obtain high molecular weights in toluene at room temperature. An experiment was carried out at −50 °C in THF (P_6). At this temperature, we observed a precipitation of the poly-ϵ-caprolactone and the proportion of low molecular weights is nearly the same as for a similar experiment made at room temperature with uncomplexed potassium *tert*-butoxide (P_4).

In conclusion, it has been shown that the addition of macrocyclic ligands leads to an increase of the reactivity of ionic species for the anionic polymerization of lactones. Use of such complexing agents for cations allows the initiation of β-propiolactone polymerization with weak nucleophiles under conditions that ordinarily do not lead to polymers. Anionic polymerization of ϵ-caprolactone in the homogeneous phase with macrobicyclic ligands leads to a higher proportion of oligomers than in the case of uncomplexed species. This is due to the enhancement of the reactivity of alkoxide end groups with cryptates as counterions. This effect is less pronounced for polymerizations occurring in the heterogeneous phase, for example, for ϵ-caprolactone polymerization at −50 °C.

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Block and Graft Copolymers of Pivalolactone. I. A New Class of Elastoplastics and Thermoplastic Elastomers

The forced union, by block and graft copolymerization of unlike polymeric segments can lead to controlled phase separation often yielding compositions with unusual and useful properties. In particular, when one of the components is elastomeric and forms a continuous phase, then separation of a glassy or crystalline component can develop tiepoint domains connecting elastomeric chains so that the resulting network exhibits the properties of a cured elastomer. Commercially important block polymers of this type offering thermoplastic processability include poly(styrene-*b*-butadiene-*b*-styrene) and the isoprene analogue, segmented polyether esters and polyether or polyester urethanes.

We wish to report on an unusual class of copolymers in which grafted blocks of polypivalolactone combine, undergo phase separation, and rapidly form highly crystalline tiepoint domains. These compositions, stable in the melt and solvent resistant, are striking examples of thermoplastic elastomers that are readily prepared.

The facile ring-opening polymerization of pivalolactone (PVL, 2,2-dimethyl propiolactone) is well known and has been recently reviewed[1] as have homopolymer properties.[2–4] Publications dealing with grafts of the type described here have, with perhaps one exception,[5] appeared only in the patent literature.[6–11] Graft polymerization of pivalolactone is readily initiated by carbanion,[7] oxyanion,[5] and in particular carboxylate[6,8,9,11] sites randomly located on the base polymer backbone. Even tertiary amine sites can initiate by reacting with monomer to form a zwitterion.[11,12] Carboxylate anions with bulky organic counterions, such as tetrabutylammonium, which form loose ion pairs in solvating solvents such as tetrahydrofuran, are sites favored for rapid initiation and propagation. The grafted chains are "living" in that the propagating group, the carboxylate anion, is quite stable in the system, undergoes no common termination reaction, and does not participate in chain transfer to monomer.[1] It can, however, transfer its activity to any available carboxyl group by simply accepting the proton.

Experimental Section

For grafting the base polymer is dissolved in tetrahydrofuran and stirred under gentle reflux. The carboxylate anion sites are developed by reaction of carboxyl containing polymers with 20–100% of the theoretical amount of tetrabutylammonium hydroxide, normally handled as a 1.0 M solution in methanol. The adequacy of partial neutralization and the distribution of pivalolactone units over all available carboxyl groups has been demonstrated by the similarity in melting behavior of graft products prepared with neutralization levels from 2 to 100%. In copolymers containing pendant ester groups the amount of base determines by saponification (1 h at reflux) the number of carboxylate ion sites. Cyclic anhydride functionality reacts rapidly, even with less than stoichiometric amounts of alcoholic base, to give the half ester initiating site.

Pivalolactone, purified by passage through a short column of neutral alumina, is added slowly enough to control the exotherm. An additional 30–60 min of heating completes the reaction, and at high modification levels the usually clear solution may gel. The system is normally acidified with 12 M HCl and the product precipitated by addition to water, ethanol, or acetone. Conversions are normally quantitative, with 95–100% of the grafted monomer recovered in the yield of the graft copolymer. For example, 50 g of pivalolactone reacted with 200 g of a base resin normally yields 247–250 g of grafted product. Homopolypivalolactone is either absent or present at low levels.

Graft polymerizations can also be carried out in the molten polymer, when it is low melting and has some degree of polarity. Further discussion of this special case will appear in a later publication.

Unpublished work at Haskell Laboratory, E. I. du Pont de Nemours and Co., has shown that pivalolactone caused skin tumors in mice when applied as a 25% solution in acetone for most of the life span of the mice. The time required for tumor formation was greater than that for β-propiolactone, a positive control in the test, and the extent of tumor formation was much less than for β-propiolactone.

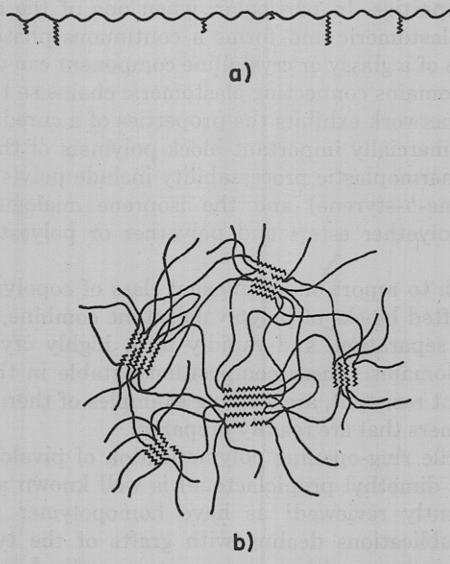

Figure 1. Schematic representation of pivalolactone graft copolymers: (a) a "stretched out" segment of a single molecule; (b) bulk polymer morphology. Crystalline domains are 50–1200 Å in diameter.

Results and Discussion

Graft Polymer Structure and Morphology. The structure of a typical pivalolactone graft polymer is visualized as a random distribution of crystallizable side chains along the base polymer chain (see Figure 1a). By analogy to polypivalolactone (living polymer, fast initiation), the side chains are expected to be present in a fairly narrow distribution of chain lengths. Since the polymer properties are so dependent upon structural features, we define two structural parameters. SSL (soft segment length) is the average distance between grafting sites in the base polymer backbone, as calculated from the weight average molecular weight and analyzed carboxylic acid content. HSL (hard segment length) is the average length of the grafted moiety, calculated as the amount of pivalolactone for each carboxyl site in the base resin.

We have chosen to identify both in molecular weight units since the backbone chains are often copolymers.

Morphology studies of several graft copolymers indicate the separation of microcrystalline domains which serve as tiepoints in a tight, three-dimensional structure as shown in Figure 1b. A typical transmission electron photomicrograph of a solvent cast film is shown in Figure 2, where it can be seen that the disperse phase has straight sides and sharp angles characteristic of crystallites. Small-angle x-ray scattering and wide-angle x-ray diffraction reveal crystallinity typical of polypivalolactone. A high degree of phase separation is indicated by differential scanning calorimetry curves showing base resin and polypivalolactone melting endotherms, the former unchanged by the grafting, the latter increasing in temperature with the calculated hard segment length to the maximum melting point for polypivalolactone (see Table I).

Processing and Properties. The melting points of these microcrystalline domains define the temperatures above which these materials may be processed (200–250 °C). Conventional compression and injection molding techniques were applied, and samples could be remolded repeatedly without loss of properties in systems with stable backbone and graft sites.

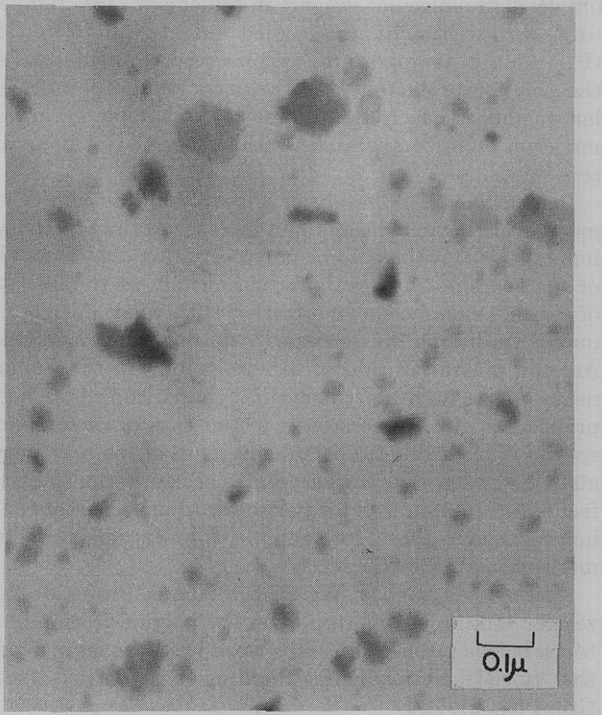

Figure 2. Transmission electron photomicrograph of a solvent cast (9:1 benzene–hexafluoroisopropanol) film of a poly-PVL graft on poly(ethylene-*co*-propylene-*co*-1,4-hexadiene)-*g*-thioglycolic acid. SSL = 3600; HSL = 1200. Poly-PVL domains are preferentially stained with phosphotungstic acid.

Table I
Composition and Selected Properties of Poly([ethylene-*co*-vinyl acetate-*co*-methacrylic acid]-*g*-PVL)

% PVL	HSL Calcd	T_m, °C[a]	Initial[b] Modulus, MPa	Yield[b] stress, MPa	Elongation[b] at Break, %
0		121	31	4.8	930
10	950	139	32	4.2	810
15	1500	170	78	5.9	674
23	2600	193		7.2	665
24.5	2800	192		8.3	645

[a] Minimum flow temperature. [b] Determined at room temperature by ASTM D-1708. Note: MPa = megapascal, S.I. unit; 1 MPa = 10^6 N/m^2 = 10.2 kg/cm^2 = 145 psi.

The effect of hard segment length on melting and mechanical behavior is illustrated in the examples of Table I, for which an experimental terpolymer of 79% ethylene, 20% vinyl acetate, and 1% methacrylic acid (SSL = 8600) with $\bar{M}_n$ = ca. 96 000 was grafted with pivalolactone by the general procedure described and in the amounts indicated. These materials have the properties of an elastoplastic and melt at the temperatures of the last endotherm in their differential scanning calorimetry curves. This coincides closely with the minimum flow temperature reported in Table I, as determined in a melt indexer with a 2.160-kg load and a 0.21-cm (0.0825 in.) orifice, the temperature being increased at 1 °C/min. Even at the high ethylene content of the example composition, the effect of PVL grafts on room temperature mechanical properties is apparent.

The data in Table II and Figure 3 illustrate the structures and selected properties of more highly elastic compositions. The discrete tiepoint domains impart to these copolymers the low Young's moduli and high tensile strengths of their conventionally cured nongrafted counterparts. However, in conventional curing high strength is obtained only in the presence of reinforcing fillers. It is therefore inferred that these polypivalolactone domains serve simultaneously as cross-linking sites and reinforcing filler particles.

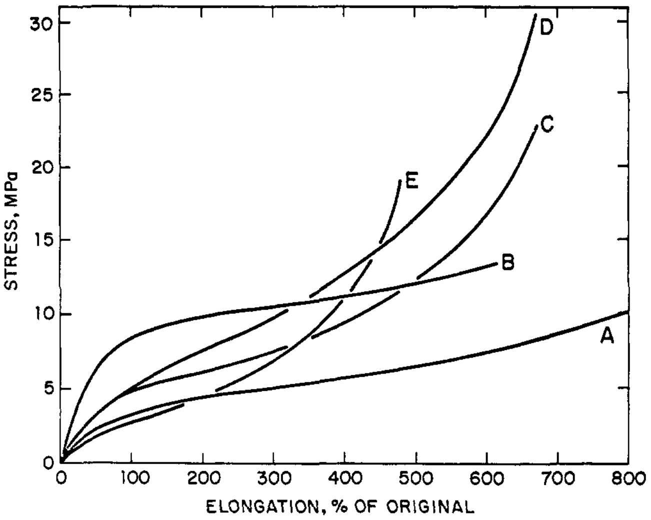

Figure 3. Stress-strain behavior of the graft copolymers identified in Table II. 1 MPa = 145 psi.

Table II
Composition and Selected Properties of Elastomeric Polypivalolactone Graft Copolymers

	Base polymer	SSL, mol wt	HSL, mol wt	Poly-PVL, wt %	T_m,[a] °C	Comp[b] set, %
A	Poly(ethyl acrylate)[c]	14 800	3700	20	195	17
B	Poly(chloroprene-*co*-methacrylic acid)[d]	3 740	1500	29	170	25
C	Poly(ethylene-*alt*-ethyl acrylate)[e]	5 000	1500	23	170	11[f]
D	Poly(ethylene-*co*-propylene-*co*-1,4,-hexadiene)-*g*-thioglycolic acid[g]	4 300	1300	26	180	23
E	Poly(ethylene-*co*-propylene-*co*-1,4-hexadiene)[h,i]					27

[a] Melting endotherm peak as determined by DSC analysis. [b] ASTM D-395, method B. All specimens were annealed 24 h at 120 °C prior to testing. [c] $\bar{M}_w \simeq 10^6$. [d] $\bar{M}_w > 100\,000$, 2.7 wt % methacrylic acid. [e] η_{inh} (0.1% in $CHCl_3$) = 2.5. [f] After 22 h at 70 °C. [g] Base polymer had the composition of sample E before addition of thioglycolic acid. Thioglycolic acid content was 2.1 wt %. [h] $\bar{M}_w \simeq 80\,000$; 55 wt % ethylene, 40 wt % propylene, 5 wt % 1,4-hexadiene. [i] Compounded and cured by conventional sulfur recipe for good compression set.

Because of the thermal integrity of the crystalline polyester tiepoint, high-temperature properties are excellent, especially in comparison to known thermoplastic elastomers. At 100 °C 65–95% of room-temperature strength at 100–300% elongation is maintained. Resistance to compression set[13] at elevated temperature is particularly good, as shown by the data of Table II. Permanent deformation is lower than that of a conventionally cured elastomer (sample E). This indicates very little network rearrangement under the combined effects of stress and temperature.

Other outstanding properties (solvent resistance, resilience, abrasion resistance, heat, and aging stability) seem related to the morphology of these unique graft copolymer systems, and will be the subject of further publications.

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(14) (a) Plastics Department; (b) Elastomer Chemicals Department; (c) Central Research and Development Department.

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Block and Graft Copolymers of Pivalolactone. II. ABA and ABA-*g*-A Copolymers with Dienes

Introduction of crystalline tie points[1] by use of pivalolactone (PVL) as the A block monomer in ABA triblock copolymers and ABA-*g*-A block-graft copolymers has demonstrated that thermally reversible cross-linking by interchain crystallization can be just as effective as chemical cross-linking. We have found that such compositions, in which the B segments are a polydiene, are unusually strong and have exceptionally stable cross-links.

The ABA products have been made from α,ω-dithio-*cis*-1,4-polydienes obtained by polymerization of isoprene or butadiene with a difunctional lithium initiator. The base polymer was prepared by polymerization of the diene in cyclohexane solution under strictly anhydrous conditions using an amount of difunctional initiator calculated to give the desired molecular weight. Polymerizations were carried out at 60 °C and were usually complete in less than 2 h. Then the reaction mixture was diluted with tetrahydrofuran and through it was bubbled a vigorous stream of dry carbon dioxide.[2] Excess carbon dioxide was removed, tetrabutylammonium hydroxide in methanol was added, and the polymer was precipitated in ethanol. The precipitated polymer was washed with ethanol, and the ethanol was removed and redissolved in tetrahydrofuran. Pivalolactone was added whereupon polymerization proceeded almost immediately and eventually gelled the solution. The gel was broken up in ethanol, acidified with acetic acid, washed well with ethanol, and dried to give PVL–isoprene–PVL triblock copolymer.

Block-graft copolymers were made by post-lithiating α,ω-dilithio-*cis*-1,4-polydienes by reaction with *n*-butyllithium at 55–60 °C or *sec*-butyllithium at 25 °C in the presence of tetramethylethylenediamine.[3] This method has been used earlier to introduce dilithio sites at allylic positions along a polydiene chain.[4] The lithiated polydiene was carboxylated by adding this solution to vigorously stirred tetrahydrofuran through which dry carbon dioxide was bubbled. This involved transfer of the polymer solution from the flask in which it was prepared through a dry tube into a second flask containing tetrahydrofuran. Conversion of carboxylated salts to tetrabutylammonium salts and use