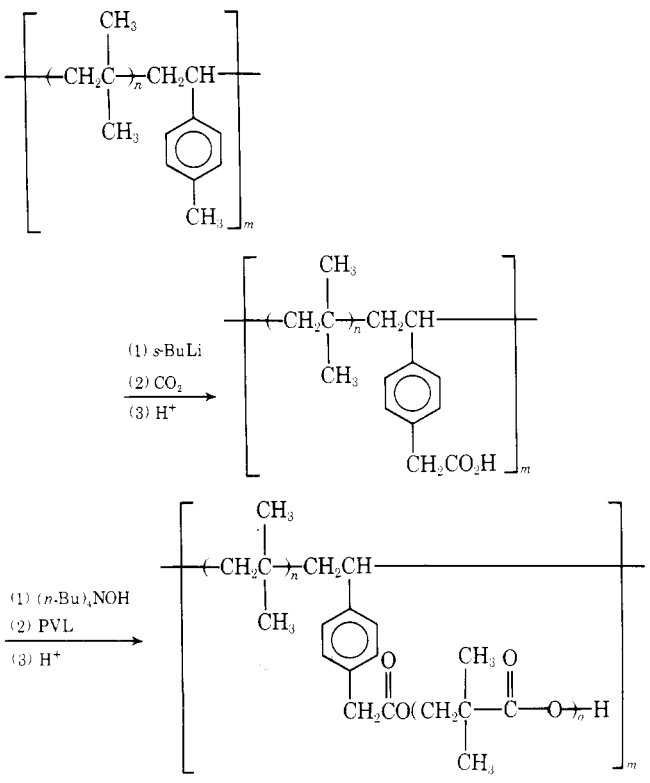
Communications to the Editor

Block and Graft Copolymers of Pivalolactone. 3. Isobutylene–Pivalolactone Graft Copolymers

The synthesis of new thermoplastic elastomers by attachment of crystalline polypivalolactone (PVL) segments to rubbery polydiene backbones as the A blocks in ABA triblock copolymers and ABA-*g*-A block graft copolymers has been described recently.[1] These compositions exhibit thermally reversible cross-linking via interchain crystallization of polypivalolactone segments. We wish to report the preparation and properties of a new type of thermoplastic elastomer comprising a polyisobutylene backbone reversibly cross-linked by means of grafted poly-PVL segments.

Chart I



The polyisobutylene backbones to which the crystalline segments are attached were prepared by cationic copolymerization of isobutylene with 4-methylstyrene, a mixture of 2-, 3-, and 4-methylstyrenes, and mixtures of 4-methylstyrene and α-methylstyrene. Copolymers with viscosity molecular weights ranging from 6 500 to 660 000 and with isobutylene:styrene mole ratios of 10:1 to 150:1 were used in this study. Polypivalolactone segments were attached through carboxyl groups that were introduced by metallation of the copolymers with secondary butyllithium, followed by reaction of the lithiated polymers with excess carbon dioxide. Acidification gave carboxylated copolymers containing alkane carboxylic acid groups. Conversion of the acid functions to the corresponding tetrakis(*n*-butyl)ammonium salt and addition of PVL resulted in the generation of pendant poly-PVL strands at the carboxyl sites.[4] A final acidification converted the carboxylate end groups to carboxylic acids.

The reactions involved, using isobutylene–4-methylstyrene copolymer as an example, are shown in Chart I.

As the PVL content is increased from very low amounts to over 60%, the products range from sticky semisolids, through a rubbery-thermoplastic region, to hard nonelastic thermoplastic solids. There is apparently a minimum PVL content of 7–8% and a minimum average number of PVL molecules per graft of about 7 required in order to obtain effective cross-linking by the intercrystallization of PVL chains. When the PVL content is much over 60%, the products are hard solids. From compositions with PVL contents between these limits, thermoplastic elastomeric films have been pressed at 180–220 °C. These materials are often tough and strong, depending upon the values of the compositional parameters.

Strips cut from films of polymers containing 20–60% of PVL had tensile strengths as good or better than conventionally

Table I
Properties of Pivalolactone/Isobutylene Graft Copolymers

Backbone properties						
Backbone copolymer[a] (mole ratio)[2]	M_v[3]	Eq wt per grafting site	% PVL	Molecules PVL per site	Tensile strength, psi	Elongation at break, %
(a) IB + 4-MeSty (110:1)	550 000	10 326	42	75	7582	220
(b) IB + 4-MeSty (88:1)	660 000	11 095	56	143	6408	123
(c) IB + VT (63:1)	305 000	12 064	37	71	4781	317
(d) IB + VT (105:1)	150 000	14 640	31	66	4043	333
(e) IB + VT (63:1)	305 000	10 905	25	36	3986	373
(f) IB + 4-MeSty (66:1)	143 000	9 469	37	56	4810	310
(g) IB + 4-MeSty (50:1)	66 500	6 115	11	7.5	970	540
(h) IB + α-MeSty + 4-MeSty (147:1.03:1)	80 500	10 565	36	60	2976	185

[a] IB = isobutylene; 4-MeSty = 4-methylstyrene; VT = vinyltoluene (a mixture of 2-, 3-, and 4-methylstyrenes in which the 3 and 4 isomers predominate); α-MeSty = α-methylstyrene.

cured polyisobutylene. When these strips were oriented by several cycles of alternate stretching and relaxing, tensile strengths increased markedly with, in most cases, a concomitant decrease in elongation. Although the relationships between tensile strength and the compositional parameters are not simple, high tensile strengths are favored by high backbone molecular weight and high PVL content. Elongations also increase with increase in backbone molecular weight, but decrease with increase in PVL content. The compositional parameters and properties of several oriented films are given in Table I.

Since these polymers contain no aliphatic hydrocarbon unsaturation and no ether oxygen, they are resistant to the easy air oxidation normally associated with many elastomeric materials. This we feel is in part responsible for the outstanding stress–decay behavior of these materials. Oxidation resistance and retention of strength under stress was indicated by stress–decay tests upon compositions that have not been treated with antioxidants. For example, oriented strips of one sample (e in Table I), stretched to 300% and held at this elongation, showed an 11% decay in stress in the first hour, followed by a further decay of only 5% in the next 22 h. A similar test on sulfur-cured natural rubber showed about 28% loss of stress in less than 20 h.

Elastic fibers have been obtained by the melt-spinning at 220–260 °C of those materials whose melt viscosity is under about 800 P at 235 °C at a shear rate of 3000 s^{-1}. For example, the polymer described in entry h of Table I has been melt spun at 240–260 °C into air-stable fibers of 85–112 denier with tensile strengths after manual orientation of about 0.5 g/denier and elongations of about 200%.

A full account of this work will be published later.

References and Notes

(1) R. P. Foss, H. W. Jacobson, H. N. Cripps, and W. H. Sharkey, *Macromolecules*, **9**, 373 (1976); *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **17** (1), 211 (1976).
(2) Determined by UV spectra of the copolymer in cyclohexane.
(3) Estimated from the Mark–Houwink equation by assuming that the inherent viscosity determined at 0.1% in toluene was equal to the intrinsic viscosity.
(4) Unpublished work at Haskell Laboratory, E. I. du Pont de Nemours and Co., has shown that PVL 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.

J. F. Harris, Jr., and W. H. Sharkey*
Contribution No. 2442 from the Central Research and Development Department, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware 19898

Received October 15, 1976