

Crosslinking of heat-curable polybutadiene resins containing pendant acetylenic groups

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SUMMARY

A copolymer of 1,3-butadiene with pendant carboxyl groups 1, was conveniently transformed into corresponding acetylenic terminal groups 2, and thermally studied. It was postulated that on heating, the polymer cures via an intermolecular cycloaddition reaction to form aromatic structures along the polymer backbone. The modified copolymer 2, exhibited better thermal and thermooxidative stability and solvent resistance than the unmodified copolymer 1.

INTRODUCTION

Improved resins are needed for functional and structural applications with properties similar to those of thermoplastics but with better solvent resistance and high-temperature dimensional stability (1). Examples for this type of resins are polymers containing acetylenic groups which react thermally to provide intra- and intermolecular reactions leading to stiffening, branching and crosslinking.

In the case of aromatic polymers containing acetylenic groups, one of the problems is their low solubility in solvents and high melting temperatures (2,3).

The work presented herein involves the thermal and thermooxidative behaviour and curing reaction of copolymers with acetylenic terminal groups, inserted at different positions in a polybutadiene chain.

They were incorporated as pendant groups along the polymer backbone (4). By this route we expect to provide effective crosslinking and thereby improvement in solvent resistance.

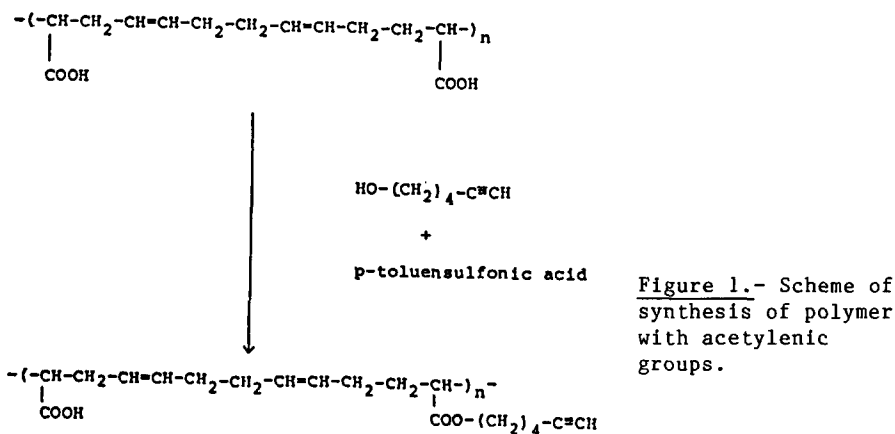
EXPERIMENTAL

The resins containing triple bonds were synthesized by using butadiene-acrylic acid copolymers as the starting material. (Polymer 1.)

The base polymer 1 was synthesized by bulk polymerization using 1,3-butadiene and acrylic acid and benzoyl peroxide catalyst (5).

In order to introduce terminal acetylenic groups, the residual carboxyl groups of the base polymer were esterified with 5-hexyn-1-ol, using p-toluenesulphonic acid as a catalyst leading to a new resin.

The resulting resin was a transparent yellow product with characteristic odour. The samples were purified by fractional



precipitation, collecting fractions F_1 , F_2 and F_3 . The principal fraction (F_2) was studied by G.P.C. The fractional precipitation was made using benzene as solvent and methanol as nonsolvent.

Determination of the carboxyl groups was carried out by titration using sodium hydroxide in a methanol solution, and thymol blue indicator. The determination was made before and after esterification permitting to know approximately the content of $\text{-C}\equiv\text{CH}$ groups.

Thermoanalytical measurements were made in a "50035 Lindberg Heavy Duty Mini Mite" furnace equipped with an internal thermocouple. It contained an aluminum pan where the sample was placed.

The results obtained were corroborated by thermogravimetric analyses (TGAs) using a Metzsch Model STA 429 apparatus.

Differential scanning calorimetry (DSC) curves were obtained on a Du Pont model 990 instrument.

IR and $^1\text{H-NMR}$ spectra were recorded in a Beckman IR 12 spectrophotometer and in a T-60 spectrometer, respectively.

RESULTS AND DISCUSSION

The base polymer 1 used as the starting material shows properties similar to those of a polybutadiene oligomer, with isolated double bonds distributed along the hydrocarbon structure. Their thermal and oxidative stability have been previously studied by us (6).

It is well known that the presence of acetylenic groups in a polymer gives it interesting thermal and oxidative properties (7); therefore, the possibility of introducing into the base polymer 1 such a group was studied. The procedure is shown in Figure 1.

According to Figure 1 the percentage of conversion of carboxyl to acetylenic groups could be changed. This is the case of the different samples obtained and given in Table 1.

Table 1.- Syntheses of polymers with different acetylenic group content.

Base Polymer 1	Conversion %	Characterization of polymer 2	
		eq. of $-C\equiv CH$	eq. of $-COOH$
Copolymer			
Butadiene-	75 (A)	0.17	0.079
acrylic acid			
containing	50 (B)	0.11	0.10
0.20 - 0.22 eq.			
$-COOH/100gr.$	25 (C)	0.06	0.15

Differential Scanning Calorimetry

The DSC scans ($\Delta T = 10^\circ C/min$) of polymers 2, (A, B and C) exhibit a strong exotherm beginning at $260^\circ C$, reaching a maximum at $T \cong 365^\circ C$. This exotherm could be attributed to reactions of the terminal acetylenic groups. (Figure 2).

From the DSC scans carried out on samples A, B and C we can observe that as the equivalent of triple bonds diminished, the peak showed a small displacement to ward higher temperatures. This could be explained by assuming that as the number of $-C\equiv CH$ increases, the probability of the triple bonds to react and to give cyclized structures also increases; in consequence, this reaction takes place at lower temperatures.

In all the samples (A, B and C) an endotherm was also observed at $450^\circ C$, and is assigned to a drastic thermal degradation of the cured polymer. In reference to the endotherm, no significant change could be observed for the polymers with different concentration of acetylenic groups.

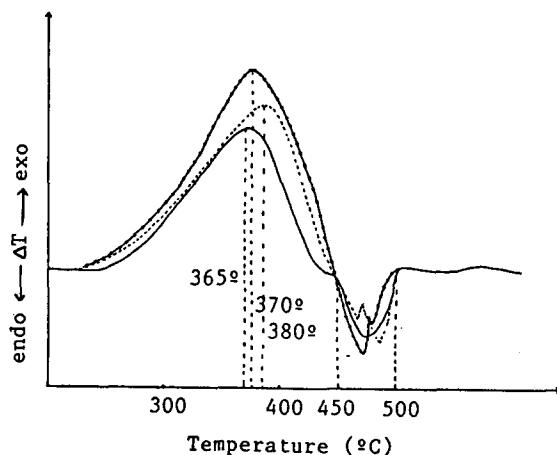


Figure 2.- DSC curves of polymers with acetylenic groups.

Polymer A ———
 Polymer B - - - - -
 Polymer C - - - - -

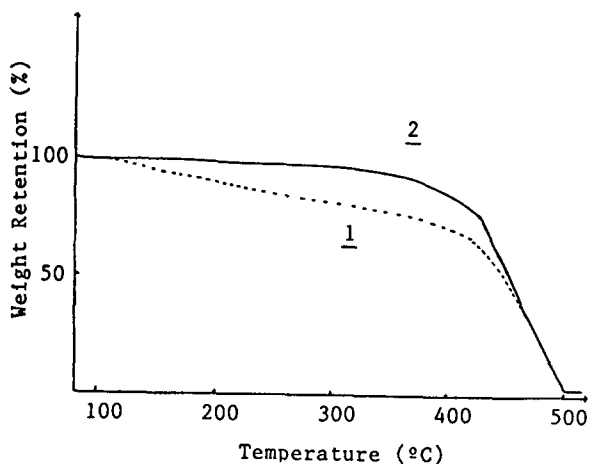


Figure 3.- TGAs curves of polymers 1 and 2 in N_2 -atmosphere

Thermogravimetric Analyses

Figure 3 shows the TGA curves of the base copolymer 1 and of the copolymer 2 with terminal acetylenic groups. The high stability of this second polymer 2 with respect to polymer 1 is remarkable.

Cyclotrimerization of the acetylenic groups may give rise to aromatic structures which results in higher thermal stability. Figure 4 helps to visualize the cyclotrimerization curing process.

According to the DSC curve this re-arrangement may take place at ≈ 360 °C. From this temperature on the shape of the TGA curve is similar to that of copolymer 1.

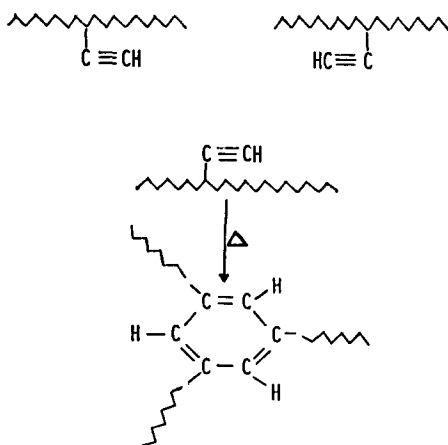


Figure 4.- Probable way of cyclotrimerization.

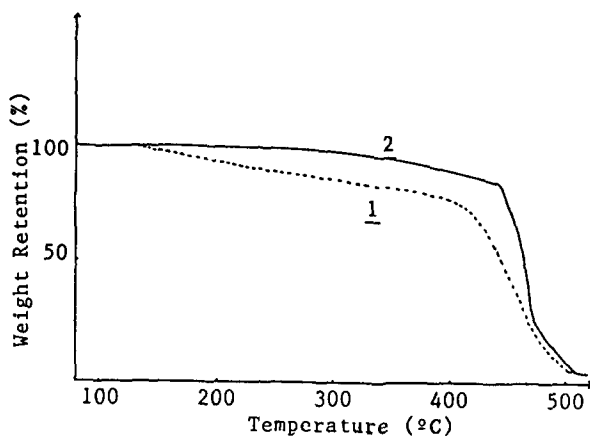


Figure 5.- TGAs curves of polymers 1 and 2 in O_2 -atmosphere.

Thermooxidative Stability

The thermooxidative stability of the copolymers were evaluated by thermogravimetric analyses. Onset of weight loss, for acetylenic copolymers, under thermogravimetric analyses in an air occurred in the 340-400 °C range with essentially complete weight loss at 500 °C.

The curves of copolymer 1 and of copolymer 2 are described in Figure 5. It can be observed that the stability of the copolymer 2 with terminal acetylenic groups in an atmosphere of oxygen is higher than the base copolymer 1.

Copolymer 1 exhibits higher stability in oxygen than in nitrogen as indicated by the displacement of the curves. This could be attributed to fragments arising during the thermal degradation up to 120 °C, followed by recombination with oxygen giving products of higher stability. At this stage of degradation there are two simultaneous processes: up to 120 °C a radical intermolecular recombination leading to molecular weight decrease and beyond 400 °C scissions leading to marked weight loss.

In the case of the acetylenic polymer 2, no difference was found in the shape of the curves in nitrogen or oxygen at less than 400 °C. The previously mentioned change observed for polymer 1 was absent and both curves were the same.

Up to 400 °C in oxygen the acetylenic polymer 2 is stabilized, probably due to some recombination of the degradation products with oxygen. At higher temperatures, up to 450 °C, the curves are similar to those of copolymer 1.

IR and NMR spectroscopy

The action of temperature on polymer 2 was followed by monitoring the disappearance of the band attributable to the acetylenic linkage at 3.05 μm .

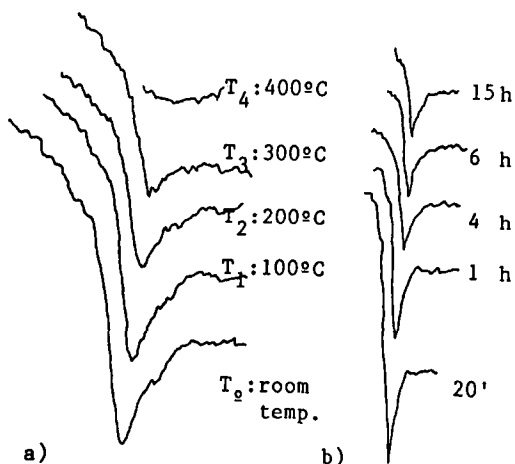


Figure 6.- a) Disappearance of the IR band (3.05 μm) at $\cong 400$ $^{\circ}\text{C}$.

b) Decrease of the IR band (3.05 μm) at 180 $^{\circ}\text{C}$.

Two different experiments were carried out in vacuum: one with a progressive increase in the temperature; the other below 180 $^{\circ}\text{C}$ and changing the time of heating.

In the first example, by increasing in the temperature the area of the peak attributable to the triple bond, decreased until it disappeared between 300 $^{\circ}\text{C}$ and 400 $^{\circ}\text{C}$. (Figure 6 and Table 2).

In the second experiment during six hours of heating the area of the peak decreased until an equilibrium was reached beyond which no further change was observed. (Figure 6).

H-NMR spectroscopy of the degradation products trapped by liquid air showed the presence of aromatic products. It is remarkable that when the same experiment was carried out with polymer 1 the presence of aromatic structures was not observed. (Figure 7).

Table 2.- Percentage of disappearance of acetylenic terminal groups by increasing temperature.

Temperature ($^{\circ}\text{C}$)	% of disappearance of IR band at 3.05 μm .
T ₀ : room temperature	---
T ₁ : 100	7.2
T ₂ : 200	39.5
T ₃ : 300	42.9
T ₄ : 400	100.0

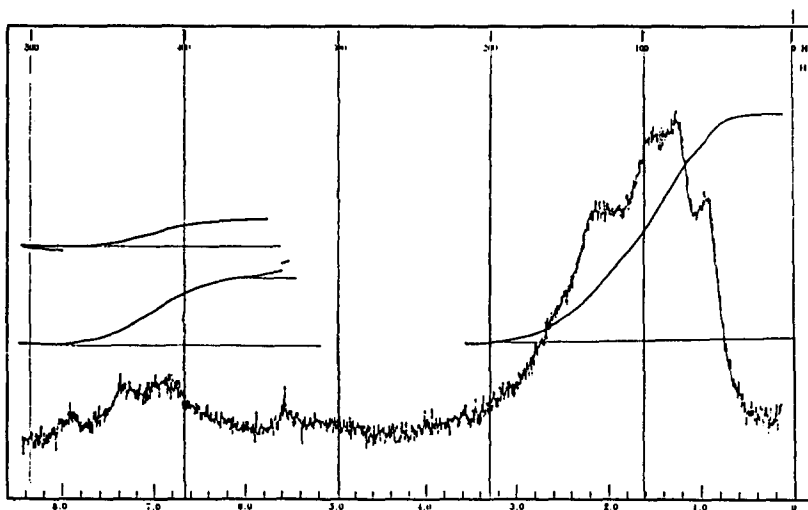


Figure 7.- NMR spectrum of the fragments originates in the thermic degradation.

CONCLUSIONS

Copolymers with pendant carboxyl groups were conveniently converted into the corresponding pendant ethynyl terminal groups. The thermally induced reaction of the acetylenic terminal groups resulted in branching and crosslinking.

The resulting polymers exhibited better thermal and thermooxidative stability than the starting polymers.

It was demonstrated by IR and NMR spectroscopies that additional stabilization could be gained by creating aromatic structures by cyclotrimerization of the triple bonds.

Thermal treatment produced an insoluble, very dark, rigid product characteristic of extensively crosslinked materials.

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