INTRODUCTION

The rapid ring-opening polymerization of pivalolactone (PVL), initiated and propagated anionically by the carboxylate anion, occurs under mild conditions relatively free of interfering reactions. The driving force for the reaction is the relief of the strain in the four-membered ring and the heat of polymerization is reported (1) as 18.4 kcal. per mole, including 2.9 kcal. for crystallization. The aliphatic polyester formed is high melting, thermally and hydrolytically stable, and highly crystalline (2-4).

These properties of pivalolactone and its polymer make it especially useful and effective for modifying carboxylated polymers through graft polymerization (5-8). The absence of a common termination reaction or chain transfer to monomer in tetrahydrofuran solution leads to grafting efficiencies and pivalolactone conversions approaching 100%.

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The purpose of this paper is to discuss the scope and technique for this facile grafting reaction, the experimental variables and the property changes observed.

EXPERIMENTAL

Pivalolactone

The pivalolactone (PVL) was 99.9+% pure by gas chromatography, stored in a freezer at -20 to -30°C as a crystalline solid, and filtered through neutral alumina just before use to remove traces of homopolymer sometimes formed during storage.

Unpublished work on its physiologic activity has been noted (5) and discussed briefly in the preceding chapter.

Poly(ethylene-α- vinyl acetate-α-methacrylic acid)

These copolymers were commercial and experimental grades of Elvax® resins, Du Pont's copolymers of ethylene and vinyl acetate. Methacrylic acid contents were determined by titration.

Poly(ethylene-α-vinyl acetate-α-methacrylic acid-g-PVL)

In a typical procedure, 200 g of base resin was dissolved in 600 ml of tetrahydrofuran, the solution warmed to a gentle reflux and 20-50% of the available carboxyl groups in the base resin were neutralized with tetrabutylammonium hydroxide (1.0 molar in methanol). The pivalolactone was then added as rapidly as the exotherm would permit (10-20 min.), and heating and stirring continued for 30-120 minutes more to complete the reaction. When the system remained fluid it was acidified with concentrated hydrochloric acid before precipitating the product in warm water in a blender. The nontacky solid was washed well with water and dried in a vacuum oven at 80°C. Conversions of the pivalolactone to polymer were normally above 95%, often complete.

Poly(ethylene-α-propylene-α-1,4-hexadiene) (EPDM)

EPDM was a commercial grade of Nordel®, Du Pont's hydrocarbon elastomer.

EPDM-g-thioglycolic acid (EPDM/T) was prepared by the reaction of EPDM with large excesses of thioglycolic acid and α,α-azobis-(δ,δ-dimethylvaleronitrile) in tetrahydrofuran (9).