

Oxidation of Styrene Popcorn Polymer

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Synopsis

Studies have been made of the oxidation of styrene popcorn polymer that was grown on butadiene popcorn seed. It was found that the solubility of the polymer increased after oxidation. This solubility was studied as a function of both temperature and butadiene content of the polymer. Oxidation of the styrene-on-butadiene popcorn occurs at the carbon atoms alpha to a double bond in the butadiene portion of the polymer. This is followed by scission of the structure and the separation of linear atactic soluble polystyrene chains.

Introduction

Polymerization of styrene popcorn polymer is readily initiated by placing styrene monomer in the presence of butadiene popcorn seed.¹ The insolubility of the resultant polymer has made any characterization of its structure by the usual methods very difficult. The polymer reacts readily with oxygen, however, and in so doing becomes partially soluble. It is the purpose of these investigations to study the oxidation of the polymer as a function of temperature and butadiene content in an attempt further to elucidate its structure.

Experimental Procedure

The styrene monomer used was from Eastman Chemical Company and contained *tert*-butylpyrocatechol as inhibitor. Butadiene was from Matheson Co., Inc., reagent grade.

Styrene popcorn polymer was propagated in the vapor phase on butadiene popcorn seed at 60°C. in the darkness of an oil bath according to the procedure previously described.¹ The butadiene seed was carefully weighed before being introduced into the reaction tube and following the polymerization the resultant polymer was evacuated (rotary high vacuum pump backed by a Dry Ice-acetone trap) for 8-10 days to remove volatiles until a constant weight was obtained, i.e., a weight loss of no more than 1 mg./day. Assuming no loss of butadiene, the polybutadiene contents of the samples used were as follows: 1.8 ± 0.4 , 6.2 ± 0.5 , 14.3 ± 0.1 , and $27.6 \pm 0.2\%$.

Oxidation was carried out by passing a stream of oxygen through a drying tube, the sample, and a Dry Ice-acetone trap at a constant flow rate

of 60 ml./min. for 72 hr. at the following temperatures respectively: 25, 40, 60, 90, and 110°C.

Solubilities of the samples were determined by treatment with benzene in a Soxhlet extractor under a nitrogen atmosphere for 24 hr. Following extraction, volatiles were removed by evacuation (rotary high-vacuum pump backed with a Dry Ice-acetone trap) until a constant weight was obtained. Treatment of unoxidized styrene-on-butadiene popcorn seeds produced negligible weight loss. The per cent solubility of each sample after oxidation was calculated by dividing the weight loss by the weight of styrene in the popcorn.

Infrared spectra of the samples in KBr pellets were taken with a Beckman IR5 spectrometer.

Refractive indices of the samples were measured by the immersion technique using a polarizing microscope. For regular polystyrene n_D^{25} is 1.5917, while that of popcorn polystyrene containing 5–25% butadiene popcorn is 1.590 ± 0.001 .

Experimental Results

When the popcorn polymer samples were evacuated in order to bring them to constant weight prior to oxidation, it was found that a greater weight loss was always obtained for the polymers that had a lower butadiene

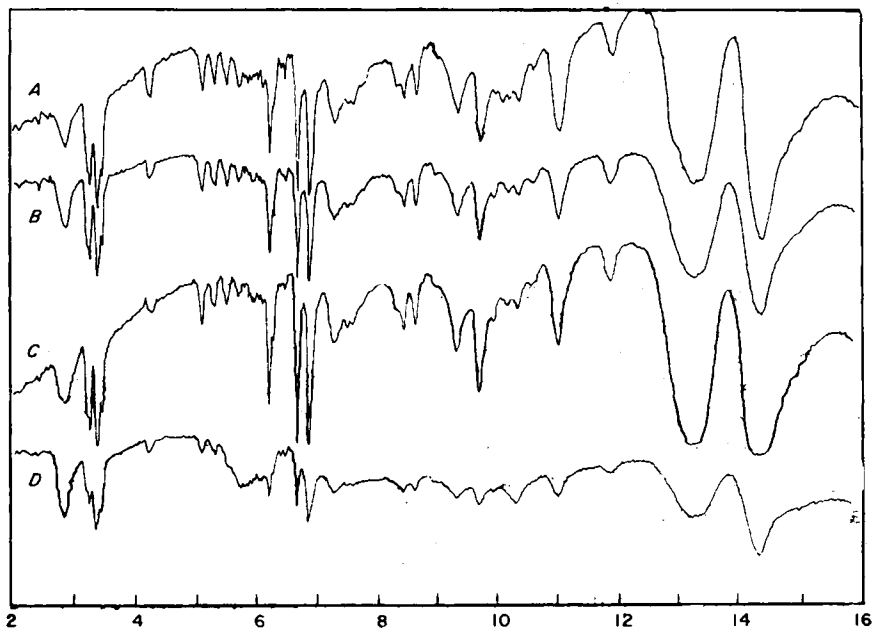


Fig. 1. Infrared spectra of styrene-on-butadiene popcorn polymers; (A) unoxidized polymer; (B) insoluble white portion of oxidized polymer; (C) soluble portion of oxidized polymer; (D) insoluble yellow fraction of oxidized polymer.

concentration. A higher degree of volatilization of styrene occurs when the concentration of butadiene crosslinking molecules is at a minimum.

The infrared spectrum of styrene-on-butadiene popcorn is shown in Figure 1A. It is identical to that for linear atactic polystyrene except for

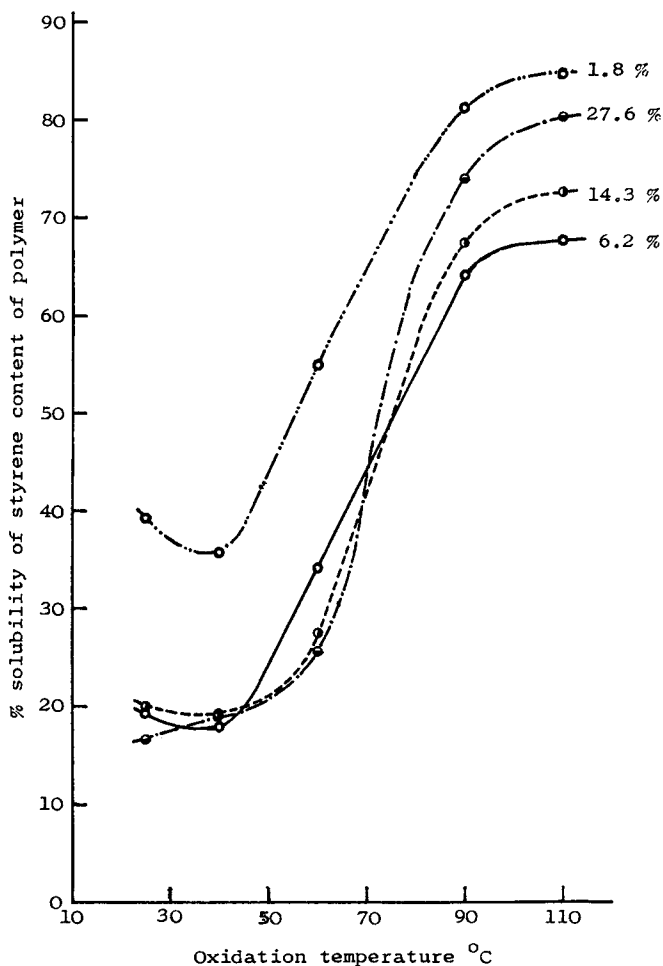


Fig. 2. Variation in solubility of styrene-on-butadiene popcorn polymer as a function of oxidation temperature. Curves are labeled according to butadiene content of unoxidized polymer.

the 10.05μ peak contribution from the $-\text{CH}=\text{CH}_2$ structure of the butadiene and a few minor peaks in the 6μ region. After oxidation, the portion of the polymer which dissolved in benzene exhibited the spectrum shown in Figure 1C (solvent removed). It differs from the spectrum of the original popcorn in that the 10.05μ peak has disappeared, thus indicating the absence of butadiene in this portion of the oxidized polymer.

The insoluble portion of the oxidized polymer was manually divided into the white and yellow-brown fractions. The infrared spectrum of the white portion is shown in Figure 1*B*. It is similar to the spectrum of the soluble portion. The yellow portion, however, showed the peaks characteristic of oxidized butadiene popcorn.² As seen in Figure 1*D*, there is the

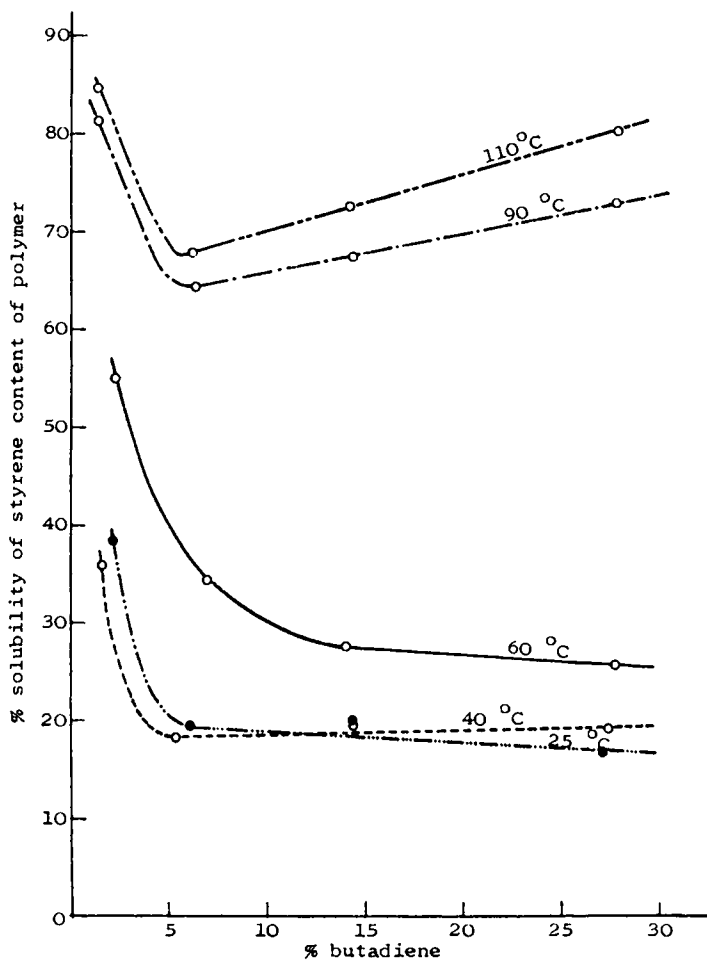


Fig. 3. Isotherms of the solubility of styrene-on-butadiene popcorn polymer as a function of butadiene content. Oxidation temperatures were maintained for 72 hr. with an O_2 flow rate of 60 ml./min.

appearance of the strong oxidation product bands in the 6μ region, and great diminution in the intensity of the styrene bands.

After oxidation, yellow particles scattered throughout the polymer bulk were found in the originally all-white popcorn. At higher temperatures these yellow particles turned brown. The weight change upon oxidation was dependent upon: (1) increase due to the addition of oxygen to the

molecules, (2) decrease due to loss of styrene. Such weight change, however, did not seem to show any regularity.

The styrene-on-butadiene popcorn is insoluble in benzene prior to oxidation but becomes partially soluble following oxidation. Figure 2 presents a plot of polymer solubility as a function of oxidation temperature for polymers of various butadiene content. Above 40°C. the solubility increases rapidly with temperature but levels off around 110°C. For a given polymer composition, the minimum solubility was obtained for a 40°C. oxidation temperature with the exception of the 27.6% butadiene popcorn.

Figure 3 shows the isotherms of percentage solubility as a function of per cent butadiene in the samples. At all temperatures there is a rapid decrease in the solubility of the oxidized polymer with increases in butadiene content up to approximately 5%. At the lower temperatures the solubility did not vary appreciably with increasing butadiene contents above 5%. At the higher temperatures the solubility showed a gradual increase with increasing butadiene content above the 5% composition.

Discussion

Oxidation of styrene-on-butadiene popcorn polymer produces an inhomogeneous mass consisting of yellow-to-brown particles scattered uniformly throughout the bulk of white polymer. Infrared analysis shows these colored portions to consist primarily of oxidized butadiene popcorn.²

Following oxidation the polymer becomes partially soluble. The portion which can be removed by solvent extraction consists of linear atactic polystyrene chains.

The extent of polymer degradation on oxidation, as measured by the per cent of soluble polystyrene chains released, increases rapidly with an increase of oxidation temperature above 40°C. For a polymer sample of fixed butadiene-styrene content and for standard oxidation conditions of time and flow rate, a point is attained where an increase in temperature produces little increase in polymer solubility. This occurs at the higher temperatures where all the available oxidation sites are rapidly utilized, as illustrated by the leveling off of the solubility versus temperature curves in Figure 2.

Between 25 and 40°C., three of the four polymer samples of different composition showed a reverse effect, i.e., a decrease in polymer degradation with an increase in oxidation temperature. At these lower temperatures the predominant reaction is undoubtedly the formation of hydroperoxide groups on the tertiary carbon atoms of the butadiene popcorn that are also alpha to a double bond. The oxidation then proceeds via the formation of free radical sites. At this point rearrangement and degradation of the molecule can occur or additional crosslinking can take place. The net result is that no overall increase in polymer solubility is noted, and a slight decrease may be obtained.

Referring to Figure 3, it is seen that at the lower oxidation temperatures there is not much change in the solubility of the oxidized polymer as the

butadiene content is changed from approximately 6 to 25%. Below 6%, however, the degradation of the polymer is much more complete. At a concentration of 1.8%, for example, the degree of crosslinking is probably less, and since there are a larger number of linear polystyrene chains associated with a given butadiene popcorn unit, the rupture of a given butadiene unit frees a relatively larger percentage of soluble polystyrene chains. An alternative explanation was suggested by one of the reviewers of this paper. Upon oxidation one can imagine an impervious shell being formed which could prevent the penetration of additional oxygen, hence when little butadiene popcorn is present this shell could exclude less oxygen and result in greater oxidative scission. The authors favor the former explanation, however, due to the known ease of penetration of popcorn polymers which must be assumed to account for the observed logarithmic growth rates.

It is evident from the distribution of the residual butadiene structures throughout the polymer mass after oxidation that the original structure of the butadiene popcorn was literally pulled apart during the addition of the styrene molecules. That such a phenomenon occurs during the growth of pure popcorn polymer is evidenced by the relatively large concentration of free radical sites which exist on the polymer under ordinary room temperature conditions as shown by electron spin resonance measurements.³

The following scheme accounts for the experimental data obtained. The styrene monomer molecules first add preferentially to the free radical sites which exist on the butadiene popcorn seed. Additional styrene monomer then forms linear atactic chains. As these chains grow, the structure is fragmented with new free radical sites being produced to carry on the process. Crosslinking also occurs to produce the insoluble network. The extent of this crosslinking, however, does not have to be extensive, e.g., in the case of insoluble poly(methyl methacrylate) popcorn the crosslinking amounts to only one for every 10^3 or 10^4 monomer units.⁴ When the resultant styrene-on-butadiene popcorn polymer is oxidized, the oxygen preferentially attacks the tertiary carbon atoms that are also alpha to the existing double bonds. This produces scission of the structure with the separation of soluble atactic polystyrene chains and an insoluble residue containing the bulk of the original butadiene popcorn structure.

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References

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Résumé

On a étudié l'oxydation du polystyrène soufflé ayant pris naissance sur un germe de butadiène (expansé). On a trouvé que la solubilité du polymère augmente après oxydation. Cette solubilité a été étudiée en fonction de la température et de la teneur en

butadiène du polymère. L'oxydation du polystyrène butadiène (expansé) s'effectue sur les atomes de carbone alpha de la double liaison de la partie butadiène du polymère. Cela est suivi d'une rupture de la structure et de la séparation des chaînes linéaires de polystyrène atactique soluble.

Zusammenfassung

Eine Untersuchung der Oxydation von Styrolpopcornpolymerem, das auf Butadienpopcornkeimen gewachsen war, wurde durchgeführt. Die Löslichkeit des Polymeren nahm nach der Oxydation zu. Diese Löslichkeit wurde als Funktion der Temperatur sowie des Butadiengehalts des Polymeren untersucht. Die Oxydation des Styrol-auf-Butadienpopcorns findet am α -Kohlenstoffatom zu einer Doppelbindung im Butadienteil des Polymeren statt. Darauf folgt eine Kettenspaltung und die Abtrennung linearer ataktischer löslicher Polystyrolketten.

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