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Polybutadiene Cross-Linked With Various Diols – Effect On Thermal Stability

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Abstract

The relationship between cross-linking and thermal stability as related to polybutadiene is the focus of current research. Cross-linked polybutadienes have been prepared using various diols as the cross-linking agent. Cross-linked polymers have been characterized by gel content, swelling ratios, infrared spectroscopy, and thermal analysis. These polymers are not highly cross-linked, as seen by gel content and swelling ratios, and cross-linking does not have a large effect on the onset temperature of the degradation. Nonetheless, extensive formation of a non-volatile residue occurs.

Keywords

Cross-linking; Thermal stability; Polybutadiene; Degradation

1. Introduction

Polybutadiene and its copolymers have been cross-linked using a variety of techniques. For example, ^{60}Co - γ -rays have been used to cross-link polybutadiene, polystyrene, and copolymers of the two.¹ Irradiation enhances the thermal stability of polystyrene, while no enhancement is observed for polybutadiene. The copolymers show an intermediate effect and one may conclude that the composition of the copolymer has some control over its thermal stability. Polybutadiene and its copolymers have also been cross-linked by chemical means, using either heat or a chemical initiator or a combination of the two.² In fact, if one heats polybutadiene in a thermogravimetric analyzer, cross-linking occurs. Since heat always effects cross-linking of this polymer, there is really no uncross-linked reference for this polymer. The most efficacious process, i.e. that which gives the largest cross-link density, is to blend the polymeric system with an initiator and then to heat this to a temperature at

which the initiator is active. There is essentially no difference in thermal stability between virgin polymer and polymers which have been cross-linked by any of these techniques.

This research group has been interested in the general question of the correlation between cross-linking and thermal stability. Radiation has been used to effect the cross-linking of polyamide-6,³ as well as the butadiene-containing copolymers while chemical initiation has been used for butadiene-containing systems and styrene–divinylbenzene copolymers, methacrylate–dimethacrylate copolymers,⁴ styrene–dimethacrylate copolymers and methacrylate–divinylbenzene copolymers.⁵ The styrene–divinylbenzene copolymers and the methacrylate–divinylbenzene copolymers show a significant enhancement of thermal stability while there is a slight enhancement for the styrene–dimethacrylate system. These investigations have led to a hypothesis that the type of cross-link is the important factor in the enhancement of thermal stability, with the number of cross-links, as long as some minimum number are present, being much less important.

In this paper, we continue to examine the question of the correlation between cross-linking and thermal stability for polybutadiene. Cross-linking is accomplished by functionalization of the polymer and then through the use of various diols as the cross-linking agents.

2. Experimental

2.1. Materials

All reagents used were purchased from Aldrich Chemical Co. Polybutadiene (PBD) that was used is described as the *cis* isomer, with a molecular weight in the range of ~2,000,000 to 3,000,000. All materials, including anhydrous tetrahydrofuran, THF, anhydrous cyclohexane, and a 2.0 M solution of *n*-butyllithium in cyclohexane, were used as received.

2.2. Instrumentation

Thermogravimetric analysis, TGA, was performed using an Omnitherm 1000 instrument under a flowing inert atmosphere at a scan rate of 20°C/min. All TGA results are the average of at least three runs; typically the temperatures are reproducible to ±3°C. Fourier-transform IR spectra were obtained using a Nicolet Magna infrared 560 spectrometer E.S.P. Nuclear magnetic resonance spectroscopy was performed on a General Electric QE 300 NMR.

2.3. Bromination of polybutadiene

Bromination of polybutadiene was accomplished by dissolving the polybutadiene in carbon tetrachloride and adding the appropriate amount of *N*-bromosuccinimide at reflux. In a typical experiment, a 500 ml 3-neck, round-bottomed flask, equipped with a mechanical stirrer and condenser, was charged with 10.35 g (0.0191 mol) of polybutadiene and 200 ml of carbon tetrachloride. This was then heated with stirring until all of the polybutadiene had dissolved. To the polybutadiene solution was added 2.34 g (0.013 mol) of *N*-bromosuccinimide and it was refluxed for 5 h. The solution was then filtered to remove succinimide and the polymer was precipitated from the solution by the addition of methanol; the recovered polymer was then dried overnight in a vacuum oven at room temperature. The brominated polymer was analyzed by proton nuclear magnetic resonance to determine the extent of bromination that had occurred. Polymers were prepared with expected bromine contents of 3, 4.5, 6, and 8.5%. The polymers were analyzed by thermogravimetric analysis, nuclear magnetic resonance, and infrared spectroscopy.

2.4. Spontaneous cross-linking of brominated polybutadiene

Brominated polybutadiene was permitted to undergo spontaneous cross-linking under several experimental conditions. A small amount of the brominated polymer was placed in each of three vials. The first was heated in an oven overnight at $\sim 90^{\circ}\text{C}$. The second vial was left at room temperature exposed to atmosphere while the third vial was kept at room temperature under nitrogen. The amount of time needed to cross-link along with the gel content and swelling ratios were determined using a Soxhlet extraction apparatus.^{6,7} Cross-linked polymers were analyzed by thermogravimetric analysis and infrared spectroscopy.

2.5. Cross-linking with various diols

The brominated polybutadiene was cross-linked by treatment with the dilithium salt of the various diols. In a typical experiment, a 100 ml 3-neck, round-bottomed flask, equipped with a condenser, was charged with 0.042 g (0.0047 mol) of butanediol and 40 ml of anhydrous tetrahydrofuran. To this was added dropwise over a 15 min period 4.5 ml (0.0090 mol) of 2.0 M butyllithium in cyclohexane. After all the butyllithium was added, the solution was allowed to stir for an additional 10 min. To this was added 0.84 g (0.0047 mol) of brominated polybutadiene dissolved in 40 ml of anhydrous cyclohexane. This solution was allowed to stir for 30 min. It was then quenched with 50 ml of $\sim 1\%$ sodium hydroxide solution. The organic layer was separated and the aqueous layer extracted with ether. The organic layer was dried with anhydrous sodium sulfate. The solvent was removed by rotary evaporation and resulting polymer dried in a vacuum oven at 80°C overnight. Gel content and swelling ratios were determined using a Soxhlet extraction apparatus. Cross-linked polymers were analyzed by thermogravimetric analysis and IR spectroscopy.

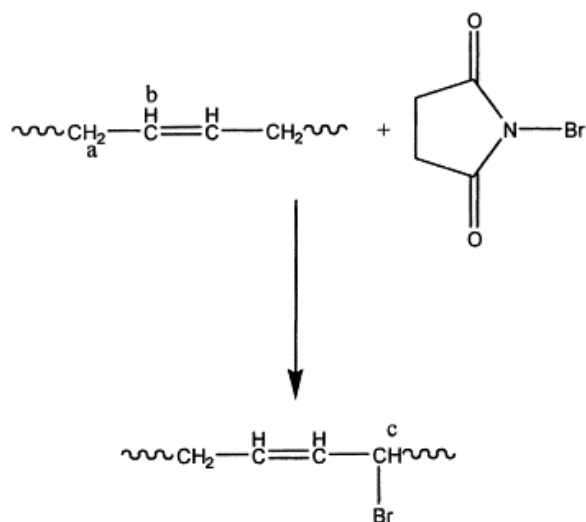
2.6. Determination of gel content and swelling ratio

Gel content and swelling ratios were determined by a 12 h extraction of the dried cross-linked polymers with tetrahydrofuran, THF, using a Soxhlet extraction apparatus. When the extraction was deemed complete, the samples were removed and patted dry. The cross-link density of the samples was determined by the ratio of the mass of swollen sample to that of the unswollen sample, termed swelling ratio. The gel content could then be determined by thoroughly drying the samples overnight at 100°C .^{6,7}

3. Results and discussion

3.1. Bromination of polybutadiene

The bromination of polybutadiene proceeds in about 65% yield as measured by NMR spectroscopy; the course of the reaction is shown in Scheme 1. The ^1H NMR spectra of virgin polybutadiene and polybutadiene containing 8.5% bromine are shown in Fig. 1. Only two peaks are observed for polybutadiene, corresponding to the methylene (a in Scheme 1) at 2.13 ppm and the methine at 5.38 ppm (b), in a ratio of 2:1. Upon bromination a new peak at 4.5 ppm appears and this may be assigned to the hydrogen attached to the brominated carbon. This peak corresponds to the hydrogen attached to the brominated carbon (c in Scheme 1). From integration of the proton resonances, one can determine the amount of bromine that has been incorporated into the polymer. The chemical shift of the brominated carbon was determined using NMR additivity rules.⁸



Scheme 1. Preparation of brominated polybutadiene.

Offset = 9 pts 8.88 Hz

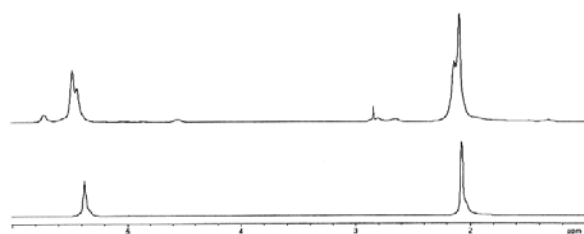


Fig. 1. NMR of polybutadiene (bottom spectra) and brominated polybutadiene (top spectra).

3.2. Thermal degradation of brominated polybutadiene

The results of thermogravimetric analysis of the brominated polymers are given in Table 1. As has been previously discussed, we use the temperature at which 10% degradation occurs as the onset temperature of the degradation. T_{max} is the temperature at which the maximum rate of degradation occurs and is another measure of the course of the degradation. It can be seen that bromination significantly lowers the onset temperature of the degradation but has little effect on the mid-point of that degradation or on the formation of char.

Table 1. Thermogravimetric analysis for brominated polybutadiene

% Bromine	$T_{10\%}$ (°C)	T_{max} (°C)	Char (%) @ 600°C
0	459	501	5
3	379	493	4
4.5	454	499	11
6	216	495	7
8.5	205	492	5

3.3. Spontaneous cross-linking of brominated polybutadiene

The spontaneous cross-linking of the brominated polybutadiene has been studied in both an air atmosphere and inert atmosphere and at room temperature as well as at somewhat elevated temperature, 90°C. The results showing gel contents, swelling ratios, as well as TGA parameters are shown in Table 2. During the course of these degradations, the evolution of HBr was observed.

Table 2. Gel content, swelling ratio, and thermogravimetric analysis for self cross-linked brominated polybutadienes

% Bromine	Temperature	Atmosphere	Gel content (%)	Swelling ratio (%)	$T_{10\%}$ (°C)	T_{max} (°C)	Char (%)
3	Room	Air, 5 days	95	1500	337	490	9
3	Room	Nitrogen, 5 days	83	800	286	481	19
3	Oven (90°)	Air, 21 h	79	600	345	494	16
4.5	Room	Air, 5 days	89	1400	302	487	10
4.5	Room	Nitrogen, 5 days	78	2200	337	491	7
4.5	Oven (90°)	Air, 21 h	92	700	300	489	12
6	Room	Air, 5 days	100	400	309	488	12
6	Room	Nitrogen, 5 days	75	900	305	489	9
6	Oven (90°)	Air, 21 h	91	600	293	488	15
8.5	Room	Air, 5 days	79	800	278	489	17
8.5	Room	Nitrogen, 5 days	75	2400	243	490	16
8.5	Oven (90°)	Air, 21 h	93	600	262	496	29

Degradation in air appears to give a higher gel content while the cross-link densities are quite variable. For instance, at 3% bromination the highest cross-link density results from cross-linking in inert atmosphere as room temperature while at 4.5%, reaction at 90°C in air gives the highest cross-link density. There does seem to be some correspondence between cross-link density and the extent of formation of non-volatile char. Fig. 2 shows the TGA curves for PBD, brominated PBD, and this same polymer after spontaneous cross-linking.

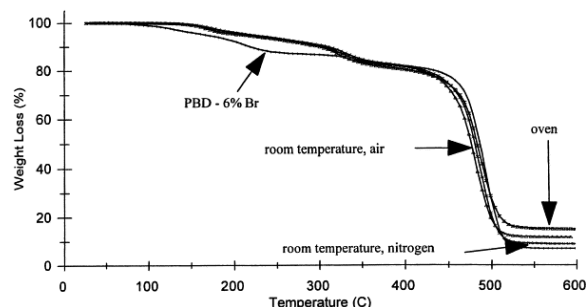


Fig. 2. TGA curves for self cross-linked brominated (6%) polybutadiene.

3.3. Brominated polybutadiene cross-linked with various diols

Brominated PBD has been cross-linked using the dilithium derivatives of the following diols, butanediol, hexanediol, octanediol, decanediol, cyclohexanediol, cyclohexanedimethanol, hydroquinone, and benzenedimethanol. These materials were chosen to permit the investigation of the effect of the alkyl chain length and the aromaticity of the cross-linker on thermal stability. The gel contents and swelling ratios for all of the systems investigated are collected in Table 3.

Table 3. Gel content and swelling ratios of PBD cross-linked with various diols

Diol	% Bromine	Gel content (%)	Swelling ratios (%)
Butanediol	3	79	600
Hexanediol	3	85	500
Octanediol	3	55	2200
Decanediol	3	44	2100
Cyclohexanediol	3	76	600
Cyclohexanedimethanol	3	60	2200
Hydroquinone	3	82	900
Benzene dimethanol	3	41	4300
Butanediol	4.5	71	1700
Hexanediol	4.5	71	600
Octanediol	4.5	40	4300
Decanediol	4.5	35	5400
Cyclohexanediol	4.5	49	3700
Cyclohexanedimethanol	4.5	61	2100
Hydroquinone	4.5	69	1500
Benzene dimethanol	4.5	58	2300
Butanediol	6	59	1000
Hexanediol	6	78	600
Octanediol	6	48	4300
Decanediol	6	27	4800
Cyclohexanediol	6	84	600
Cyclohexanedimethanol	6	69	600
Hydroquinone	6	99	600
Benzene dimethanol	6	57	900
Butanediol	8.5	88	1200
Hexanediol	8.5	56	3100
Octanediol	8.5	33	5500
Decanediol	8.5	61	2900
Cyclohexanediol	8.5	79	1200
Cyclohexanedimethanol	8.5	67	1500
Hydroquinone	8.5	71	800
Benzene dimethanol	8.5	74	1800

From Table 3, it is obvious that increasing the length of the alkyl chain is disadvantageous for good cross-linking. Butanediol and hexanediol give somewhat comparable results for all polymers, but, as the alkyl chain is lengthened to eight carbons and to ten carbons, the extent of gel formation and the cross-

link density drop dramatically. The aromatic compounds and the cyclic aliphatics are roughly comparable to the four and six carbon chains, probably since all of these species are small enough to be able to effectively interact at both reactive ends with the polymers. Apparently the chain length controls the cross-linking process.

The thermal stability of all of these cross-linked systems has been followed by thermogravimetry and the results are presented in Table 4 and the TGA curves for representative systems are shown in Fig. 3. The onset temperature of the degradation is almost always lower for the cross-linked polymers than for virgin PBD, while T_{max} is more or less comparable for the cross-linked polymers and virgin PBD. As the amount of bromination increases, the onset temperature of the cross-linked polymer decreases. This is attributable to the inability of the cross-linking agent to interact with all of the bromine so that some bromine always remains in the cross-linked polymer. The onset temperature of the degradation is due more to the loss of bromine than to the actual degradation of the cross-linked polymer.

Table 4. Temperatures of degradation for PBD cross-linked with various diols^a

Diol	% Bromine	$T_{10\%}$ (°C)	T_{max} (°C)	Char (%)	$T_{2nd\ pt.}$ (°C)
Butanediol	3	467	496	59	769
Hexanediol	3	359	493	16	–
Octanediol	3	318	482	15	746
Decanediol	3	271	490	22	743
Cyclohexanediol	3	371	494	13	772
Cyclohexanedimethanol	3	315	494	12	–
Hydroquinone	3	419	497	13	–
Benzene dimethanol	3	411	496	36	760
Butanediol	4.5	428	494	26	–
Hexanediol	4.5	266	492	17	–
Octanediol	4.5	321	488	46	–
Decanediol	4.5	244	483	27	–
Cyclohexanediol	4.5	433	500	31	749
Cyclohexanedimethanol	4.5	242	485	30	–
Hydroquinone	4.5	433	496	38	740
Benzene dimethanol	4.5	436	502	42	753
Butanediol	6	406	497	33	–
Hexanediol	6	263	482	29	–
Octanediol	6	198	479	25	–
Decanediol	6	404	486	34	742
Cyclohexanediol	6	415	492	18	861
Cyclohexanedimethanol	6	388	501	25	–
Hydroquinone	6	386	499	29	722
Benzene dimethanol	6	268	486	22	–
Butanediol	8.5	353	454	56	759
Hexanediol	8.5	244	459	50	–
Octanediol	8.5	243	478	35	–
Decanediol	8.5	282	489	15	–
Cyclohexanediol	8.5	439	503	59	746
Cyclohexanedimethanol	8.5	302	495	17	748

Hydroquinone	8.5	327	501	24	–
Benzene dimethanol	8.5	204	505	27	–

^a Average of three TGA runs.

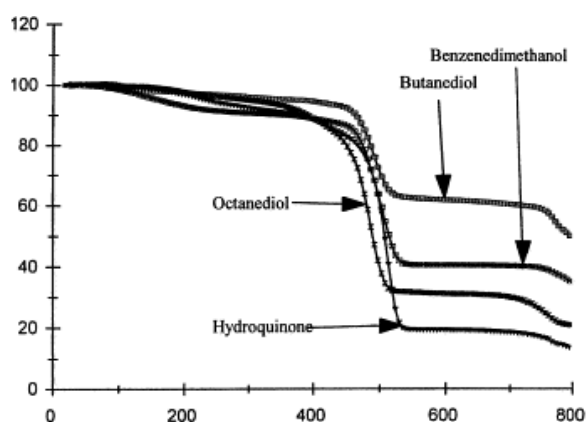


Fig. 3. Cross-linked PBD (3% Br) with various diols.

There are two areas where a rather large difference is observed, the extent to which a non-volatile char is produced and the presence of a new feature in the degradation curve above 700°C. It is a surprise to observe that the aromatic systems do not show the greatest thermal stability, since aromatics are usually considered to have greater thermal stability than aliphatics. This calls into question the truth of this assumption. There does seem to be a relationship between cross-link density and the extent of formation of non-volatile char. As a general observation, one can say that there appears to be no correlation between gel content, cross-link density, onset temperature, fraction of non-volatile residue, and the structure of the diol. Butanediol does appear to give the highest onset temperature and a large fraction of non-volatile residue along with a high gel content and cross-link density, but there is a good deal of variability in the data. It is believed that the amount of residual bromine in the sample is most likely responsible for the onset temperature of the degradation and the non-volatile residue. Butanediol may more easily couple with the multiple sites at which bromine had been present and lead to lower bromine content and therefore higher onset temperatures. This is consistent with the observation that the onset temperature decreases as the amount of bromine in the butadiene increases.

3.4. Infrared spectroscopy

The cross-linked polymers, and the chars produced from them, were analyzed by IR spectroscopy. Spectra of brominated PBD cross-linked with hydroquinone and its char at 600°C and 900°C are shown in Fig. 4. The vibration due to the C=C linkage near 1100 cm⁻¹ is clearly visible in the starting cross-linked polymer and is still evident at 600°C but it does vanish from the material recovered at 900°C. This indicates that in these cross-linked systems, the cross-links do impart substantial thermal stability to the system.

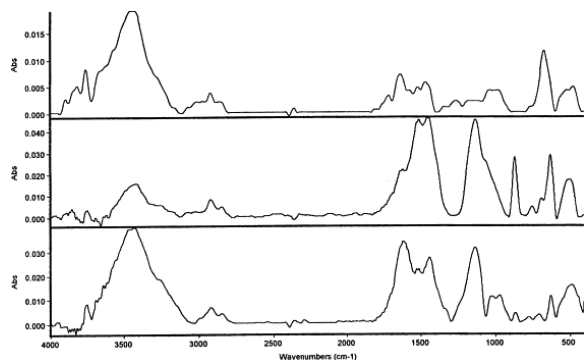
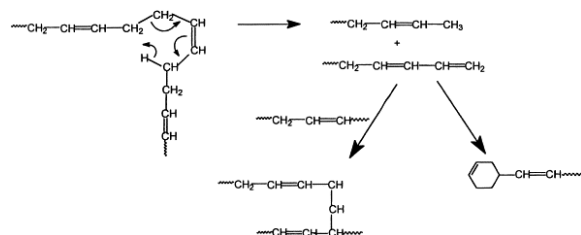


Fig. 4. Infrared spectra of the reaction product from brominated polybutadiene with dilithiohydroquinone (bottom) and the char produced by heating to 600°C (middle) and 900°C (top).

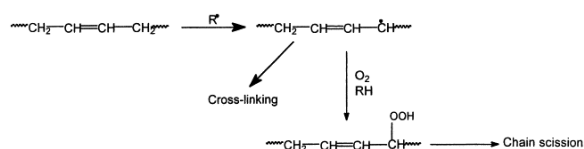
3.5. Mechanism of char formation

The mechanism of degradation of polybutadiene has been shown to occur in several steps. The first step, *cis-trans* isomerization, occurs around 250°C. Cyclization and cross-linking, the second step, occurs about 370°C. When polybutadiene is heated in the absence of oxygen, hydrogen transfer reactions can occur and the transfer of an allylic hydrogen can lead to chain scissions. The newly formed vinyl chain ends are capable of undergoing a cyclization or branching reaction and this branching reaction can lead to cross-linking, as shown in Scheme 2.^{1,3,6,7}



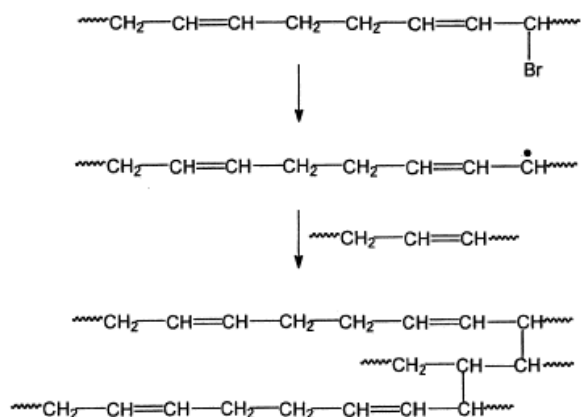
Scheme 2. Possible modes of degradation of polybutadiene.

In the presence of air, oxygen can react with the radicals that are produced, with the initial formation of a peroxy or epoxy linkage. Epoxy and peroxy linkages can undergo cleavage reaction, followed by hydrogen abstraction, to produce $C=O$ and $O-H$ bonds, as shown in Scheme 3.²



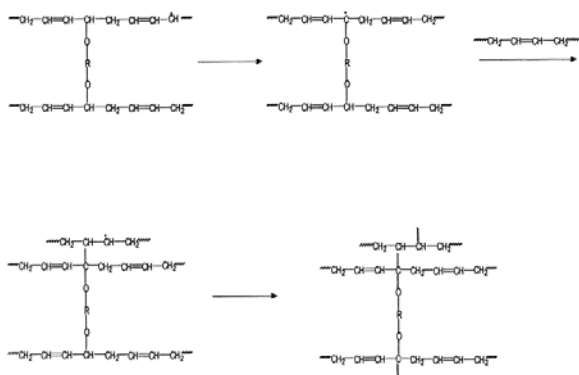
Scheme 3. Degradation of polybutadiene in the presence of oxygen.

The spontaneous cross-linking of brominated polybutadiene occurs at room temperature and above; a possible pathway to account for this degradation is shown in Scheme 4. An initial loss of a bromine atom occurs, giving a radical site along the polymeric chain. This polymeric radical can interact with a double bond in another polymer chain to give a new polymeric radical. This can then again interact with an adjacent chain to give a cross-linked system. Since the chain is only partially brominated, all of the cross-linking pathways outlined for virgin PBD are also possible.



Scheme 4. Degradation of brominated polybutadiene.

A pathway for the degradation of brominated PBD, cross-linked with diols, is depicted in Scheme 5. Since all of these materials still contain bromine, the initial reaction is likely the loss of a bromine atom with the formation of a polymeric radical. This polymeric radical can now back-bite to give a tertiary radical at the site at which the diol is attached. This new polymeric radical can attack a double bond, in the same way as has been shown for the degradation of brominated PBD, to add polybutadiene units around the carbon which is bonded to the diol. Thus the diol will be well-protected and may exist to relatively high temperatures.



Scheme 5. Degradation of polybutadiene cross-linked with various diols.

4. Conclusion

Brominated PBD can be easily cross-linked via reaction with the dilithio derivatives of diols. Brominated PBD has a much lower thermal stability than does virgin PBD, since a bromine atom can be very easily lost. Since the bromine is never completely removed from the cross-linked polymers, a lower thermal stability invariably results from the cross-linking. The primary reactions, which produce the onset of the degradation, give rise to reactive species which can apparently facilely react to form significant amounts of a non-volatile residue. The ether linkage is the most thermally stable moiety in these cross-linked polymers.

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