

Azeotropic Graft Polymerizations of Dienes and Acrylonitrile onto Poly(propylene Oxide)

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Synopsis

Graft copolymerizations of isoprene or butadiene with acrylonitrile in an approximately 2:1 weight ratio onto poly(propylene oxide) are azeotropic. These products, when vulcanized with sulfur, yield elastomers with excellent tensile properties.

INTRODUCTION

The grafting of isoprene or a comonomer mixture of isoprene and acrylonitrile onto a backbone of poly(propylene oxide) has been shown to produce an unsaturated polymer with interesting elastomeric properties when cured in a recipe containing sulfur.¹ Since the use of acrylonitrile greatly reduces the reaction time necessary for the incorporation of isoprene, its effect in the grafting reaction was investigated further. The results of this investigation were then extended to similar graft rubbers made with butadiene.

EXPERIMENTAL

Materials

Propylene oxide was polymerized to a high molecular weight polymer with a diethyl zinc-water catalyst. The polymer, to which no antioxidant had been added, was stored in brown jars under nitrogen. All other chemicals were commercial materials used as obtained.

Graft Polymerization Procedure

An approximately 4% reaction cement was prepared by dissolving 100.0 parts of poly(propylene oxide) (PPO) in benzene. At the same time, the various compositions of the monomers to be grafted were added. The cement was usually made by stirring overnight in a constant temperature bath set at the reaction temperature. Reactions which were made in a 5-gallon reactor were maintained at 70°C. However, on the smaller 2-liter laboratory runs, the temperature fluctuated and the range was recorded (Table I). The reaction was initiated by the addition of 4.25 parts (on 100 of PPO) of *tertiary*-butyl peroxoate in benzene solution. Grafting was terminated by the addition of phenyl- β -naphthylamine (1% based on estimated product weight).

TABLE I
Effect of Acrylonitrile in Graft Copolymerization with Isoprene^a

Run no.	1	2	3	4	5	6
PPO, g	100	100	100	100	100	100
Isoprene, g	100	100	100	100	50	10
Acrylonitrile, g	5	12.5	25	50	25	5
Temp., °C	67.0-71.0	66.5-73.0	67.0-72.0	66.5-70.5	59.5-66.5	58.0-75.0
Time, hr	48	48	48	48	47	48
Weight gain, g	20.6	28.1	35.7	54.3	24.0	6.6
DSV, dl/g						
Original	10.9	10.9	10.9	10.9	14.7	12.6
Final	3.4	3.6	3.4	3.6	3.6	—
Nitrogen, %	0.61	0.99		3.02	1.63	
Acrylonitrile, %	2.08	3.52		11.2	6.18	
Product composition ^d						
PPO	100	100		100	100	
Isoprene	18.2	23.6		37.0	16	
Acrylonitrile	2.5	4.5		17.3	8	
Vulcanizate properties ^c						
300% Modulus, psi	405	460	690 ^a	950	865	445 ^b
Tensile, psi	1770	1640	1650 ^b	1310	2250	1275 ^b
% Elongation	590	550	425 ^b	325	490	570 ^b
% Insoluble ^c	87.2	87.9	89.4	89.2	88.8	86.2

^a All charges included 2.5 liter benzene and 4.25 g tertiary-butyl peroxoate.

^b Thirty min at 275°F.

^c In benzene.

^d PPO degrades completely when treated by itself with perester catalyst.

^e Ungrafted PPO has insignificant properties when incorporated in a sulfur cure recipe.

TABLE II
Graft Copolymerizations of Acrylonitrile with Isoprene or Butadiene^a

Run no.	7	8	9	10	11
PPO, g	100	100	100	100	100
Isoprene, g	20	15	10		
Butadiene, g				20	20
Acrylonitrile, g	10	15	20	10	10
Weight gain, g	17.4	13.7	14.7	12.0	14.3
DSV, dl/g					
Original	14.1	10.5	12.2	15.6	12.6
Final	4.4	2.8	2.0	4.2	—
Vulcanizate properties					
300% Modulus, psi	475	465	475 ^b	625	860
Tensile, psi	2875	2500	2250 ^b	3588	4175
% Elongation	710	715	725 ^b	700	650
% Insoluble	91.9	89.4	87.9	91.1	87.8

^a All charges included 4 l. benzene and 4.25 g. of tertiary-butyl peroctoate. All reactions were run at 70°C for 48 hours.

^b Thirty min at 275°F.

The solid product was recovered by steam stripping followed by drying in vacuo to constant weight.

The reaction conditions and results along with pertinent physical data of derived vulcanizates are listed in Tables I and II. Analytical data as well as the derived polymer compositions are also listed in Table I.

Vulcanization

All products recovered in this investigation were milled according to the following 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; and sulfur, 2.0 parts.

Press cures were usually run for 20 min at 275°F. Where significantly better results were obtained with 30-min curing, these are so reported in the tables.

RESULTS AND DISCUSSION

Butadiene (BD) is known to form an "azeotropic" copolymerization mixture with acrylonitrile (AN).² The possible azeotropic composition for isoprene (I) with AN can be calculated. The copolymerization eq. (1)²

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1 [M_1] + [M_2]}{[M_1] + r_2 [M_2]} \quad (1)$$

where $[M_1]$, $[M_2]$ and r_1, r_2 are, respectively, the molar concentrations and the reactivity ratios of the monomers M_1 and M_2 , can be reduced to eq. (2) in an azeotropic polymerization system:

$$[M_1]/[M_2] = \frac{r_2 - 1}{r_1 - 1} \quad (2)$$

Thus, only a knowledge of the copolymerization parameters r_1 and r_2 is needed to calculate the molar ratios of the monomer pairs charged for an azeotro-

pic polymerization. Furthermore, it would appear that both r_1 and r_2 should be either greater than or less than 1 for this equation to be meaningful as otherwise a negative number is obtained.

There are many values given in the literature³ for the reactivity ratios of the isoprene/acrylonitrile and the butadiene/acrylonitrile copolymerization systems. In order to make initial calculations, the published values of $r_1 = 0.03 \pm 0.03$ for acrylonitrile and $r_2 = 0.45 \pm 0.05$ for isoprene were chosen, giving an azeotropic I/AN weight ratio of 2.3. Since there were errors inherent in the determination of the original copolymerization parameters as published, it was decided that a 2:1 weight ratio of isoprene/AN was a convenient starting point.

The original finding that acrylonitrile served as an "intercessory" monomer for isoprene came from graft polymerizations using a charge weight ratio of PPO/I/AN 100/100/5. (The term intercessory monomer identifies a monomer which functions as an aid to the graft polymerization of another monomer.) Hence, it was decided to begin the investigation at this point and increase the concentration of AN until a final charge weight ratio I/AN 100/50 was reached. This was accomplished in the first series of four experiments listed in Table I.

As the concentration of AN in the charge increased the modulus more than doubled, the tensile at break dropped somewhat, while the elongation at break was reduced to almost half its original value. The striking increase in modulus could be a direct manifestation of an increase in the crosslink density as a result of a much greater incorporation of isoprene into the graft polymer with increasing AN concentration.

Of these four products, three of them (runs 1, 2, and 4) were analyzed for nitrogen content. These values were then converted to AN contents. From these it was possible to calculate the compositions of the polymers. In this way, the composition of product from run 4 in which the charge was 100/100/50 was calculated to be 100/37/17. For our purposes, this was sufficiently close to the desired 2:1 ratio to be a verification of the potential azeotropic nature of the graft copolymerization.

From the results of the investigation thus far, it appeared that the change in the nature of the product began when 25 parts of AN were in the charge. For this reason, the charge of the next experiment, run 5, was set at 25 parts of AN; and to keep the I/AN ratio at 2, it also included 50 parts of isoprene. As is shown in Table I, the tensile properties of this run were all superior to those of the preceding runs. In addition, the calculation of the product composition from the nitrogen analysis indicated a polymer of PPO/I/AN 100/16/8. This is conclusive evidence of the azeotropic nature of the graft copolymerization using a charge with I/AN in a 2/1 weight ratio.

With this established, it was of interest to determine the minimum concentration of the grafting monomers which would produce a desirable elastomer. Since 5 parts of AN had been so effective as an intercessory monomer with 100 parts of isoprene,¹ the last experiment in the series listed in Table I, run 6, in which the charge was 100/10/5 was undertaken. In evaluating the results of this run with the other five experiments, it might be observed that optimum tensile properties for the vulcanizates probably could be achieved by grafting between a monomers weight ratio of 10/5 and 50/25.

In order to test this observation, a monomers charge I/AN of 20/10 was arbitrarily chosen (run 7, Table II). The yield indicated a 58% incorporation of the monomers into the grafted product. The tensile at break, 2875 psi, and the elongation at break, 710%, were superior to any product previously made. In addition, these properties for a gum vulcanizate compare most favorably with published results—maximum tensile of 2650 psi with 540% elongation for a black filled propylene oxide rubber.⁴ It should also be noted that the gum tensile of this particular rubber, which is essentially amorphous, is in the range of 400 to 600 psi.

It was now decided to maintain the concentration of the grafted monomers in the charge at 30 parts and to determine the effect, if any, of a change in the AN concentration upon the product. This was done in runs 8 and 9, Table II, by increasing the amount of AN with a concomitant reduction in the amount of isoprene, 15/15 and 10/20, respectively. The result was a significant reduction in the tensile although modulus and elongation remained essentially constant.

Finally, the application of an azeotropic graft copolymerization to a BD system was undertaken. Calculations from published copolymerization parameters^{2,3} for BD and AN gave a value of 1.7 parts of BD for each part of AN as the azeotropic polymerization concentration. The 2/1 weight ratio used so successfully with isoprene was also used with BD. Duplicate experiments, runs 10 and 11, were made in which the charge ratio of PPO/BD/AN was 100/20/10. The tensile properties of the gum vulcanizates prepared from these products are outstanding and exceed those already published of propylene oxide rubber reinforced with either black or silica fillers.⁴ The effect of fillers on the graft rubber was not part of this investigation. Later work with BD grafts, also not included in this study, indicated that the 2/1 BD/AN graft copolymerization is likewise an azeotropic reaction.

CONCLUSIONS

This work has shown that graft copolymerizations of isoprene or butadiene with acrylonitrile at a weight ratio of 2:1 diene to acrylonitrile onto poly(propylene oxide) are apparently azeotropic copolymerizations.

The tensile properties of gum vulcanizates prepared from charges of 100/20/10 poly(propylene oxide)/diene/acrylonitrile far exceed those of propylene oxide rubber and are equal to or exceed those of propylene oxide rubber with a variety of fillers.

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