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Sulfomaleation of EPDM Polymers

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ABSTRACT: The introduction of polar functionality into hydrocarbon polymers has been studied extensively in our laboratory as a means of producing sulfonate ionomers. Another method for introducing polar functionality is the maleation of hydrocarbon polymers, the anhydride functionality being useful for bonding polar molecules such as amines. Sulfonation is quite vigorous and, under the proper circumstances, is very effective with the low level of unsaturated sites present in a number of hydrocarbon elastomers. Maleic anhydride, to the contrary, exhibits low reactivity, and alternative measures such as prior halogenation–dehydrohalogenation or free radical grafting are required. We wish to report a process called "sulfomaleation" to simultaneously introduce sulfonate ionomer functionality and reactive anhydride groups into elastomers. To accomplish this, we have used sulfonate-substituted maleic anhydrides. The presence of the strongly electrophilic sulfonate activates the maleic group and substantially increases its reactivity with low functionality hydrocarbon rubbers, presumably via an Alder–ene type of reaction. In this preliminary report, we have attempted to elucidate the structures of sulfomaleic anhydride and derivatives and have conducted some screening experiments to demonstrate the formation of polymer adducts and their ability to covalently bond amine to polymers.

The sulfonation[1-3] of low-functionality elastomers such as ethylene–propylene terpolymer (EPDM rubber) has been used extensively in our laboratory to produce ionomers. The introduction of low levels of metal or amine sulfonate results in ionomers[4] with remarkable physical properties. Another chemical modification, the reaction of polymers with maleic anhydride, is used extensively to introduce reactive anhydride functionality into hydrocarbon polymers. An Alder–ene reaction can be utilized to react with the olefin sites of polymers such as low molecular weight ($M_n \sim 1000$) polyisobutylene; however, with many polymers such as EPDM the olefin is not sufficiently reactive. Thus, free radical grafting of maleic anhydride onto saturated hydrocarbon polymers, usually initiated by peroxides, is a major means of introduction of reactive functionality. There are numerous problems connected with free radical grafting of maleic anhydride onto hydrocarbon polymers. The process is nonselective and reactions in solution give extensive maleic grafting to solvent. Furthermore, the hydrocarbon polymer radicals can combine and/or undergo scission, resulting in cross-linking or molecular weight breakdown, depending on the polymer structure. This is a serious disadvantage for some applications.

We wish to report a novel chemical technique that enables us to readily introduce both sulfonate and maleic anhydride functionality in EPDM polymers. The reagents that we have investigated are sulfomaleic anhydride and its derivatives.

A salt derived from sulfomaleic anhydride was first described in 1930,[5] but it was not until 1973 that French workers[6] first reported the preparation of sulfomaleic anhydride free acid (1) by the reaction of SO_3 and maleic anhydride. A search of the literature turned up little regarding this compound. Several patents have been issued covering detergent compositions prepared by reacting alcohols with sulfomaleic anhydride. Some work by Gruzdev[7] on the preparation of some derivatives was published in 1979. No reactions of sulfomaleic anhydride

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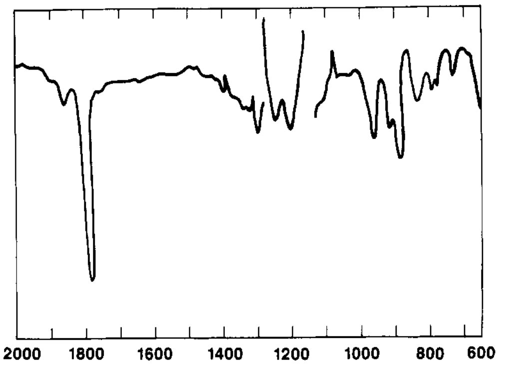


Figure 1. Infrared spectrum of sulfomaleic anhydride in dioxane.

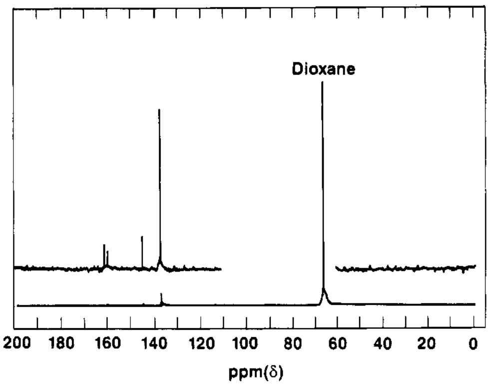
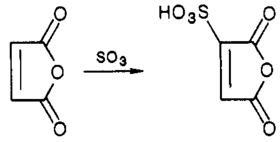


Figure 2. ^{13}C NMR spectrum of sulfomaleic anhydride in dioxane.

or its derivatives with polymers were reported.

Results and Discussion

Sulfomaleic Anhydride and Derivatives. Sulfomaleic anhydride was prepared readily by combining sulfur trioxide and maleic anhydride.[3] A purified product was obtained by recrystallization from hot dichloroethane. The product was extremely hydroscopic and was handled in a dry nitrogen atmosphere.



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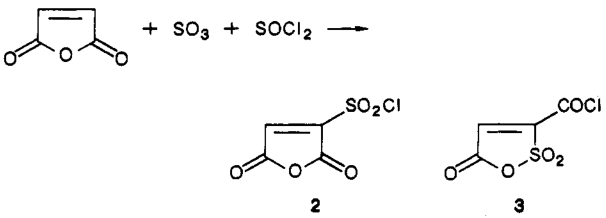
(1)

Infrared analysis showed a typical anhydride carbonyl absorption (1780 and 1843 cm^{-1}) (Figure 1) and ^{13}C NMR confirmed that this product was essentially a single isomer with two carbonyl carbons and two olefinic carbons (Figure 2).

Utilizing thionyl chloride and sulfur trioxide, French workers reported the synthesis of the sulfonyl chloride derivative of sulfomaleic anhydride. Repeating their work, we obtained instead a mixture of two products. ^{13}C NMR (Figure 3) showed two sets of four carbons. Distillation led to the enrichment of the higher boiling component corresponding to the NMR peaks designated by the letter "H". Infrared analysis (Figure 4) showed carbonyl absorptions consistent with a mixture of isomers (eq 2).



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(2)

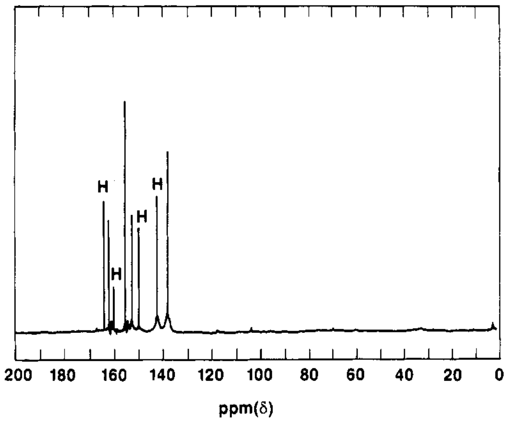


Figure 3. ^{13}C NMR spectrum of a mixture of 2 (high boiler) and 3 prepared according to eq 2.

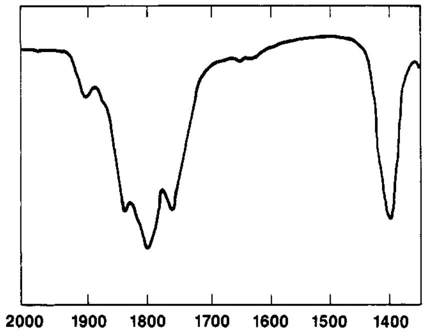


Figure 4. Infrared spectrum of mixture of 2 and 3.

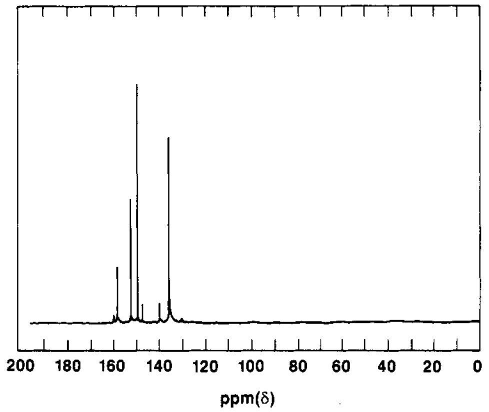
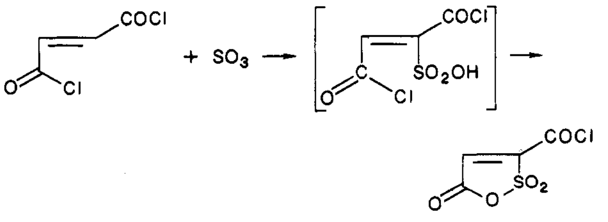


Figure 5. ^{13}C NMR spectrum of low boiler 3 concentrate prepared according to eq 3.

Gruzdev[7] reported the production of (chlorocarbonyl)-β-sulfoacrylic anhydride (3) as the sole product of the sulfonation of fumaryl chloride (eq 3).



3

(3)

In our hands, this reaction also produced a mixture of two products, which according to ^{13}C NMR and infrared analysis, were the same product mixture shown in eq 2. Careful distillation in an efficient packed column utilizing a high reflux ratio enabled us to collect the nearly pure low-boiling compound whose NMR (Figure 5) and infrared

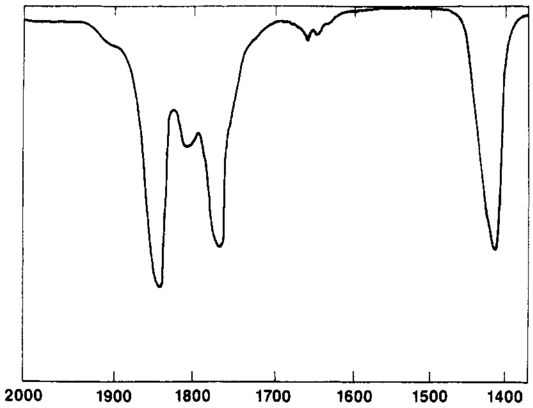


Figure 6. Infrared spectrum of low boiler 3 concentrate.

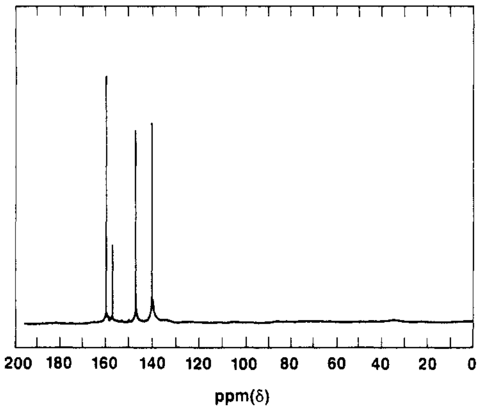


Figure 7. ^{13}C NMR spectrum of high boiler 2 prepared according to eq 6.

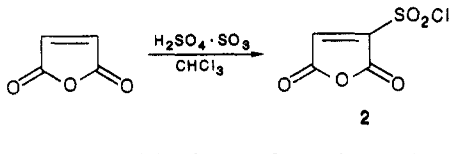
(Figure 6) are shown. The assignment of the (chlorocarbonyl)-β-sulfoacrylic anhydride (mixed anhydride) structure 3 to this material is consistent with the reported infrared absorption of β-sulfoacrylic anhydride.[8]

A rather ingenious technique was developed by Gruzdev (eq 5) to circumvent the troublesome equilibrium between chlorosulfonic acid and sulfuric acid (eq 4) encountered

$$RSO_3H + ClSO_3H \rightleftharpoons RSO_2Cl + H_2SO_4 \quad (4)$$

$$H_2SO_4{\cdot}SO_3 + CHCl_3 \rightarrow 2ClSO_3H + HCl + CO \quad (5)$$

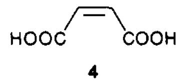
in chlorosulfonations. Maleic anhydride was chlorosulfonated with oleum and chloroform, and a single product was obtained (eq 6), which proved to be the higher



(6)

boiling component (2) observed in the earlier chlorosulfonations. The ^{13}C NMR (Figure 7) and infrared carbonyl absorption band (Figure 8) confirm this.

Reactions of maleic acid (4) or fumaric acid (5) with oleum in chloroform also yield 2 as the principal product.



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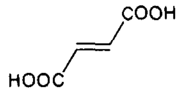

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The presence of strong electron-withdrawing substituents should activate maleic anhydride and enable ene chemistry to be carried out on a variety of hydrocarbon polymers. Our objective was to bond sulfomaleic anhydride derivatives to unsaturated hydrocarbon polymers via an ene reaction and utilize the reactive functionality to subsequently bond polar molecules to the polymer.

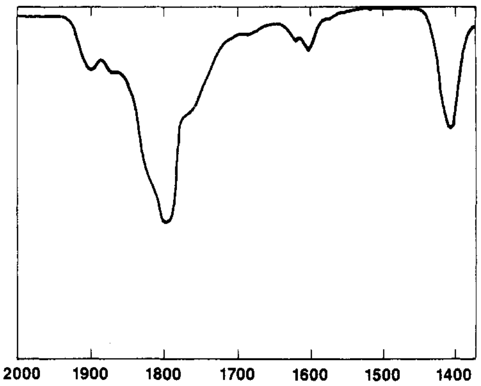
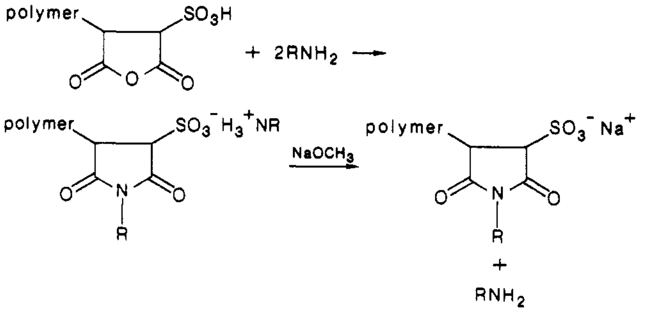


Figure 8. Infrared spectrum of high boiler 2.

In addition to neutralizing the sulfonic acid group, primary amines are known to react with cyclic anhydride functionality to give amic acid first and then imide with subsequent heating and the elimination of H_2O. Thus we anticipated that 2 mol of a primary amine would combine with each mole of polymer-bonded sulfomaleic anhydride.

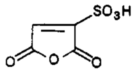
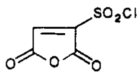
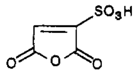
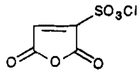
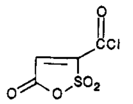


Subsequent treatment with a strong base such as metal alkoxides or hydroxides should remove ionically bound nitrogen and leave covalently bound nitrogen.

Sulfomaleation and Subsequent Amidation of Hydrocarbon Polymers. A series of screening experiments was conducted in which sulfomaleic anhydride or its derivatives were reacted with a hydrocarbon solution of a low-functionality polymer such as EPDM, butyl rubber, conjugated diene butyl rubber, Vistanex J, etc. The resulting product was then treated with excess methylamine in methanol, and the product was isolated by precipitation from excess alcohol, dried in vacuo, and analyzed for sulfur and nitrogen. Methylamine was selected because it is extremely volatile, thereby minimizing any confusion in the nitrogen analysis caused by entrained amine.

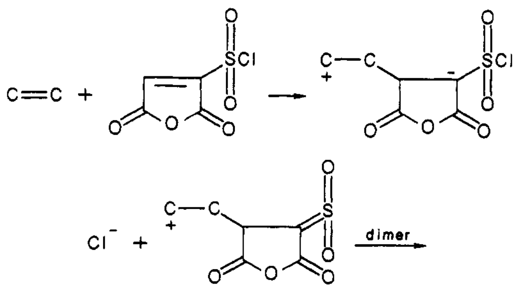
The isolated polymer products were redissolved, treated with sodium methoxide in methanol to free ionically bound amine, and isolated and purified as before. The results shown in Table I demonstrate that sulfomaleic anhydride and its derivatives react with low-functionality hydrocarbon polymer and can further serve to covalently bond polar molecules such as amines to these polymers. Treatment with sodium methoxide generally caused a loss of about half of the bound nitrogen with little effect on sulfur, which was consistent with the mechanism depicted. Sulfomaleic anhydride was also reacted with EPDM rubber in the bulk by milling the two together. Subsequent incorporation of 5 wt % zinc stearate generated a tough ionomer. Solubility in hot 95:5 (v/v) toluene–methanol confirmed the presence of physical ionomer rather than covalent cross-links.

Table I
Reaction of Sulfomaleic Derivatives with Hydrocarbon Polymers

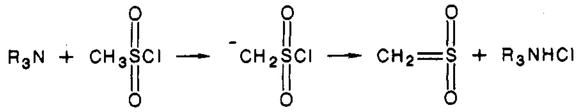
polymer	reagent[a]	methoxide treatment[b]	% S	mequiv of S/100 g	% N	mequiv of N/100 g
EPDM 2504		pre	0.46	14.2	0.265	18.9
		post	0.41	12.8	0.102	7.3
EPDM 2504		pre	0.46	14.2	0.359	25.6
		post	0.39	12.2	0.194	13.8
CD butyl[d]		pre	0.38	11.9	0.248	17.7
butyl rubber 365		pre	0.47	14.7	0.468	33.4
		post	0.45	14.1	0.215	15.3
EPDM 2504	methyl ester[c]	pre	0.38	11.9	0.179	12.8
		post	0.36	11.2	0.089	6.4
EPDM 2504		pre	0.40	12.5	0.445	32.1
		post	0.52	16.3	0.205	14.6

[a] 30 mequiv/100 g of polymer followed by methylamine. [b] Before and after sodium methoxide treatment. [c] Reaction product of sulfomaleic anhydride–methanol, 1:1. [d] CD butyl is conjugated diene butyl rubber.

Some observations of these screening experiments were not readily explained. The sulfomaleic anhydride with its strong acid functionality produced soluble polymer adducts, while use of the sulfonyl chloride resulted in extensive gelation. Gelation was also observed from the mixed anhydride (**3**); however, this material always contained significant quantities of the sulfonyl chloride isomer (**2**). Alternative explanations include the possibility that the sulfonyl chloride is a more electrophilic reagent capable of initiating alkylation reactions at olefin sites which would result in linking of polymer chains. Donation of electrons from the hydroxyl oxygen to the sulfonyl group of the sulfonic acid could serve to attenuate the electrophilicity, making the sulfonic acid less electrophilic than the sulfonyl chloride. Paradoxically, the sulfomaleic anhydride containing the free sulfonic acid would be a weaker Lewis acid than the sulfonyl chloride. Another possibility involves the loss of chlorine from the sulfonyl chloride due to the formation of a negative charge on the α carbon and subsequent dimerization of the reactive intermediate.



Precedent for this mechanism can be found in the tertiary amine catalyzed reaction of sulfonyl chloride.



$$R_3N + CH_3\overset{O}{\underset{O}{S}}Cl \longrightarrow {}^{-}CH_2\overset{O}{\underset{O}{S}}Cl \longrightarrow CH_2{=}\overset{O}{\underset{O}{S}} + R_3NHCl$$

The reactions of sulfomaleic anhydride with alkylchloroformate can produce sulfonate esters and offer a convenient route to capping the sulfonic acid group. The resulting esters are distillable, easily purified products with substantially improved hydrocarbon solubility. An essentially pure methyl ester (**6**) was obtained upon distillation of the reaction product of SMA with methyl chloroformate (Figure 9).

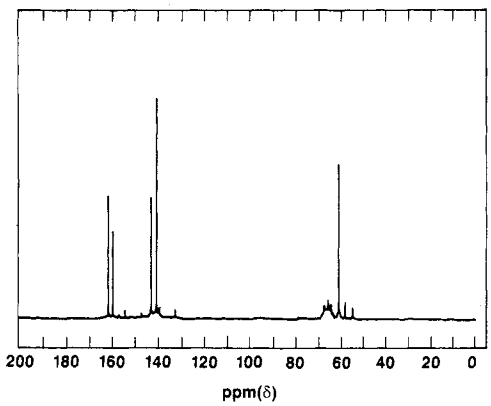
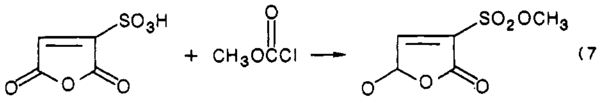


Figure 9. ^{13}C NMR spectrum of sulfomaleic anhydride methyl ester **6** (dioxane-d_8).



1 **6** (7)

Methyl sulfonate esters are excellent alkylating agents; thus subsequent to polymer modification, the sulfonate is regenerated by reaction with amines.

$$-SO_2OCH_3 + H_2NR \rightarrow -SO_3^- \; H_2N^+(CH_3)R$$

We are currently exploring the chemistry of these sulfomaleic esters with unsaturated hydrocarbon polymers as well as some small-molecule models mimicking the unsaturated sites on EPDM polymers. The results will be reported shortly.

Experimental Section

Sulfomaleic anhydride (1) was prepared by the reaction of maleic anhydride and liquid SO_3 according to the method of Le Berre.[6] The product was crystallized from dichloroethane and dried under vacuum in a drybox.

(Chlorosulfonyl)maleic anhydride (2) was prepared by the reaction of oleum–chloroform on maleic anhydride according to the Russian procedure.[7]

(Chlorocarbonyl)-β-sulfoacrylic anhydride (3) was prepared by the reaction of fumaryl chloride with SO_3.[7] The lower boiling isomer was collected by careful fractionation through a packed column using a high reflux ratio. The fraction bp 91 °C, $n^{20}{}_D$ 1.5162 contained the desired product with only a small amount of contamination by the high boiler (**2**). (See Figures 5 and 6.)

(Methoxysulfonyl)maleic anhydride (6) was prepared by the reaction of methylchloroformate on purified sulfomaleic anhydride (method A) and by addition of methyl chloroformate to a mixture of SO_3 and maleic anhydride (method B).

Method A: A combination of sulfomaleic anhydride (15 g (0.084 mol)) and methyl chloroformate (19.8 g (0.21 mol)) was heated at reflux under a nitrogen purge overnight. Evolution of CO_2 and HCl was observed. The mixture was distilled, and 12.1 g (75% yield) of **6** was obtained, bp 120–123 °C (0.6 mm).

Method B: Under a nitrogen blanket or a drybox, 98.06 g (1 mol) of maleic anhydride and 80.06 g (1.01 mol) of SO_3 were combined and heated in a ~55 °C oil bath. When the temperature rose past 60 °C, cooling was provided until the exotherm ceased. Heating was maintained for about 20 h.

The reaction mixture was cooled at ambient, and 236.3 g (2.5 mol) of methyl chloroformate was added in two portions. After the exotherm ceased the mixture was heated at ~75 °C overnight. Excess methyl chloroformate was removed on a rotary evaporator. Distillation gave 35.6 g of unreacted maleic anhydride (63.7% conversion) and 110–122 g of product, 90–101% selectivity.

Polymer Modification with Sulfomaleic Anhydride. A typical polymer modification reaction was conducted as follows. A solution of 50 g of a dry EPDM rubber such as Vistalon 2504 in 1000 mL of dry xylene was heated at 130 °C and stirred under nitrogen and 2.67 g (15 mmol) of sulfomaleic anhydride was added. The anhydride was tightly wrapped in a parafinic film to prevent moisture pickup. Heating was continued for 4 h. After cooling, excess methylamine was added (21 g) to neutralize the sulfonic acid and react with the anhydride. The polymer solution became extremely viscous and 50 mL of methanol was added to attenuate the viscosity. After standing overnight, the polymer was precipitated in a high-speed mixer with 4000 mL of isopropyl alcohol–water (70:30), collected by filtration, and washed again in the mixer with another portion of IPA–H_2O. A small quantity of Irganox 1010 (~0.1 g) antioxidant was added, and the polymer was filtered and vacuum-dried at 50 °C.

Microanalysis indicated that the polymer contained 0.46% S (14.2 mmol/100 g) and 0.265% N (19.9 mmol/100 g). Treatment of a solution of the modified polymer with excess sodium methoxide in methanol to free ionically bound methylamine and isolation of the polymer by the above procedure gave the sodium sulfonate product, whose analysis showed 0.40% S (12.5 mmol/100 g) and 0.115% N (8.2 mmol/100 g).

All polymer samples used in this study contained about 1.5–2.0 mol % unsaturated monomer. Thus the available unsaturated monomer was in excess of the sulfomaleic anhydride reagent utilized. The unsaturation in EPDM is obtained from ethylidenenorbornene while butyl rubber utilizes isoprene as the comonomer. Conjugated diene butyl is made by chlorination and dehydrohalogenation of butyl rubber.

Registry No. 6, 40336-90-1.

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Conducting Polyquinolines

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ABSTRACT: Polyquinolines containing stilbene, diphenyl sulfide, thianthrene, and biphenyl connecting groups as well as AB polyquinolines, with either phenyl or a thiophene pendent group, were prepared and doped with arsenic pentafluoride, iodine, sodium naphthalide, or sodium anthracide. The highest conductivities obtained were for the right-rod polyquinolines poly[2,6-(4-phenylquinoline)] and poly[2,2′-(*p,p*′-biphenyl)-6,6′-bis(4-phenylquinoline)], both of which gave conductivities of approximately 10 S/cm on doping with sodium anthracide. Modification of these two polyquinolines resulted in lower conductivities.

Introduction

Many polymers and metals have a number of characteristics in common such as strength, elasticity, plasticity, and toughness. However, one of the more important properties of metals, their high conductivity, is not shared with polymers except for a few isolated examples. The possibility of conducting polymers was suggested[1] over 20 years ago, although only recently have organic polymers with conductivities approaching those of metals been synthesized.

The discovery that a free-standing film of polyacetylene, prepared by a Ziegler–Natta polymerization of acetylene,[2] could be oxidized with strong oxidants to give a conducting organic polymer[3] and the discovery that poly(*p*-phenylene) could be oxidized to an organic conducting polymer[4] stimulated research on a series of conducting organic polymers. These polymers, including poly(*p*-phenylene),[4] poly(*p*-phenylene sulfide),[5] polypyrrole,[6] polythiophene,[7] and polyaniline,[8] can be doped to give conductivities of up to 10^2 S/cm (conductivity is expressed in Siemens per centimeter, S/cm). Recently, it has been shown that polyquinolines can be doped to give conductivities of approximately 10 S/cm.[9,10]

High molecular weight polyquinolines ($M_n = 5 \times 10^5$) can be prepared by an acid-catalyzed reaction of aromatic *o*-amino ketones with keto methylene compounds.[11] The polymerization reaction is versatile, and the synthetic pathways to the monomers are abundant, such that a wide variety of structural features can be incorporated into the polymer (vide infra). Rigid-rod polyquinolines such as poly[2,2′-(*p,p*′-biphenyl)-6,6′-bis(4-phenylquinoline)] are highly crystalline ($T_m \sim 500$ °C) and are soluble in the

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