

Radiation-Induced Graft Polymerization of Vinyl Benzyltrimethylammonium Chloride onto Polyethylene Film

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SYNOPSIS

An attempt was made to introduce a strong base anion-exchange group by radiation-induced grafting of vinyl benzyltrimethylammonium chloride (VBTAC) onto polyethylene film. Both two-step grafting and comonomer grafting techniques were tried owing to the difficulty of direct graft polymerization of VBTAC onto polyethylene. 2-Hydroxyethyl methacrylate (HEMA) and ethyl methacrylate (EMA), having the same backbone structure except that the hydroxyl group of HEMA was grafted onto the polyethylene film and then VBTAC was grafted to examine the reactivity of VBTAC with each grafted polyethylene film. Co-grafting of the binary mixtures of VBTAC and HEMA, or EMA, onto polyethylene film was also carried out. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Graft polymerization of vinyl monomer onto the polyethylene substrates has attracted considerable interest because it imparts some desirable properties such as biocompatibility,¹ ion exchange,²⁻⁴ dyeability, and protein adsorption.⁵

Graft polymerization can be carried out by ionization radiation, ultraviolet light, plasma, or chemical initiators. Among these techniques, radiation-induced grafting is one of the most effective methods because of its large penetration in the matrix and its rapid and uniform creation of active radical sites on the existing polymer matrix. The methods of achieving graft polymerization using radiation include (1) simultaneous irradiation⁶ of the backbone polymer in the presence of the monomer, (2) preirradiation⁷ of the backbone polymer in vacuum or nitrogen gas and subsequent monomer grafting by trapped radicals, and (3) preirradiation of the backbone polymer in the presence of oxygen and subsequent monomer grafting by polymeric peroxides.⁸

In this experiment, a preirradiation grafting method in the presence of nitrogen gas was used to synthesize a strong base anion-exchange membrane, which is important for electro dialysis. It has been reported that an indirect method to introduce a strong base anion-exchange group such as quaternary ammonium salt could be carried out by grafting of styrene onto a polymer substrate, followed by chloromethylation and amination with a tertiary amine.⁹ However, a strong base resin frequently shows abnormalities that are not observed with a cation-exchange resin because of the harsh reaction of chloromethylation. In the present study, an attempt was made to graft vinyl benzyltrimethylammonium chloride (VBTAC) containing quaternary ammonium salt onto a polyethylene film radiolytically using a preirradiation method. Both two-step grafting and comonomer grafting methods were used owing to the difficulty of grafting VBTAC onto the polyethylene film directly.

EXPERIMENTAL

Materials

Commercial high-density polyethylene film (Asahi Chemicals Co.) with a thickness of 25 microns was

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used as a substrate for graft polymerization. A technical grade of vinyl benzyltrimethylammonium chloride (VBTAC, $\text{CH}_2=\text{CHC}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_3\text{Cl}$) (Seimi Chemical Co.), 2-hydroxyethyl methacrylate (HEMA, $\text{CH}_2\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{OH}$), and ethyl methacrylate (EMA, $\text{CH}_2\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_3$) (Kishida Chemical Co.) were used as received. Other chemicals were of reagent grade.

Grafting Procedure

The films were irradiated by passing them under the electron beams of a cascade-type accelerator (Dynamitron IEA 300-25-2, Radiation Dynamics Ltd.) operating at beam energy of 1.5 MeV and current of 1 mA. The irradiation was carried out under a nitrogen gas atmosphere. The irradiated films were immersed in the monomer solution that was prepared with given monomers with solvents and deaerated by bubbling nitrogen. A mixture of methanol/dimethylformamide (1/1 volume ratio) was used as a diluent in these experiments. After the prescribed time, the grafted films were removed from the monomer solution in glass ampules and washed with methanol to remove the remaining homopolymer. The degree of grafting was determined as the following:

Degree of grafting (%)

$$= (W_g - W_0)/W_0 \times 100 \quad (1)$$

where W_g and W_0 are the weights of the grafted and the starting film, respectively. The extent of VBTAC grafted onto the polyethylene substrates was determined by measuring the salt-splitting capacity of the final grafted polyethylene. The grafted polyethylene was immersed into 2 M NaOH solution to convert the Cl form of VBTAC into the OH form and then washed with distilled water. The quantity of NaOH liberated by immersing the grafted polyethylene film with the OH form into 5 wt % NaCl solution was calculated by titration with 1/50 M HCl. The amounts of HEMA and EMA grafted onto the polyethylene substrates were determined by subtracting the VBTAC content in the copolymer from the total amount of grafted copolymer.

ESR Measurement

The radical concentration was measured by an ESR spectrometer (JES-FE3X, JEOL). Immediately after the irradiation at a dose of 100 kGy, the irradiated polyethylene film was stored at 195 K in a dry ice

box. The irradiated polyethylene film was sealed in an ESR tube with a silicone stopper. The tube was placed in a TE011 cylindrical cavity. A microwave of the X band (9 kHz band) was applied at 10^{-3} mA output and 100 kHz frequency of a magnetic field of modulation. All measurements were carried out at 77 K in liquid nitrogen.

X-ray Microanalysis

The graft distribution in the polymer substrate was observed by an X-ray microanalyzer (JXA-superprobe 773, JEOL) after the VBTAC/HEMA-grafted polyethylene film with the Cl form was dried under reduced pressure. The grafted film was cut perpendicularly to its surface at the liquid nitrogen temperature and its cross section was observed. The X-ray microanalyzer was operated at an accelerating voltage of 25 kV and current of 2.5×10^{-8} A.

RESULTS AND DISCUSSION

An attempt in the present work was made to introduce the strong base anion-exchange group by radiation-induced grafting of VBTAC onto the polyethylene film. Both the two-step grafting and comonomer grafting techniques^{10,11} were tried owing to the difficulty of direct graft polymerization of VBTAC onto the polyethylene film.

HEMA and EMA, having the same backbone structures except for the hydroxyl group of HEMA, were grafted first onto the polyethylene film and then VBTAC was grafted after a second irradiation onto each grafted film to examine the reactivity of VBTAC with the hydrophilic monomer (HEMA)-grafted polyethylene film or the hydrophobic monomer (EMA)-grafted polyethylene film. As shown in Figure 1, VBTAC cannot be directly grafted onto polyethylene because the VBTAC monomer with a highly ionized $\text{N}(\text{CH}_3)_3$ group is hardly compatible with hydrophobic polyethylene. However, it was possible to induce the grafting of VBTAC by improving the compatibility by the hydrophilization of polyethylene with HEMA. The degree of grafting of VBTAC after the second irradiation onto the HEMA-grafted polyethylene film increased with the increasing of the degree of HEMA grafting onto the polyethylene film. On the other hand, in the case of the polyethylene film modified by the hydrophobic EMA monomer, the grafting reaction of VBTAC with the EMA-grafted polyethylene film was poor compared to that of VBTAC with the hydrophilic HEMA-grafted polyethylene film.

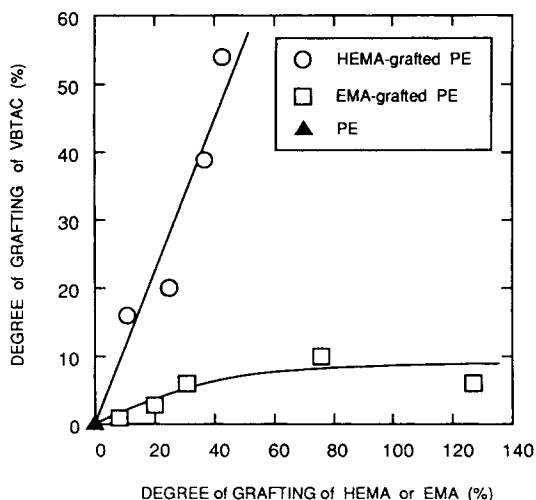


Figure 1 Degree of grafting of VBTAC onto the polyethylene film pregrafted with HEMA and EMA. VBTAC concentration: 1 M; grafting temperature: 70°C; radiation dose: 100 kGy.

The radical concentration of HEMA- or EMA-grafted polyethylene film after irradiation with an electron beam at a dose of 100 kGy was measured by ESR. Figure 2 shows the variation of radical concentrations vs. the degree of grafting of HEMA and EMA onto the polyethylene film. The radical concentration decreased in general with increasing degree of grafting regardless of the HEMA- or EMA-grafted polyethylene film, since most of the radicals were expected to be trapped more in the crystalline

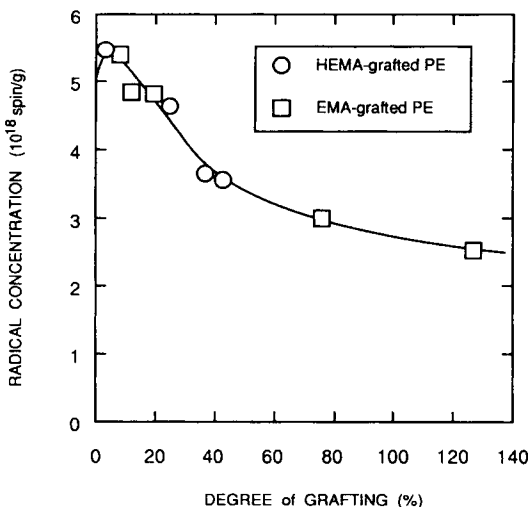


Figure 2 Relation between radical concentration and the degree of grafting when HEMA-grafted PE and EMA-grafted PE were irradiated at a total dose of 100 kGy under nitrogen gas.

region of polyethylene than in the amorphous region formed by pregrafting. It is expected that some radicals decay when the molecular chains in the amorphous region are sufficiently mobile to cause the recombination of radicals. We can find that the degree of VBTAC grafting depends directly on the hydrophilicity of the pregrafted film from the fact that the degree of VBTAC grafting onto the HEMA-grafted polyethylene film was much higher than that of VBTAC grafting onto the EMA-grafted polyethylene film even though two grafted chain polymers have almost the same radical concentration.

To demonstrate further the reactivities of VBTAC onto the hydrophilic and hydrophobic polymer substrates, direct preirradiation graft polymerization of VBTAC was tried onto the hydrophilic polymer, such as HEMA-grafted polyethylene and cellulose, and onto the hydrophobic polymer, such as polyethylene, polypropylene, and polytetrafluoroethylene (PTFE), as shown in Figure 3. As expected, direct grafting of VBTAC onto the hydrophobic polymer substrates was impossible except for only a little grafting yield on the EMA-grafted polyethylene film that has a polar carbonyl group.

Cografting of VBTAC with HEMA or EMA onto the polyethylene film was carried out to introduce the quaternary ammonium salt group onto the polyethylene film effectively. Individual HEMA and EMA were also used for grafting to examine the variation of the degree of grafting between mixed monomers and an unitary monomer (Fig. 4). The

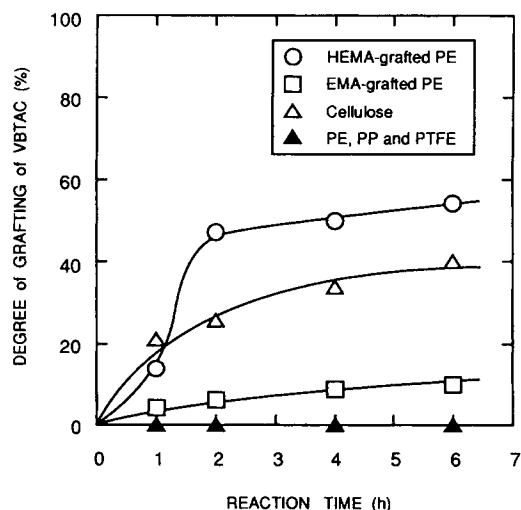


Figure 3 Degree of grafting of VBTAC onto 43% HEMA-grafted polyethylene, 76% EMA-grafted polyethylene, cellulose, polyethylene, polypropylene, and polytetrafluoroethylene. Grafting conditions are the same as in Figure 1.

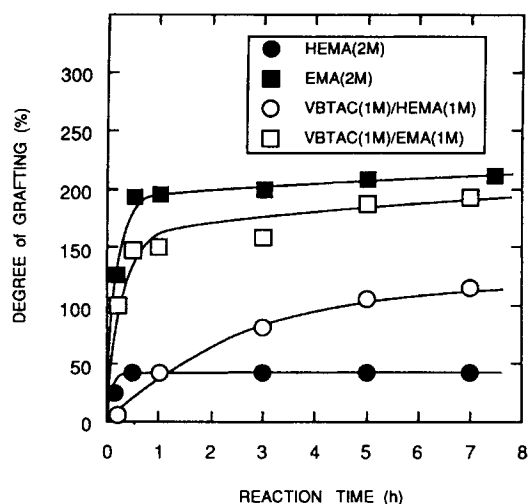


Figure 4 Effect of reaction time on the degree of grafting of HEMA, EMA, VBTAC/HEMA mixture, and VBTAC/EMA mixture onto the polyethylene film. Grafting temperature: 70°C; radiation dose: 200 kGy.

degree of grafting of the grafted copolymers obtained from HEMA and EMA increased sharply with the reaction time and leveled off within 30 min. EMA had higher grafting yield compared to that of HEMA. The degree of grafting of VBTAC/EMA increased drastically at the initial reaction time under the influence of a high grafting rate of EMA. The grafting rate of VBTAC/EMA was also higher than that of VBTAC/HEMA.

Figure 5 shows the respective molar ratios of VBTAC/HEMA and VBTAC/EMA in the copol-

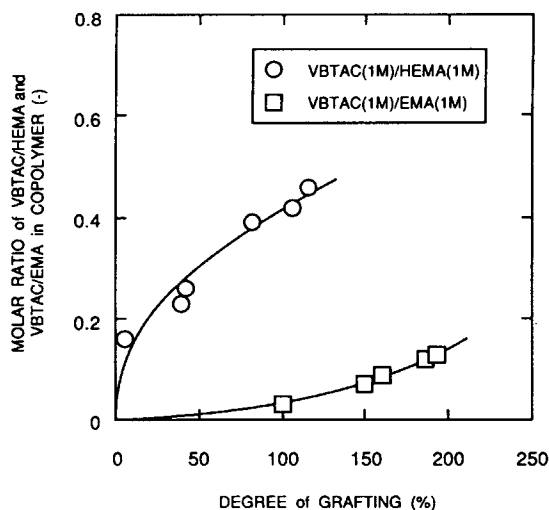


Figure 5 Molar ratios of VBTAC/HEMA and VBTAC/EMA in the copolymer vs. the degree of grafting. Grafting conditions are the same as in Figure 4.

mer vs. the total degree of grafting when VBTAC(1M)/HEMA(1M) and VBTAC(1M)/EMA(1M) were grafted onto the polyethylene film, respectively, as shown in Figure 4. The molar ratios of VBTAC/HEMA or VBTAC/EMA in the copolymer increased with increasing the total degree of grafting. The reason for the continuous increase in molar ratios of VBTAC/HEMA or, in particular, VBTAC/HEMA, in the copolymer with increasing the total degree of grafting can be attributable to the following fact that VBTAC in the beginning of grafting reaction can hardly be grafted onto the polyethylene film owing to the extremely low accessibility of VBTAC with the hydrophobic polyethylene film, but can be easily grafted onto the HEMA-grafted polyethylene film only after HEMA is grafted onto the polyethylene film. The molar ratios of VBTAC/HEMA in the copolymer were higher than those of VBTAC/EMA since it is assumed that reactivity of VBTAC with HEMA is larger than that of VBTAC with EMA. The schematic illustration of grafting of VBTAC/HEMA mixtures onto the polyethylene film is shown in Figure 6.

When the binary mixtures of VBTAC and HEMA were used for graft polymerization onto polyethylene, grafting begins at the surface and then proceeds to the inner side of the polymer substrate with a continuous diffusion of VBTAC and HEMA. To examine the distribution of the grafted layer when the VBTAC (1M)/HEMA (1M) mixture was used for grafting, the cross section of the VBTAC/HEMA-grafted film was observed using an X-ray microanalyzer. As shown in Figure 7, the grafting proceeds from the both surface to the central part of the film. With a 101% grafting yield, the grafting proceeds thoroughly to the inner side of the polyethylene substrate with a high distribution at the outside layer of the film.

Figure 8 shows the total degree of grafting with respect to the VBTAC/HEMA mixture of varying proportions and the addition of trimethylolpropane

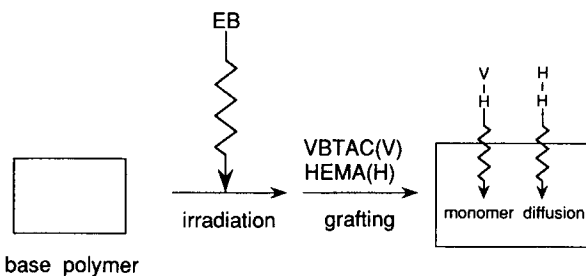


Figure 6 Schematic illustration of grafting of VBTAC/HEMA comonomer onto polyethylene.

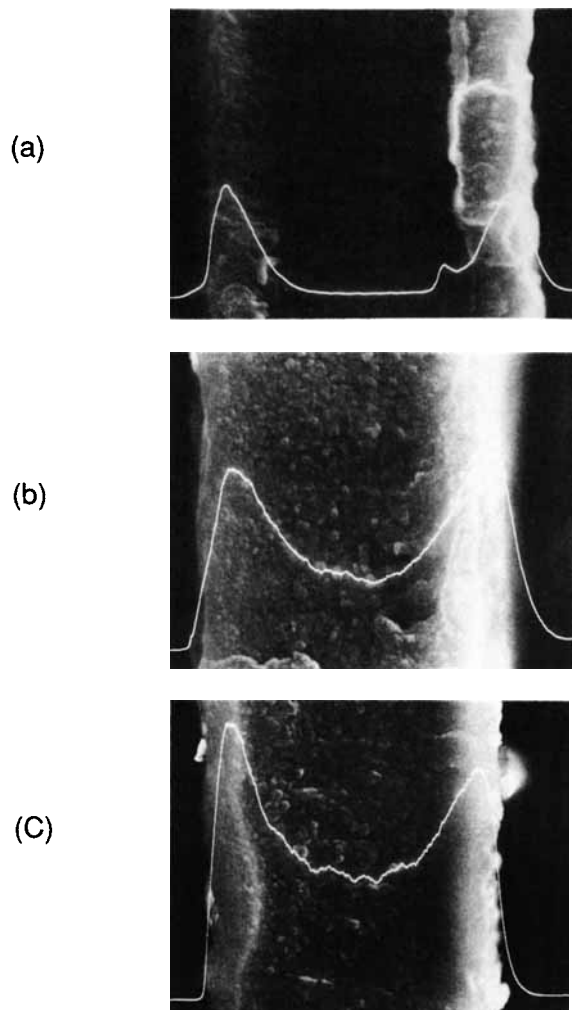


Figure 7 XMA micrographs of VBTA C/HEMA-grafted polyethylene films: (a) degree of grafting 18%; (b) degree of grafting 57%; (c) degree of grafting 101%.

triacrylate (TMPTA). The degree of grafting increased with increase in the proportion of HEMA and the reaction time. The use of TMPTA as an additive was shown to enhance the grafting yield of VBTA C/HEMA onto the polyethylene film. Dworjanyn and Garnett¹² reported that a number of different classes of additives such as mineral acid and polyfunctional monomers are useful for accelerating the grafting reactions initiated by UV and ionizing reaction. In this experiment, TMPTA appears to have dual functions that involve the enhancement of the grafting rate and the cross-linking of the grafted poly-VBTA C/HEMA chains. The cross-linking can be formed when one end of TMPTA is bonded to the growing VBTA C/HEMA chains or polyethylene and the other unsaturated end initiates

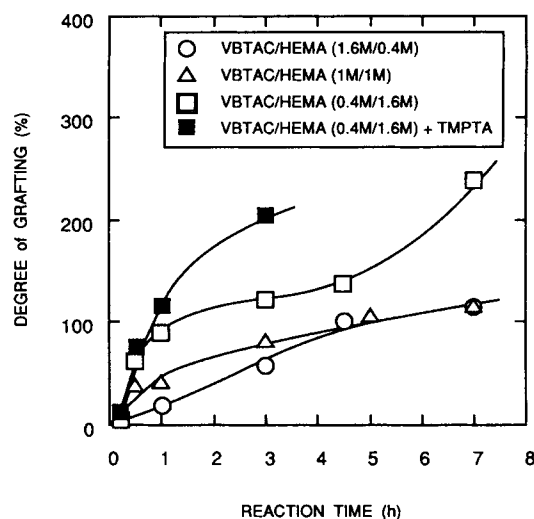


Figure 8 Degree of grafting of comonomer vs. comonomer composition. Grafting temperature: 70°C; radiation dose: 200 kGy; TMPTA concentration: 0.01 M.

a new chain growth. The new branched VBTA C/HEMA might eventually be cross-linked by reacting with another poly-VBTA C/HEMA chain. The grafting rate increases mainly through the branching of the growing grafted chains. Figure 9 shows the respective molar ratios of VBTA C/HEMA in the copolymer vs. the degree of grafting when varying proportions of VBTA C/HEMA were grafted onto the polyethylene film, as shown in Figure 8. In the case of low grafting yield, the amount of VBTA C entering the copolymer is much lower than that of HEMA irrespective of the feed ratio of the mono-

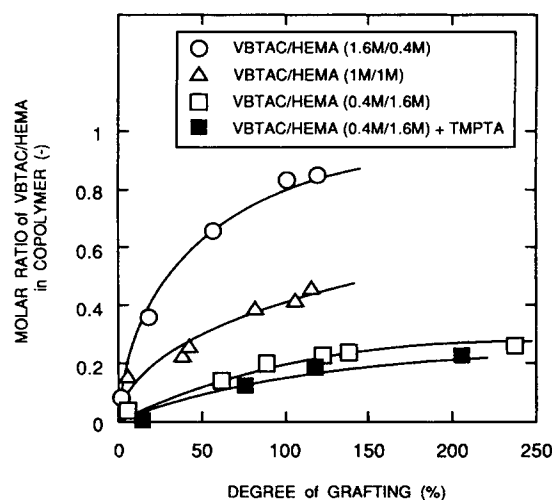


Figure 9 Molar ratios of VBTA C and HEMA in the copolymer for various feed ratios. Grafting conditions are the same as in Figure 8.

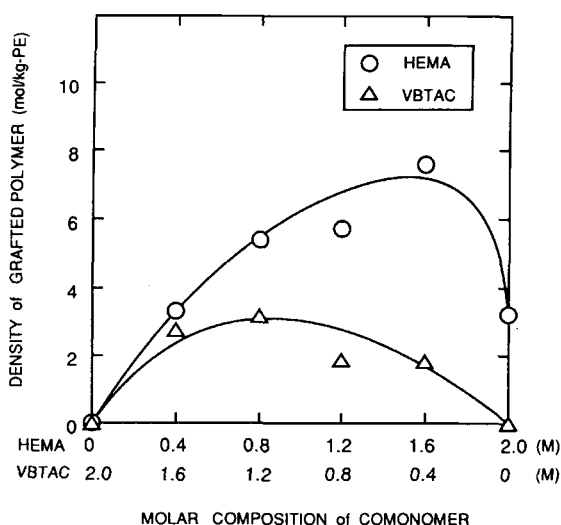


Figure 10 Density of VBTAC/HEMA grafted onto the polyethylene film vs. the comonomer composition. Grafting temperature: 70°C; radiation dose: 200 kGy; reaction time: 4.5 h.

mers. However, the molar ratios of VBTAC/HEMA in the copolymer were directly proportional to those of the VBTAC/HEMA feed. It was found that the addition of TMPTA in the grafting solution reduced the content of VBTAC in the copolymer. This may be attributed to the lower reactivity of TMPTA with VBTAC than that of TMPTA with HEMA. In Figure 10, the density of VBTAC and HEMA in the copolymer was shown by mol/kg of polyethylene substrate as a function of feed ratios of VBTAC and HEMA. The optimum comonomer composition, at

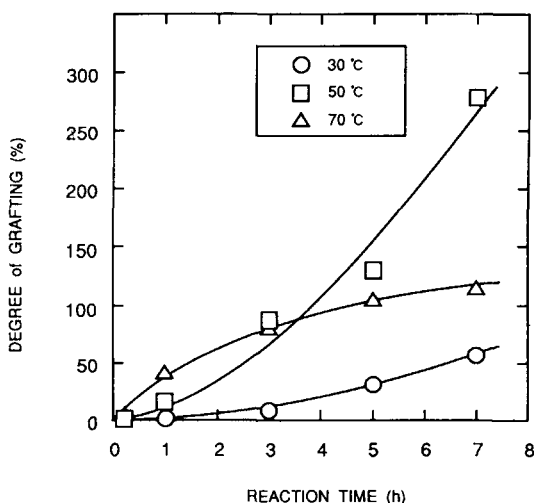


Figure 11 Effect of reaction temperature on the degree of grafting of VBTAC/HEMA onto the polyethylene film. Grafting conditions are the same as in Figure 4.

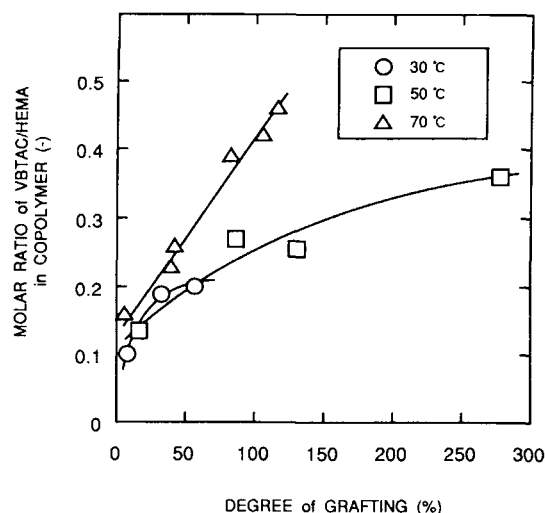


Figure 12 Effect of reaction temperature on molar ratios of VBTAC/HEMA in the copolymer. Grafting conditions are the same as in Figure 4.

which a high content of VBTAC in the copolymer was obtained, was found at the feed ratio of VBTAC (1.2M)/HEMA (0.8M). When HEMA (2M) alone was taken in the grafting solution, the grafting yield was about 3 mol/kg of polyethylene substrate. However, when HEMA was used in the binary mixtures of VBTAC, the synergistic effect of HEMA was observed at all proportions of monomers in the binary mixtures.

Figure 11 shows the degree of grafting-time curves of VBTAC (1M)/HEMA (1M) at temperatures of 30, 50 and 70°C. The initial rate of grafting increases drastically at 70°C and then gradually levels off. Since the decay of trapped radicals is enhanced at a higher temperature, the grafting reaches the final grafting yield faster. On the other hand, although the initial grafting rate at low temperature was low, the grafting yield continued to increase until 7 h because the amount of trapped radicals decreased slowly with increasing reaction time. The molar ratios of VBTAC/HEMA in the grafted chain obtained at 30, 50 and 70°C are shown in Figure 12. The molar ratios of VBTAC and HEMA in the grafted chain changed at a high degree of grafting. A higher molar ratio of VBTAC/HEMA was obtained at a higher temperature. This may be attributed to the change in diffusion rate of monomers into the polyethylene film.

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