

The Grafting of Isoprene onto Poly(propylene Oxide)*

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Synopsis

The grafting of isoprene as well as a comonomer mixture of isoprene and acrylonitrile onto a backbone of high molecular weight poly(propylene oxide) with tertiary-butyl peroxoate gave a gumstock which is sulfur curable to a product having interesting elastomeric properties.

INTRODUCTION

Propylene oxide rubber is a copolymer of propylene oxide and an unsaturated epoxide, usually allyl glycidyl ether. The latter is necessary to allow vulcanization by sulfur. This rubber has aroused considerable interest through its good physical properties, resistance to swelling by aliphatic hydrocarbon oils, and excellent low-temperature properties and ozone resistance.¹ However, the cost of the available unsaturated epoxides limits the scope of useful applications of the rubber. For this reason, other means of preparing a sulfur-curable propylene oxide rubber have been investigated. This report covers the successful grafting of a diene, isoprene, as well as a comonomer mixture of isoprene and acrylonitrile onto poly(propylene oxide) by the perester, tertiary-butyl peroxoate.

EXPERIMENTAL

Materials

Propylene oxide was polymerized to a high molecular weight polymer with a diethyl zinc-water catalyst.² Since the solid polymer was to be used subsequently in grafting, no antioxidant was added. The polymer was stored in brown jars under nitrogen. All other chemicals were commercial materials used as obtained, including tertiary-butyl peroxoate, a product of the Lucidol Division, Wallace and Tiernan, Inc.

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Graft Polymerization Procedure

The reaction cement was prepared by dissolving 100.0 parts of poly(propylene oxide) in sufficient benzene to make an approximately 4% solution. At the same time, 100 parts of the monomer to be grafted was added. Usually, the cement was prepared by stirring overnight while heating to the reaction temperature. The reaction was begun by the addition of 4.25 parts of tertiary-butyl peroctoate in benzene solution. Grafting was terminated by the addition of phenyl- β -naphthylamine (1% based on estimated product weight) and removal of heat. The solid product was recovered by steam stripping. The product was then dried in vacuo to constant weight.

In two experiments, samples were removed during the course of the reaction. These were obtained through a dip leg in the reactor by applying nitrogen pressure. Sufficient quantities were removed and processed for curing and the determination of the physical properties of the samples.

The reaction conditions and results are given in Table I. Physical properties are listed in Table II; included also are those for a propylene oxide rubber.

TABLE I
Reaction Conditions for Graft Polymerizations

Run	1	2	3	4
PPO, g	100.0	100.0	100.0	10.00
Isoprene, g	100.0	100.0	100.0	100.0
Acrylonitrile, g	—	5.0	—	5.0
Benzene, liters	2.5	2.5	2.5	2.5
<i>t</i> -Butyl peroctoate, g	4.25	4.25	4.25	4.25
Temp., °C	60	60	70	70
Time, hr	143	143	^a	
Yield, g	115.8	124.0		
DSV, dl/g				
Original	17.0	17.0	11.1	11.7
Final	3.68	4.43	^b	

^a See Table II.

^b No final DSV's were obtained.

Curing

The products which were recovered from the four experiments described in Table I were milled according to the following cure recipe: gum stock, 100.0 parts; zinc oxide, 5.0 parts; stearic acid, 3.0 parts; phenyl- β -naphthylamine, 1.0 part; tetramethylthiuram disulfide, 1.0 part; mercaptobenzothiazole 1.0 part; sulfur, 2.0 parts.

Cures were generally run at 310°F for 20 mins in a Pasadena Hydraulics, Inc., laboratory press. Tensile properties were obtained on the cured stocks and are recorded in Table II.

TABLE II
Properties of Graft Polymers

Run	Fraction ^a	Time, hr	Conv. ^b	Wt, g	Cure, min/°F	300% Mod. ^c	500% Mod. ^c	Tensile, psi	Elong., %	% Insol.
1	—	143	16		20/305	370	1111	1814	625	—
2	—	143	14		15/305	400	1280	1710	590	89.2
3	1	1	3.4							
	2	4	—							
	3	8	3.4							
	4	10	4.3							
	5	14	6.5							
	6	26	9.6							
	7	30	13.0							
4	1	1	2.5	75.1	20/305	360	—	450	350	49.1
	2	4	6.1	73.9	20/305	430	—	1160	490	70.0
	3	7	11.3	67.6	20/305	390	1160	1300	525	83.0
	4	10	13.1	63.5	20/305	360	1060	1430	575	85.1
	5	14	16.0	81.0	20/305	350	1140	1740	600	85.6
	6	24	21.2	312.6	20/305	420	1240	2000	600	86.8
5 ^d					22/315	210	465	1560	695	96.4

^a Sample removed from reaction cement at stated time interval.

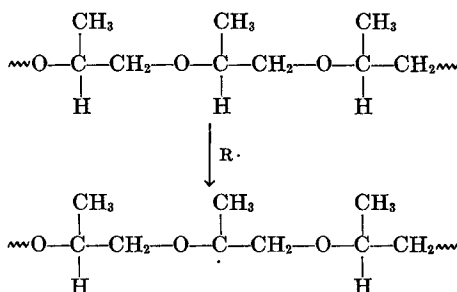
^b Per cent conversion of isoprene or comonomers.

^c Modulus in psi

^d Gum tensile properties of a propylene oxide rubber vulcanizate.

RESULTS AND DISCUSSION

Poly(propylene oxide) is a saturated polymer and cannot be sulfur cured by the usual techniques. However, each propylene oxide unit has a tertiary hydrogen which is susceptible to abstraction by free radicals. The presence of an alkoxy group alpha to each tertiary hydrogen on the polymer chain should enhance this susceptibility:



Once formed on the backbone, this free-radical site can react with dienes. The product so obtained would have a pendent type of unsaturation, as does propylene oxide rubber, capable of being sulfur cured. Such a product would also leave the polyether backbone virtually intact, thereby retaining its desirable physical properties.

Thus, sulfur curing becomes the criterion of grafting. However, this in itself completes only one requirement of this effort. Not only must vulcanization be possible, but the properties of the cured rubber must also be comparable to those of propylene oxide rubber. Obviously, then, the diene, which in this investigation is isoprene, must be grafted onto the backbone in sufficient quantities and also in an adequate distribution along the backbone to achieve these results.

Virtually all free radicals have, to some degree, the capability to abstract hydrogen atoms. We began the experiments using catalysts with half-life characteristics similar to those of benzoyl peroxide for the following reasons:

1. Poly(propylene oxide) has one sensitive tertiary hydrogen in each repeat unit. This being so, it was felt that too high a temperature in forming the free-radical sites on the backbone would tend to cause chain scission to become the predominant subsequent reaction rather than grafting.

2. A temperature range of 60°-70°C was selected for this investigation. At 70°C, the half-life of these catalysts would cause the reaction to be accomplished within a reasonable period of time.³

3. Aromatic hydrocarbons are excellent solvents for poly(propylene oxide). The use of these catalysts in the contemplated temperature range permits the use of benzene as the solvent. This reduces the possibility of chain transfer to the solvent to a minimum.⁴

The three catalysts examined in the initial phase were benzoyl peroxide, lauroyl peroxide, and azobisisobutyronitrile.

Results indicated that benzoyl peroxide was the most effective of the three catalysts. About 25% of the isoprene charged was converted to polymer. The presumed graft polymer, when cured, gave a tensile sheet which was only 46% insoluble in benzene and had very poor physical properties. Obviously, some grafting had occurred but in insufficient amount to realize the second requirement of good elastomeric properties.

It was then apparent that other catalysts had to be examined. Among those looked at in a screening program to find a suitable catalyst was tertiary-butyl peroctoate. This was the catalyst which caused isoprene to be grafted onto poly(propylene oxide) in sufficient amounts and with the proper distribution along the polymer chain to yield a sulfur-cured product with substantial elastomeric properties.

Four key experiments are listed in Tables I and II. Run 1 shows the conditions and results of a typical graft experiment. In this case, 15.8 g isoprene was converted to polymer for every 100 g poly(propylene oxide). Assuming that this is 100% graft, which we freely admit cannot be realized in practice, then there are, on the average, about 11 isoprene units grafted for every 5000 molecular weight of the backbone polymer. The tensile properties of 1800 psi tensile at break and 625% elongation at break indicate that the product has indeed undergone vulcanization and does have substantial elastomeric properties. There is a drop in the dilute solution viscosity (DSV) from 17.0 dl/g of the original material to 3.68 dl/g for the graft. This is an approximate reduction in molecular weight from 5,400,000 to 760,000. Thus, it is very evident that in addition to grafting, a considerable amount of chain scission does occur.

During the initial phase of this work, it was discovered that the presence of a small amount of acrylonitrile in the grafting charge seemed to improve both the yield and properties of the product. Run 2 was an attempt to confirm this. This was a duplicate of run 1 in the presence of 5 phr acrylonitrile. The yield of product does increase, reflecting a higher conversion of isoprene. And the DSV of 4.43 represents an approximate product molecular weight of 930,000. However, the tensile properties of the cured product do not show any significant differences over run 1.

Two additional experiments, runs 3 and 4, were performed at 70°C and were otherwise similar to runs 1 and 2. The 10°C increase causes a four-fold increase in the reactivity of the peroctoate catalyst.² As shown in Table II, samples were removed at specific intervals, and the conversions were calculated from the determined solids contents. Now the effect of including 5 phr acrylonitrile, run 4, is striking. Without acrylonitrile there is only a 13.0% conversion in 30 hr, while this same conversion is accomplished in 10 hr in the presence of acrylonitrile, and the total conversion in 23 hr is 21%. The fractions obtained in run 4 were processed and cured as described above. Tensile properties were secured and are listed in Table II. It is apparent that after a 7-hr reaction period, the product manifests substantial elastomeric properties which are enhanced by the subsequent continued grafting of isoprene.

CONCLUSIONS

Thus, we have demonstrated that the grafting of isoprene onto the backbone of poly(propylene oxide) using tertiary-butyl peroctoate as the grafting catalyst provides a product which can be sulfur cured. In addition, the cured gumstock exhibits interesting elastomeric properties.

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References

1. D. A. Meyer and E. F. Gruber, *SAE J.*, **73**, 76 (1965).
2. J. Furukawa, T. Tsuruta, T. Saegusa, R. Sakata, G. Kakogawa, A. Kawasaki, and I. Harada, *J. Chem. Soc., Ind. Chem. Sect.*, **62**, 1269 (1959); R. Sakata, T. Tsuruta, T. Saegusa, and J. Furukawa, *ibid.*, **63**, 1817 (1960); J. Furukawa, T. Tsuruta, R. Sakata, and T. Saegusa, *Makromol. Chem.*, **32**, 90 (1959); R. Sakata, T. Tsuruta, T. Saegusa, and J. Furukawa, *ibid.*, **40**, 64 (1960).
3. Lucidol Product Bulletin 6.701 and 30.30, March, 1966.
4. G. E. Ham, *Copolymerization*, Interscience, New York, 1964.

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