Aromatic Rings as Cure Sites for EPM Elastomers

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Synopsis

Terpolymers of ethylene and propylene with 4-phenyl-, 4-*o*-tolyl, 4-*p*-tolyl, and 4-(1-naphthyl)-1-butenes were vulcanized with bisbenzylic halides in the presence of highly acidic clays. The halides include bischloromethyldurene, *p*-bischloromethylbenzene, and *p*-bisbromomethylbenzene. Since the polymers contain no olefinic unsaturation, the crosslinking is achieved by electrophilic attack of the halide on the pendant aromatic rings. The order of activity is naphthyl > tolyl > phenyl. The new curing system also reacts with olefinic unsaturation. Thus, an EPDM elastomer and SBR rubber, the latter containing both aromatic rings and double bonds, were also readily crosslinked.

INTRODUCTION

Copolymers of ethylene and propylene, having no unsaturation, can be crosslinked through radical formation induced by peroxides. Terpolymers of the ethylene–propylene–diene (EPDM) type contain dienes as third monomers; the double bond not incorporated in the polymer chain acts as a cure site toward sulfur recipes. The possibility of aromatic rings serving as cure sites has not previously been investigated. Potential curing agents would be polyfunctional electrophilic reagents, such as a bisbenzylic halide. This type of halide has been shown to crosslink polymers (styrene–butadiene, polybutadiene) with double bonds in the chain.[1]

EXPERIMENTAL

Materials

Catalysts, Crosslinking Agents, and Solvents. Generous samples of Montmorillonite K Clays were supplied at no cost by the Girdler Division, Chemetron Corporation. Bischloromethyldurene is available from Aldrich Chemical Co., and *p*-bischloromethyl- and *p*-bisbromomethylbenzene, from Eastman Organic Chemicals. Reagent-grade Perclene (du Pont registered trademark) perchloroethylene was sparged with nitrogen and stored over silica gel. Solutions of polymerization catalysts in Perclene were handled under nitrogen.

Monomers. Ethylene, propylene, and nitrogen were purified by passing through molecular sieve. 4-Phenyl-1-butene was purchased from Aldrich

Chemical Co. and distilled before use.   The other 4-aryl-1-butenes were prepared by Grignard coupling reactions as described in the literature.[2-4]

Preparation of Polymers.   Copolymers of ethylene and propylene with 4-aryl-1-butenes were prepared by coordination catalysis in batch runs. The following is a typical example: In a 2-liter resin kettle, 1 liter of Perclene was rapidly stirred and sparged with nitrogen for at least 10 min while being cooled externally to 0°C.   The contents of the kettle were maintained at this temperature for the entire run.   Streams of ethylene and propylene were introduced.   Feed rates of 1.0, 0.5, and 2.5 liters/min for ethylene, propylene, and nitrogen, respectively, were maintained throughout the run. After at least 20 min, 1 ml of 4-phenyl-1-butene, 20 ml of an $0.5M$ solution of diisobutylaluminum chloride in Perclene, and 10 ml of an $0.1M$ solution of vanadium trisacetylacetonate in Perclene were added in rapid succession to give a bright orange solution which gradually changed to dull orange-brown.   Some gelation on the walls at the top of the solution usually occured within 5 min.   Five additional 0.6-ml portions of 1-phenyl-3-butene were added at 5-min intervals, the first of them 5 min after addition of the $V(AA)_3$ solution.   The polymerization was allowed to proceed another 10 min after the final addition; then 10 ml of isopropyl alcohol was added to deactivate the catalyst.   The solution was poured into 2 liters of methanol to precipitate the polymer, which was washed three times with methanol in an Osterizer mixer and dried in a vacuum oven at 70°; wt. 30–35 g.

The   ethylene–propylene–4-aryl-1-butene   terpolymers   had   30–40% propylene and inherent viscosities 1.6 to 2.0.   Incorporation of the arylbutenes was demonstrated by the presence of characteristic absorption bands in the infrared spectra of the polymers.   A terpolymer from 4-(p-chlorophenyl)-1-butene contained 6.6% of the arylbutene as shown by chlorine analysis.

Vulcanization Experiments

Formulations containing E/P/arylbutene terpolymers were blended on a mill at or below room temperature, those containing Nordel (du Pont registered trademark for its hydrocarbon rubber), an ethylene-propylene-1,4-hexadiene terpolymer, at about 40°C and those with SBR rubber at about 60°C.   They were molded at 40,000 lb of pressure at the times and temperatures indicated in the Results and Discussion section. Concentrations are expressed in parts per 100 parts of polymer (phr).

RESULTS AND DISCUSSION

Polymers with pendant aromatic rings were prepared by copolymerizing ethylene and propylene with 4-aryl-1-butenes in the presence of a vanadium trisacetylacetonate–diisobutylaluminum   chloride   catalyst   at   catalyst efficiencies of 30,000 (g polymers/mole vanadium).   They were crosslinked by bifunctional electrophilic reagents such as bisbenzylic halides in the presence of acid-treated clays of the Montmorillonite K series. The reaction, involving attack on the aromatic ring by a cation, is thus of the

Friedel-Crafts type. Ferric chloride was also effective as acidic catalyst but its hygroscopic nature made processing.more difficult.

Montmorillonite is an aluminum silicate of the bentonite type $(Al_2O_3.-4SiO_2.H_2O+xH_2O)$, containing 50–70% SiO_2, 15–20% Al_2O_3, 3–5% Fe_2O_3, 1–3% CaO, and 1–3% MgO. The Montmorillonite K series of clays have all been acid treated and are available with different degrees of acidity. Five members of this series were evaluated as vulcanization catalysts for the terpolymer containing 4-phenyl-1-butene in formulations containing 22 phr bischloromethyldurene and 19 phr Montmorillonite and pressed at 180°C for 1 hr. Only KSF, the most acidic member of the series, gave a full cure. The second most acidic, K10SF, gave a partial cure, but the still less acidic KSFO, K20M, and K10 were almost completely ineffective. The importance of acidity was also shown by the fact that the presence in the KSF formulation of as little as 2% magnesium oxide as potential hydrogen chloride acceptor prevented vulcanization.

The bifunctional electrophilic reagents most effective as curing agents for these polymers are bischloromethyldurene (BCMD), the slightly mord reactive p-bischloromethylbenzene $(\alpha,\alpha'$-dichloro-p-xylene; DCPX), ans the much more reactive p-bisbromomethylbenzene (DBPX). As little as 3 phr of the bromo compound gave full gum stock cure of E/P/4-o-tolyl-1-butene terpolymer when used in conjunction with 14 phr of KSF at 180°C for 1 hr (Table I) while the chlorides require more than 6 phr. When 14 phr each of the bromo compound and catalysts were used, the less acidic Montmorillonite K10SF gave overcure and the even less acidic KSFO effected complete curing. In the absence of catalyst there was no cure at all; thus, some acidity is necessary even when this more active electrophile was used.

When large excesses (35 and 70 phr) of Montmorillonite KSF were used, terephthaloyl chloride cured E/P/tolylbutene terpolymer to weak vulcanizates that were 70 and 93% insoluble in boiling toluene, respectively.

With terpolymers containing 4-o- and p-tolyl-1-butenes smaller amounts of both curing ingredients were required to effect vulcanization than with phenylbutene terpolymers, thus demonstrating the ring-activating effect of the methyl group. The effect was much more pronounced in the o-tolyl polymer than in the p-tolyl, however, as evidenced by the relative amounts of curing ingredients required to effect complete vulcanization. Thus, with the p-tolyl polymer, 17 phr bischloromethyldurene gave a cure but 11 phr did not; while with the o-tolyl polymer, 6 phr gave complete cure and 11 phr gave overcure (all with 14 phr of KSF).

These results can be explained by the fact that though the ring is activated equally in each case, the p-methyl group blocks a position more sterically favored for attack by the benzylic cation.

The ring-deactivating effect of a chlorine substituent was also demonstrated. Thus, ethylene–propylene–4-p-chlorophenyl-1-butene terpolymer with 22 phr bischloromethyldurene and 19 phr KSF gave an incomplete cure to a vulcanizate with 85–89% permanent set.

TABLE I
Properties of Typical Gum Stock Vulcanizates[a]

	Nordel 1040 cured with Sulfur[b]	E/P/o-Tolyl-butene cured with Dicup[1]	E/P/Phenylbutene cured with		E/P/o-Tolylbutene cured with		
			Dicup[c]	BCMD	BCMD	DCPX	DBPX
Parts curing agent, phr	1.5[b]	10	10	13	9	6	3
Parts KSF, phr	—	—	—	17	14	14	14
Curing temp, °C	160	160	160	180	180	180	180
Curing time, min	30	60	60	60	60	60	60
M_{100}, psi	130	190	155	240	215	200	195
T_B, psi	200	250	195	350	240	220	210
E_B, %	260	200	140	370	140	140	120

[a] BCMD = Bischloromethyldurene; DCPX = α,α'-dichloro-p-xylene; DBPX = α,α'-dibromo-p-xylene.
[b] Also 1.5 phr Thionex, 0.8 phr MBT, 5 phr ZnO, 1 phr stearic acid.
[c] 40% on CaCO₃.

E/P/4-α-naphthyl-1-butene terpolymers are even more readily cured by bisbenzylic halides and KSF than are E/P/4-o-tolyl-1-butene polymers owing to greater number of available sites. Thus, E/P/naphthylbutene with bischloromethyldurene (14 phr) or p-bisbromomethylbenzene (9 phr), each with KSF (14 phr), gave overcured vulcanizates.

Properties of Gum Stock Vulcanizates from E/P/Arylbutene Terpolymers

Gum stock vulcanizates of ethylene–propylene–arylbutene terpolymers with bisbenzylic halides and Montmorillonite KSF are short-breaking elastomers of hardness 60 (Durometer A-2), with M_{100} 195–240 and T_B 210–350 lb/sq in. (psi) at 120–370% elongation (see Table I).

Ferric chloride (hexahydrate) can be used in place of Montmorillonite KSF as the acidic vulcanization catalyst. A typical E/P/phenylbutene–bischloromethyldurene–FeCl$_3$ example had stress–strain properties similar to KSF vulcanizates: M_{100} 200, T_B 340 psi, E_B 230%. This catalyst was effective over a wide range of concentrations (5 to 35 phr). High concentrations gave vulcanizates of a little more strength, but extraction with boiling toluene for 24 hr revealed no significant differences in degree of cure. By this method, vulcanizates with FeCl$_3$ and with KSF each were found to be over 90% insoluble.

It was also shown that free-radical gum stock curing of E/P/arylbutene terpolymers results in vulcanizates very similar to those obtained from E/P/arylbutene–bisbenzylic halide–KSF systems (Table I).

E/P/Arylbutene Vulcanizates Containing Carbon Black Fillers

Addition of certain carbon blacks to E/P/arylbutene–bisbenzylic chloride–KSF formulations resulted in vulcanizates that have greatly increased tensile strength and hardness. In the presence of carbon black fillers, much larger quantities of Montmorillonite KSF were required to catalyze vulcanization. Five carbon blacks with various pH's were examined for their reinforcing action in vulcanizates of E/P/o-tolyl-butene with BCMD and KSF. The reinforcing effects of the blacks varied greatly, but not solely with pH. Since some alkaline blacks reinforced better than acidic ones, partial

TABLE II
Effect of Type of Carbon Black on Tensile Properties[a]

	Micronex W-6 (pH 4.8)	Micronex MPC (pH 4.4)	Shawinigan Acetylene (pH 7–8)	Philblack ISAF (pH ~9)	HAF (pH 9)
Durometer A-2 hardness	77	75	76	78	78
M_{100}, psi	—	350	530	—	550
T_B, psi	290	390	800	320	720
E_B, %	40	260	260	60	320

[a] In each experiment, 26 phr carbon black, 22 phr BCMD, and 50 phr KSF were used per 100 parts of E/P/tolylbutene terpolymer (180° for 1 hr).

TABLE III

Properties of Typical E/P/Arylbutene–Carbon Black Vulcanizates

E/P/o-Tolylbutene, parts	100	—	—	—	100	100	100	100	100	100	100	100	100	100	100	100	100
E/P/α-Naphthylbutene, parts	—	100	100	100	—	—	—	—	—	—	—	—	—	—	—	—	—
Carbon black HAF, phr	26	25	25	25	25	25	25	26	26	26	50	50ᵃ	26	50	50	26	50
Curing agent	BCMD	BCMD	BCMD	BCMD	BCMD	BCMD	BCMD	BCMD	BCMD	BCMD	BCMD	BCMD	DCPX	DCPX	DCPX	DBPX	DBPX
Parts curing agent, phr	22	17	17	17	17	21	21	22	22	22	22	22	18	18	18	14	14
Parts KSF, phr	50	67	67	67	67	83	83	54	60	64	64	60	60	60	60	60	70
Curing temp, °C	180	180	180	180	160	180	160	180	180	180	180	180	180	180	180	180	180
Curing time, min	60	60	60	30	60	30	60	60	60	60	60	60	60	60	60	60	60
Durometer A hardness	74	75	73	73	65	71	73	78	78	85	75	75	75	87	87	78	87
M_{100}, psi	600	710	570	600	485	640	590	490	510	—	770	570	570	540	—	660	—
T_B, psi	1110	1190	990	1000	675	830	720	700	700	490	830	800	800	800	540	960	800
E_B, %	320	240	280	300	300	270	260	330	300	60	140	240	240	60	60	230	100
Yerzley resilience (25°C), %	—	76	70	68	65	68	63	—	—	—	—	—	—	—	—	—	—
Compression set (70°C), %	—	17	33	49	93	48	74	—	—	—	—	—	—	—	—	—	—

ᵃ Shawinigan acetylene black used in place of HAF black.

neutralization of the acidic catalyst must not be the only factor involved. Data are in Table II.

Most of the optimization work was carried out using 25–26 phr carbon black HAF, since at 50 phr the vulcanizates were too hard (Durometer A-2 hardness 85–87). At the 26 phr concentration, E/P/4-o-tolyl-1-butene terpolymer was poorly cured by 20 phr bischloromethyldurene and 30 or 40 phr KSF. Increasing the KSF concentration to 54, 60, 67, and 83 phr with 25–26 phr HAF black resulted in tensile properties similar to those given in Table II for the example containing 50 phr KSF. The use of 50 phr HAF black, however, results in shorter-breaking vulcanizates; KSF was varied from 50 to 70 phr without causing significant changes. Shawinigan acetylene black, however, gave a somewhat more attractive vulcanizate in a single experiment. Results of the same magnitude were obtained by replacing BCMD with α,α'-dichloro-p-xylene (DCPX) or α,α'-dibromo-p-xylene (DBPX). Typical data are in Table III. Temperatures less than 180°C are inadequate for complete cure, as shown by compression set data. It should also be noted that the naphthyl group was again shown to be more active toward the electrophilic reagent than the o-tolyl ring.

The amount of bisbenzylic halide needed for curing must also be increased slightly over that required for gum stock vulcanization. Thus, 8 phr DBPX, 12 phr DCPX, or 4–14 phr BCMD were insufficient when 50 phr carbon black HAF were present even when high KSF concentrations were used.

In a single pair of experiments, to determine effect of moisture, a typical milled formulation containing HAF black was allowed to remain exposed to the atmosphere in humid weather for 4 hr before molding. It was only slightly less cured than its counterpart molded immediately after milling.

In control experiments utilizing free-radical vulcanization, the o-tolyl-butene and phenylbutene terpolymers each with 50 parts HAF black and 10 parts DICUP (40% on $CaCO_3$), were cured at 160° for 1 hr to vulcanizates with M_{100} 850 and 500 psi and T_B 2900 and 2200 psi at E_B 200% and 240%, respectively.

E/P/Arylbutene Vulcanizates Containing Carbon Black and Compounding Oil

The use of a compounding oil (Flexone 765) with carbon black HAF in E/P/tolylbutene–bisbenzylic halide–KSF vulcanizates did not have a beneficial effect on properties. Vulcanizates are softer, but tend to be less cured and require even higher concentrations of KSF. In only one example was the expected increased elongation at break achieved. In vulcanizates with 50 phr HAF black, addition of 20 or 40 phr of the oil lowered the Durometer A-2 hardness from 85 to 56–59. Some typical examples are listed in Table IV for comparison with their counterparts in Table III.

TABLE IV
Properties of Typical E/P/Arylbutene–Carbon
Black Vulcanizates Containing Oil

Carbon black HAF[a]	26	50	26	50
Flexone 765 oil[a]	14	20	14	20
BCMD[a]	22	24	—	—
DCPX[a]	—	—	14	16
KSF[a]	50	90	70	80
M_{100}, psi	440	—	550	—
T_B, psi	880	180	600	150
E_B, %	430	60	160	20

[a] Parts per 100 parts E/P/o-tolylbutene (180° for 1 hr).

E/P/Arylbutene Vulcanizates Containing Clay Fillers

Inert clays provided reinforcement for E/P/arylbutene–BCMD–KSF vulcanizates. The best examples had properties approaching those of clay-filled sulfur-cured "Nordel" vulcanizates. Both hard (Crown, Suprex) and soft (McNamee) clays were utilized. The vulcanizates had Durometer A-2 hardnesses between 60 and 67. Best reinforcement was achieved at the 50 phr concentration. Unlike carbon blacks, clay fillers did not require the use of excessive amounts of KSF catalyst, but only slightly more than required for gum stock vulcanization. Properties of typical vulcanizates are detailed in Table V.

TABLE V
Properties of Typical Clay-Filled E/P/Arylbutene Vulcanizates

E/P/p-Tolylbutene, parts	100	100	—	—	—	—	—
E/P/o-Tolylbutene, parts	—	—	100	100	100	100	100
Crown clay, phr	50	—	—	50	100	—	—
Suprex clay, phr	—	50	—	—	—	100	—
McNamee clay, phr	—	—	50	—	—	—	100
BCMD, phr	26	26	26	26	26	26	26
KSF, phr	22	22	22	34	44	50	44
M_{100}, psi	480	480	320	240	570	530	380
M_{300}, psi	885	890	500	370	—	—	—
T_B, psi	930	970	550	460	590	545	480
E_B, %	340	380	420	600	120	120	200

Gum Stock Vulcanizates of Nordel EPDM Elastomer

Crosslinking of Nordel 1040 has been accomplished at 180°C by reaction with bischloromethyldurene or p-bisbromomethylbenzene in the presence of the strongly acidic clay Montmorillonite KSF. This is the same curing system described above for ethylene–propylene–arylalkene terpolymers, but in this case the benzylic halide reacts with a double bond rather than with an aromatic nucleus.

Nordel 1040 appears to be more easily vulcanizable than E/P/arylalkene terpolymers under these conditions. Thus, 7 phr bischloromethyldurene

TABLE VI

Properties of Nordel–Carbon Black–Oil Vulcanizates Cured with BCMD–KSF[a]

Nordel 1040, parts	100									100	100	100	100
Carbon black HAF, phr	50									50	50	50	50
Flexone 765 oil, phr	8									8	8	10	10
BCMD, phr	17									17	17	26	12
KSF, phr	83									83	67	80	80
Curing temp., °C	140	160	160	160	180	180	200	200	200	180	180	180	180
Curing time, min	60	10	30	60	10	30	10	30	60	60	60	60	60
Durometer A hardness	61	60	71	74	69	72	71	76	75	79	72	—	—
M_{100}, psi	—	—	220	400	180	580	580	550	520	620	580	560	400
T_B, psi	190	140	640	750	580	950	800	1020	1050	1090	1180	990	420
E_B, %	40	20	230	240	240	225	300	300	310	280	300	300	160
Yerzley resiliance (25°), %	56	56	53	56	59	60	57	57	57	61	58	—	—
Compression set (70°), %	96	99	89	45	35	26	56	26	30	18	48	—	—

[a] The first ten vulcanizates in this table were all from the same master batch. The last three samples were molded 13 days after the first seven samples, i.e., after milling.

(BCMD) and 10 KSF gave an overcured sample, 88% insoluble in boiling toluene for 24 hr, while only 4 phr BCMD with 10 phr KSF gave an almost fully cured vulcanizate, 82% insoluble. The latter represents the correct stoichiometric amount of BCMD to react with all the double bonds in Nordel. This vulcanizate had M_{100} 100, M_{300} 135, T_B 175 psi, E_B 560%.

In contrast to its behavior toward E/P/arylalkene terpolymers, α,α'-dibromo-p-xylene is a less active curing agent for Nordel 1040 than is bischloromethyldurene. Thus, 10 phr of the bromo compound with 14 phr KSF gave an undercured gum stock vulcanizate, 58% insoluble in boiling toluene for 24 hr.

Nordel 1040 Vulcanizates Containing Carbon Black, Compounding Oil, and Clay Fillers

Addition of carbon black HAF and compounding oil to Nordel/BCMD/-KSF formulations was found to give vulcanizates with T_B about 1000 psi at 300% elongation.

Carbon black interfered with the cure just as it did when E/P/arylalkene terpolymers were vulcanized with this system, and the use of higher catalyst concentration is necessitated. Even when 20 phr BCMD was used with Nordel containing 50 phr HAF black and 8–10 phr Flexone 765 oil, up to 25 phr KSF gave no cure, 33 phr very slight cure, and 50 phr undercure, in marked contrast to the gum stock results above. Use of 4 phr BCMD (the stoichiometric amount) gave undercure even with 83 phr KSF. Good cures were obtained, however, using 67–83 phr of the catalyst, but even with 67 phr, crosslinking is not complete as shown by compression set data (see Table VI).

Optimum conditions for vulcanization of Nordel 1040 formulations containing 50 phr carbon black and 8–10 phr of oil are thus similar to those required for E/P/arylbutene formulations containing only 25–26 phr carbon black. This implies that more acidity is needed to catalyze attack by benzylic cations on aromatic rings than on double bonds.

As with gum stock cures, Nordel 1040 vulcanizates loaded with black and oil were cured better by BCMD than by DBPX. In a series of vulcanizates

TABLE VII
Properties of Clay-Filled Nordel Vulcanizates[a]

Parts BCMD, phr	17	17	17	20	20	20
Parts KSF, phr	21	21	21	25	25	25
Type inert clay[b]	Crown	Suprex	McNamee	Crown	Suprex	McNamee
Durometer A hardness	50	52	55	51	55	59
M_{100}, psi	190	225	210	190	220	270
T_B, psi	500	460	320	340	460	430
E_B, %	360	270	230	220	250	220
Compression set (70°), %	46	43	34	39	33	28
Yerzley resilience (25°), %	71	70	70	70	68	70

[a] All pressure molded at 180° for 1 hr.
[b] 50 phr of each.

TABLE VIII
Properties of SBR Vulcanizates

SBR-1500, parts	100	100	100	—	—	—	—	—	—	—	—
SBR-1502, parts	—	—	—	100	100	100	—	—	—	—	—
SBR-3750, parts	—	—	—	—	—	—	162	162	162	162	162
BCMD, phr[a]	24	21	16	24	21	16	22	22	22	22	22
KSF, phr[a]	20	17	14	20	17	14	70	65	60	54	48
Curing temp., °C	166	180	180	166	180	180	180	180	180	180	180
Curing time, min	30	60	60	30	60	60	60	60	60	60	60
Durometer A-2 hardness	—	—	—	—	—	—	96	—	—	84	86
T_B, psi	550	350	270	1850	1320	620	2200	1970	1970	1200	1260
E_B, %	60	150	80	40	40	50	20	20	20	75	40

[a] Per 100 parts of polymer exclusive of fillers for easier comparison with other tables present.

each containing 50 phr carbon black HAF, 10 phr oil (Flexone 765), and 80 phr KSF, samples containing 26 and 12 phr BCMD were well cured while samples with 22 and 10 phr DBPX were badly undercured.

Properties of typical vulcanizates are detailed in Table VI, which includes a time–temperature curing study. This showed that 180°C for 60 min or 200°C for 30 min is necessary for complete cure, 160° for 60 min and 180° for 30 min give marginal cures, and that milder conditions are inadequate.

Nordel 1040/BCMD/KSF vulcanizates containing clay fillers are softer and more resilient than the corresponding carbon black vulcanizates. Properties are set forth in Table VII.

SBR Rubber Vulcanizates

SBR (styrene–butadiene copolymer) is similar to E/P/arylbutene terpolymers in that it contains pendant aromatic rings and similar to Nordel in that it contains double bonds. It is therefore potentially capable of being crosslinked by bifunctional electrophilic reagents through either site. It has now been found that SBR can be cured by bischloromethyldurene under the catalytic influence of Montmorillonite KSF at 166°–180°C for 30–60 min but it is not known by which route.

Vulcanizates of gum stocks SBR-1500 and SBR-1502 with BCMD and KSF were tough but short breaking. They are probably somewhat over-cured, even at 166°C for 30 min.

The curing of SBR-3750 (which contains 50 phr carbon black HAF and 12 parts oil) with BCMD and KSF at 180° for 1 hr gave extremely hard, short-breaking vulcanizates with very little resilience. This apparent over-cure was accomplished with much smaller catalyst concentrations then were used with Nordel with similar amounts of fillers, so it is clear that SBR is the most active polymer toward this curing system. Properties are tabulated in Table VIII.

CONCLUSIONS

A new approach to the curing of EPM elastomers, involving crosslinking through pendant aromatic rings, has been demonstrated. The elastomers used for this purpose, terpolymers of ethylene and propylene with 4-aryl-1-butenes, were readily prepared by a conventional coordination catalyst system. Crosslinking was achieved by acid-catalyzed attack on the aromatic rings by bifunctional electrophilic reagents.

References

1. V. G. Epshtein, A. A. Chekanova. T. N. Istomina, M. I. Farberov, and A. A. Bondarenko, *Soviet Rubber Technology*. 31, October (1967).
2. M. M. Martin and G. J. Gleicher, *J. Amer. Chem. Soc.*, 86, 233 (1964).
3. J. A. Price, M. R. Lytton, and B. G. Ranby, *J. Polym. Sci.*, 51, 541 (1961).
4. F. J. Welch and C. W. McGary, U.S. Pat. 3,164,575 (1965).