

Ethylene-Propylene Terpolymers with Conjugated Double Bonds

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Synopsis

A study was made of ethylene-propylene terpolymerization with fulvenes and various acetylenes. Vinylacetylene, 2-methyl-1-buten-3-yne (isopropenyl-acetylene) or 6,6-dimethylfulvene in conjunction with ethylene and propylene formed terpolymers which contained conjugated double bonds. The presence of conjugated double bonds was established by infrared and ultraviolet analyses. The terpolymers were randomly unsaturated with sufficient unsaturation to be sulfur-vulcanized.

INTRODUCTION

Various nonconjugated dienes have been reported¹⁻⁴ as termonomers to introduce unsaturation into ethylene-propylene terpolymers. In our studies of ethylene-propylene terpolymerization, a number of fulvenes and acetylenic compounds were evaluated as termonomers.^{5,6} Two acetylenes (vinylacetylene and isopropenylacetylene), and 6,6-dimethylfulvene copolymerized in such a manner as to introduce units of conjugated double bonds into the polymer. Sufficient random unsaturation was attained to permit sulfur vulcanization.

EXPERIMENTAL

Polymer Preparation

Polymerizations were conducted in 7-oz beverage bottles fitted with three-hole crown caps over self-sealing liners. The bottles were agitated in a modified Parr hydrogenation apparatus. Dry toluene was added to oven-dried bottles and then purged with prepurified nitrogen. The termonomer and ethylaluminum sesquichloride were injected by syringe. Each bottle was placed in the Parr apparatus cradle and an ethylene-propylene gas mixture (1:3 mole ratio) at 45 psig was introduced from the gas reservoir through a copper line and hypodermic needle. The bottle was agitated for 5 min to solubilize the monomers. Polymerization was then initiated by injection of either vanadium tetrachloride or vanadium oxychloride. After 30 min, polymerization was terminated by injecting a 10% solution of Cyanox SS in isopropyl alcohol at an estimated antioxidant level of 1%. The polymers were recovered by coagulating in isopropyl alcohol and drying *in vacuo* at 60°C.

Samples for evaluation studies were prepared in similar recipes in a one-liter stainless steel autoclave.

Compounding

The polymers for evaluation were compounded in the common recipe shown in Table I and were cured 45 min at 320°F.

TABLE I
Terpolymer Compounding Recipe

	Parts by weight
Ethylene-propylene terpolymer	100
High abrasion furnace black	50
Zinc oxide	5
Stearic acid	1
Circosol 2XH ^a	30
Sulfur	1.5
Captax ^b	0.5
Monex ^c	1.5

^a Petroleum hydrocarbon softener.

^b 2-Mercaptobenzothiazole.

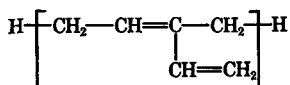
^c Tetramethylthiuram monosulfide.

RESULTS AND DISCUSSION

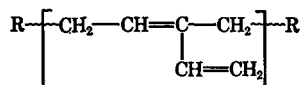
Polymer Structure

Infrared spectra of the terpolymers were obtained with a Model 21 Perkin-Elmer spectrometer, ultraviolet spectra by means of a Model 14 Cary recording spectrometer.

The infrared spectra of terpolymers prepared with the acetylenic monomers had no absorption attributable to an acetylenic triple bond (Fig. 1). The vinylacetylene terpolymer produced infrared absorption bands similar to those found by Marvel and Williams⁷ in the spectrum of 3-methyl-1,3-pentadiene, indicating similar structure.



3-methyl-1,3-pentadiene



Termonomer segment of polymer

Absorption bands at 10.15, 11.12 and 12.30 μ indicate the presence of pendant vinyl and branched internal double bonds.

The infrared spectra of the isopropenyl terpolymer had absorption bands at 6.11 and 11.17 μ indicative of a disubstituted vinyl group.

Ultraviolet light scanning of the two acetylenic terpolymers showed an absorption maximum at about 2200 Å. This is an indication of conjugated double bonds of the butadiene type. Conjugated bonds of this type arise from preferential addition across the carbon-carbon triple bond.

Infrared and ultraviolet spectra of the terpolymer from ethylene, propylene, and 6,6-dimethylfulvene also indicate conjugated olefinic structure

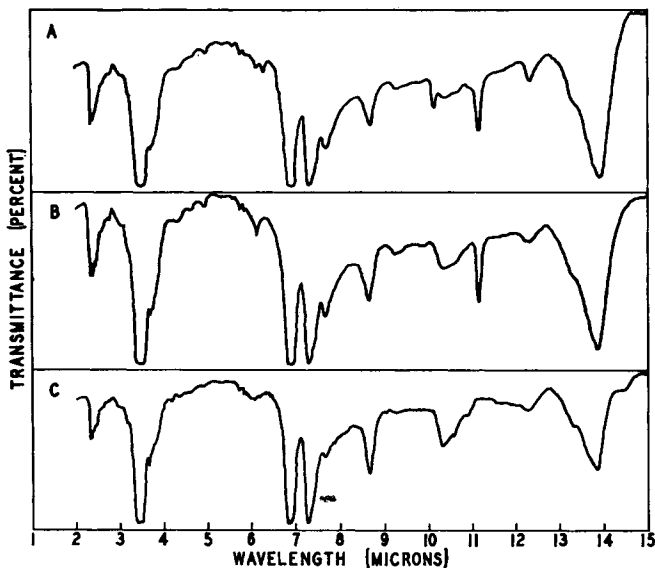
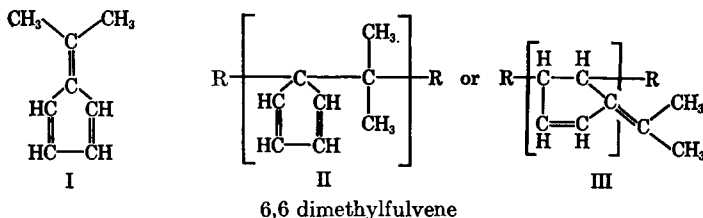


Fig. 1. Infrared spectra of ethylene-propylene terpolymers: (A) vinylacetylene monomer; (B) isopropenylacetylene monomer; (C) 6,6-dimethylfulvene monomer.

(Fig. 1). Polymerization by 1,2-addition of the fulvene (I) could result in structure II, structure III, or both.



A conjugated double bond system could also arise by a variant of 1,4 addition involving the 2,6- or 3,6-carbons in fulvene. The most prominent infrared absorption band in the C=C stretching region occurs at 6.20μ with two other very weak bands at 6.12 and 6.17μ . These bands disappear on bromination. The relatively low C=C frequency for the principal band suggests conjugation in the C=C structure. An ultraviolet absorption maxima occurs at 2500 \AA further indicating conjugation.

Presence of the single prominent band at 6.20μ suggests that formula II probably represents the predominating conjugated structure. The two weak bands mentioned above indicate the possibility of some III structure. Precedent for addition across the double bonds of carbons 5 and 6 of 6,6-dimethylfulvene in preference to carbons 1 and 2 of the ring can be found in the literature. Reaction of phenyllithium with this fulvene leads to 5-lithio-5(dimethylphenyl)-methylcyclopentadiene.⁸ Hydrolysis of the intermediate complex of the reaction of dimethylfulvene and lithium aluminum hydride gives 70–80% of the reduction product, 5-isopropylcyclopentadiene.⁹

Compounding Results

Physical properties of cured black stocks of typical polymers are shown in Table II.

TABLE II
Polymer Characterization and Physical Properties

Polymer	Ethylene-propylene terpolymer		
	Vinyl-acetylene	Isopropenyl-acetylene	6,6-Dimethyl-fulvene
Propylene, wt-%	33	44	61
Inherent viscosity (toluene, 25°C)	1.04	1.54	1.51
Unsaturation, mmole ICl/g polymer	0.33	0.22	0.55
Cured stock			
300% Modulus, psi	1580	360	860
Tensile, psi	2850	2020	3110
Elongation, %	505	875	710
Resilience, %	62	65	65
Shore A hardness	88	58	59
Gehman freeze point, °F	—	—56	—54

The data in Table II demonstrates that sufficient termonomer was incorporated in a random manner in the three polymers to permit vulcanization. Differences in properties probably arise from differences in ethylene/propylene/termonomer ratios, molecular weight, randomness of unsaturation, and differences in the type of conjugated structure. It is noteworthy that a very good balance of properties was obtained with the fulvene terpolymer. The vulcanizate properties of this polymer compare favorably with those of commercial EPDM.

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