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Solvent Effects in the Graft Copolymerization of Methyl Methacrylate to Polypropylene

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ABSTRACT

Methyl methacrylate can be readily graft copolymerized to polypropylene film by mutual γ -irradiation in vacuo. Graft yields in excess of 1000% can be obtained at low total doses (0.1 Mrad) and dose rates (0.05 Mrad/hr). When the monomer is diluted with solvent mixtures, similar yields can be obtained at lower monomer concentrations due to an accelerative effect. Besides swelling of the polypropylene, the results indicate the importance of solvent on the reaction kinetics of the growing poly(methyl methacrylate) radicals. A possible explanation of the effect of diluent is presented in terms of polymer chain entanglement.

INTRODUCTION

Although radiation-initiated grafting of monomers to polymer substrates by the mutual irradiation technique has been extensively studied [1-3], the influence of diluents on the process is still not satisfactorily explained. An accelerative effect of diluent on the rate of grafting was first reported by Dobo [4], and since then extensively

explored by Odian [5, 6] in the system polyethylene-styrene-methanol. Silverman [7] concluded from his studies of this system that the observed maximum graft rate is an optimum resulting from a high concentration of absorbed monomer and a low viscosity for the poorly swelled polymer matrix. However, this seems to be insufficient as a general explanation since high graft rates can be found for systems in which the diluent, and not the monomer, swells the substrate. This is shown by the effect of water or alcohols on the grafting of styrene to nylon [8]. Thus these systems indicate the importance of swelling of the substrate and effect of solvent on the grafted polymer. Wilson [9] has attempted to rationalize the observations by using monomer-solvent mixtures which should swell the substrate in a predictable manner based on their Hildebrand solubility parameter. For mixtures with the same solubility parameter, the graft rate was found to increase as the monomer concentration increased.

The effect of diluent mixtures on the grafting yield has received little attention. The reports that do exist are those involving aqueous systems in the grafting of monomer to poly(vinyl alcohol) [10], cellulose [11], and nylon [12]. Recent work by the present authors has shown that an accelerative effect of diluent can be obtained over a range of monomer concentrations by the use of diluent mixtures.

EXPERIMENTAL

Methyl methacrylate monomer was washed with a 5% aqueous solution of sodium hydroxide, 10% aqueous solution of sodium chloride, and distilled water, dried with anhydrous magnesium sulfate, and vacuum distilled just before use. Blown polypropylene film (50 μm), produced from unpigmented polymer containing no antislip, antistatic, or antiblock additives, was supplied by Shell Chemical (Aust.) Pty. Ltd. The film was extracted with acetone in a hot Soxhlet extractor for 48 hr and dried before use. Specimen size for each irradiation experiment was 25 mm \times 15 mm. All irradiations were conducted at 25°C under vacuum (10^{-4} mm Hg) in 13 mm \times 100 mm borosilicate glass ampoules with a ^{60}Co γ -ray source at a dose rate of 6×10^4 rad/hr. All monomer solutions were prepared on a weight percent basis, and 5 ml of grafting solution was used. The graft yield, expressed as $(W - W_0)/W_0$, where W_0 is the initial weight of the film, was determined from the weight increase after removal of homopolymer by extraction with acetone.

Swelling was determined by measurement of the change in linear dimensions of strips of film immersed in the grafting mixtures.

RESULTS AND DISCUSSION

When methyl methacrylate is grafted to polypropylene from methanol or benzene solution the results shown in Fig. 1 are obtained.

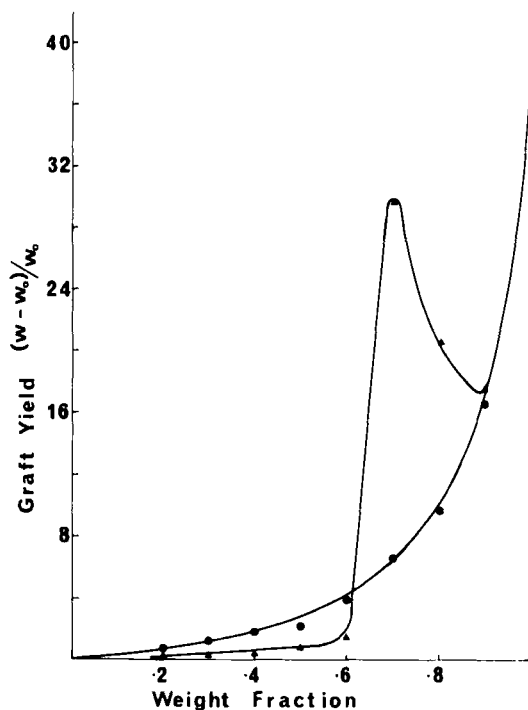


FIG. 1. Variation of graft yield with concentration of methyl methacrylate when diluted with (●) benzene or (▲) methanol.

Unlike methanol, on using benzene as a diluent no accelerative effect is observed as the monomer concentration is reduced. However, when some of the methanol in a 1:1 mixture of methanol with methyl methacrylate is replaced by benzene, an optimum is found at 10% benzene as shown in Fig. 2. Similar data are obtained for grafting reactions at other methyl methacrylate concentrations, as expressed in Fig. 3 which shows how the yield varies for the whole range of concentrations of monomer, methanol, and benzene.

The swelling of polypropylene by the range of mixtures methyl methacrylate 50%-methanol $(50-x)\%$ -benzene $x\%$ is shown in Fig. 4, which indicates that a gradual increase in volume of the polymer film is found as the benzene concentration increases. Thus it appears unlikely that the very sharp increase in graft rate, as seen in Fig. 2, can be explained on the basis of a sharp increase in monomer concentration in the polymer, especially as with benzene concentrations greater than 10% the graft yield again falls. Benzene, besides being a swelling agent for polypropylene, is also a good solvent for poly(methyl

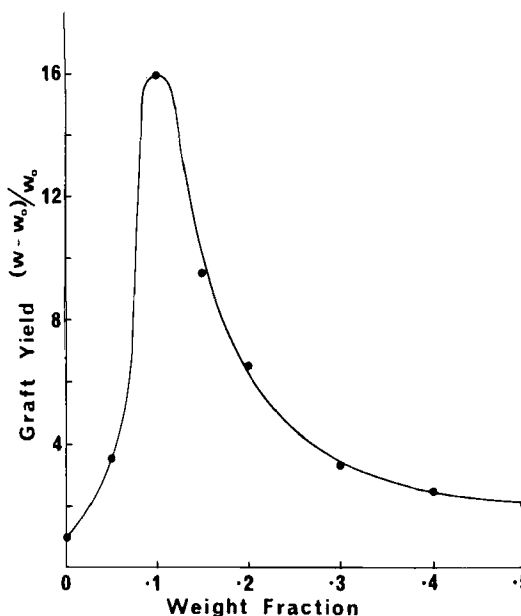


FIG. 2. Variation of graft yield with benzene concentration; methyl methacrylate fixed at 0.5 weight fraction, and the weight balance provided by methanol.

methacrylate) (PMMA) and thus the change in graft yield with benzene concentration will therefore be a reflection of how the propagation and termination rate constants of polymerization vary with swelling of the substrate and the grafted monomer.

The high grafting rates which are shown at the optima in this system may be due to the same factors which produce the well known gel effect in the bulk polymerization of methyl methacrylate. This phenomenon has recently been elaborated by Cardenas [13] in terms of polymer chain entanglement. The extent of entanglement is dependent on the molecular weight. Once the propagating polymer chain length exceeds a critical value at which entanglement can occur, the termination rate constant is greatly reduced while the propagation rate constant is hardly affected, so giving rise to a large increase in polymerization rate. Entanglement would also be expected to be medium dependent in that polymer chain extension will vary with the composition of the solvent mixture. For good solvents the entanglement will be reduced, thus allowing easier termination and a reduction in rate as observed at high benzene concentrations. At low benzene concentrations the low rate of grafting would then be due to a reduced propagation rate constant such as that found in bulk polymerizations

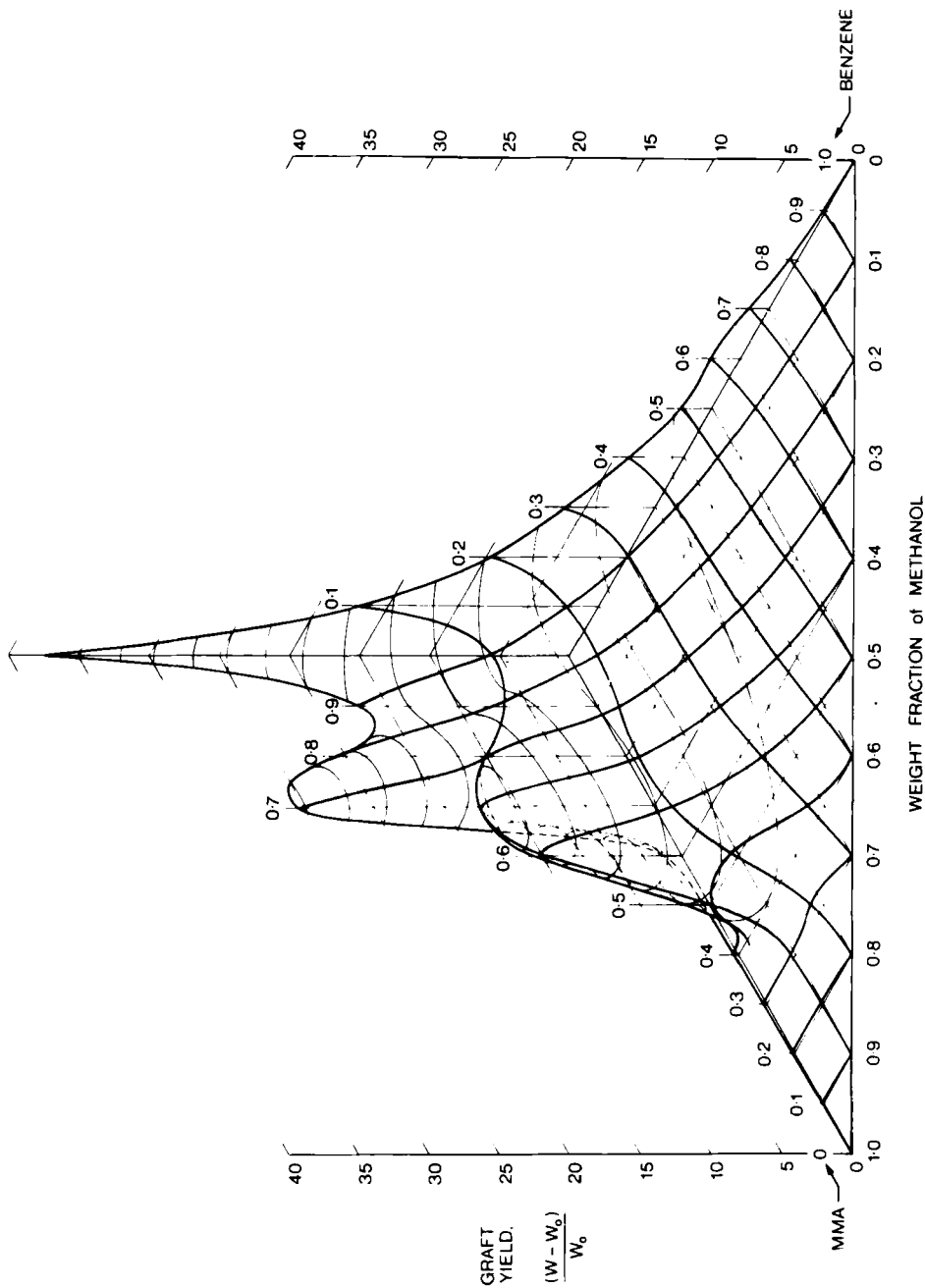


FIG. 3. Variation of graft yield with change in the concentrations of methyl methacrylate (MMA), methanol, and benzene.

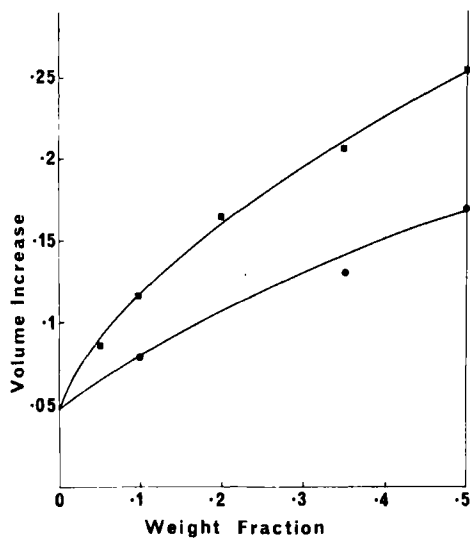


FIG. 4. Relative increase in the volume of polypropylene film with change in (●) benzene or (■) hexane concentration; methyl methacrylate fixed at 0.5 weight fraction, remaining weight is methanol.

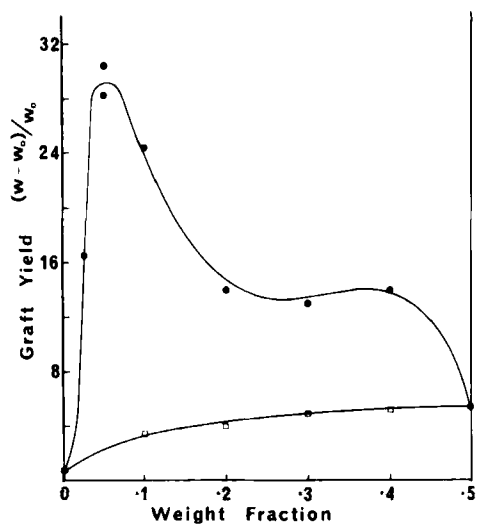


FIG. 5. Variation in graft yield with concentration of (●) hexane or (□) acetone; methyl methacrylate weight fraction 0.5, weight balance with methanol.

which are approaching the glassy state. Where the optimum grafting rate is observed, conditions must be such that entanglement limits the termination rate to a greater extent than the propagation rate.

When benzene is replaced by hexane, which is a nonsolvent for PMMA, but a better swelling agent (Fig. 4) for polypropylene than benzene, the results shown in Fig. 5 are obtained. The decrease in graft yield at high hexane concentrations is probably due to the propagation rate being limited by increased entanglement of the grafted polymer. In contrast, when a solvent for PMMA is used which does not swell polypropylene, no accelerative effect is observed. This is shown by the methyl methacrylate-methanol-acetone system (Fig. 5) where the increase in graft yield as the methanol is replaced by acetone is due to an increase in the propagation rate constant.

In addition, when the conditions are favorable for a high polymerization rate, the presence of the grafted PMMA is also contributing to the rate due to new grafting sites located on the grafted PMMA. This will also result in an acceleration [14].

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