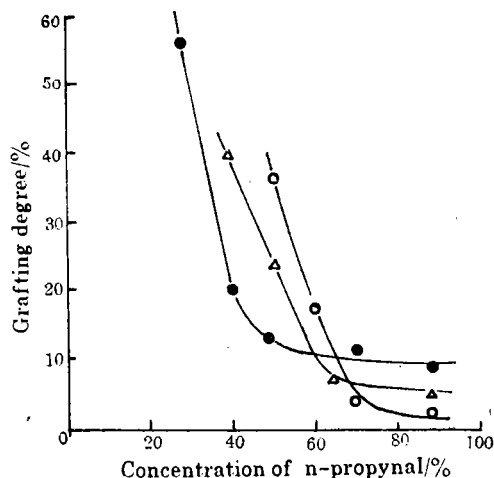


Fig 5. The influence of solvent on grafting degree
 (●) acrylic acid
 (△) ethylene glycol acrylate
 (○) condensation diethylene acrylate

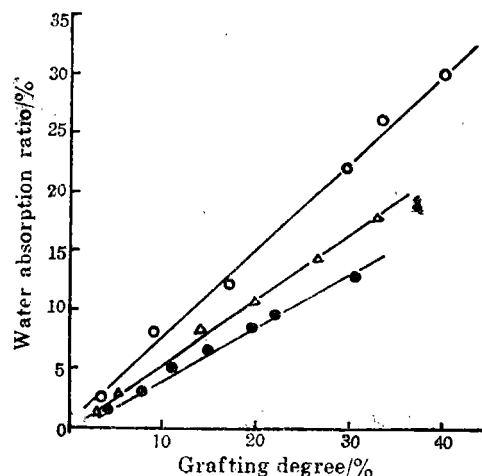


Fig 6. The relationship between the water absorption ratio and grafting degree
 (○) acrylic acid (△) ethylene glycol acrylate (●) condensation diethylene glycol acrylate

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 difficult 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).

1.4 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:

$$K = \frac{H}{G} = \frac{w_w - w_d}{w_d - w_0} 100\%$$

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

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KINETIC OBSERVATION OF RAPID ELECTRON TRANSFER BETWEEN THYMINE AND THYMIDINE ANION RADICALS AND CAFFEIC ACID:

A PULSE RADIOLYSIS STUDY

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ABSTRACT Utilizing pulse radiolysis and kinetic spectrophotometric monitoring techniques, rapid electron transfer reaction from thymine and thymidine anion radicals to caffeic acid was observed respectively. Anion radicals of caffeic acid with absorption maximum at 360 nm have been generated via foregoing electron transfer reaction with rate constant of $1 \times 10^9 \text{ mol}^{-1} \text{ L s}^{-1}$. Accordingly the subsequent protonation of thymine anion radicals should be prevented by the electrophilic protector. These kinetic demonstrations have provided direct evidence of charge transfer protection mechanism.

KEYWORDS Caffeic acid, Thymine, Electron transfer, Charge transfer, Radiation protection

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不同分子量的丙烯酸酯对聚乙烯辐射接枝的研究

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摘要 利用预辐射方法, 在聚乙烯薄膜上接枝不同分子量的缩乙二醇丙烯酸酯单体。研究单体不同分子量的变化对接枝反应和接枝样品亲水性等的影响。结果表明: 摩尔接枝率随单体分子量增加而非线性地降低; 接枝基材的溶胀程度对分子量较大的单体的接枝反应影响较大; 试片溶胀度越大, 接枝率越高; 单体分子量增加, 接枝反应初速度下降。

关键词 预辐射, 接枝聚合, 生物医用材料, 聚乙烯, 丙烯酸酯