

Benzocyclobutenes as Styrene Monomer Scavengers and Molecular Weight “Stabilizers” in Atactic and Syndiotactic Polystyrenes

JOHN M. WARAKOMSKI,¹ WILLIAM C. PIKE,² ROBERT A. DEVRIES³

¹ Engineering Compounds Research and Development, 433 Building, The Dow Chemical Company, Midland, Michigan 48667

² Polystyrene Research and Development, 438 Building, The Dow Chemical Company, Midland, Michigan 48667

³ Organic Chemicals Research, 677 Building, The Dow Chemical Company, Midland, Michigan 48667

Received 23 November 1999; accepted 15 March 2000

ABSTRACT: Syndiotactic polystyrene (SPS) is a semicrystalline polymer with a melting point of 270°C. At processing temperatures of 300°C or higher, SPS begins to decompose with loss of molecular weight and the formation of styrene monomer. Under these conditions, atactic polystyrene also decomposes. One approach to controlling this generation and buildup of styrene and the molecular weight loss during processing is to add a compound that will react with styrene and/or with the polymer decomposition products at the processing conditions. This report describes the use of three benzocyclobutene (BCB) compounds (ethylene *bis*-BCB, divinyl disiloxane *bis*-BCB, and a copolymer of styrene and 4-vinyl BCB) during SPS and atactic polystyrene processing. The conclusions are: 1. BCB moieties, when extruded with SPS at the 2 wt % level, caused a substantial decrease in residual styrene compared with a control SPS; 2. BCB compounds, when extruded with SPS, resulted in high molecular weight fractions. The result with the divinyl disiloxane *bis*-BCB was especially dramatic; and 3. BCB functionalized materials may find utility as additives in SPS during processing to minimize loss of molecular weight and buildup of styrene. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2008–2015, 2000

Key words: monomer scavengers; syndiotactic polystyrene; atactic polystyrene; benzocyclobutene

INTRODUCTION

Benzocyclobutenes (BCBs) are a family of thermally polymerizable monomers that can react with sites of unsaturation or with themselves to form high polymers.^{1–4} When heated to approximately 200°C (Fig. 1) the cyclobutene ring of

BCB, **1**, opens to form a highly reactive *o*-quinodimethane intermediate **2**. If unsaturation is present, this intermediate reacts to form stable Diels-Alder adducts. In the absence of other unsaturation, BCB can form an unstable spiro-dimer, **3**, which decomposes to polymer. The BCB group can also be incorporated into polymers via other functional groups to provide latent reaction sites. For example (Fig. 2), 4-vinylbenzocyclobutene (VBCB), **4** (4-vinylbenzocyclobutene has CAS #99717-87-0 and name 3-ethenyl(bicyclo[4.2.0]-octa-1,3,5-triene)), can be copolymer-

Correspondence to: J. M. Warakomski (warakomski@dow.com).

Journal of Applied Polymer Science, Vol. 78, 2008–2015 (2000)
© 2000 John Wiley & Sons, Inc.

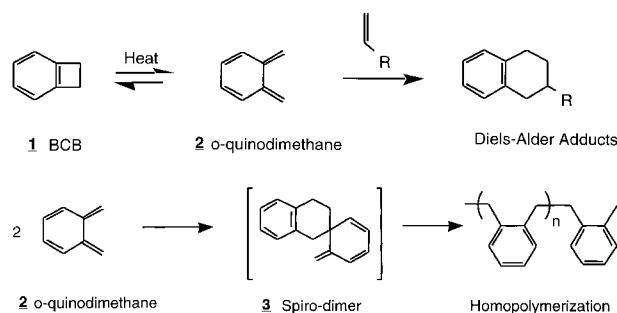


Figure 1 Reactions of benzocyclobutenes.

ized with styrene by conventional means leaving the pendant BCB units intact.^{5–10} Another method in which BCBs have been used in polymers is to blend in bisbenzocyclobutenes (or polybenzocyclobutenes) which can thermally react with residual unsaturation upon heating. The two bisbenzocyclobutene monomers used in this study (Fig. 3) were ethylene-bisbenzocyclobutene (Et-*bis* BCB), **6**,¹¹ and tetramethyldivinylsiloxane-bisbenzocyclobutene (DVS-*bis* BCB), **7** (Et-*bis* BCB has CAS #67237-37-0 and name *trans*-3,3'-(1,2-ethenediyl) *bis*(bicyclo[4.2.0]octa-1,3,5-triene)), made from 4-bromobenzocyclobutene (BrBCB), **5** (DVS-*bis* BCB has CAS #117732-87-3 and name mixed isomers of disiloxane-1,3-*bis*(2-bicyclo[4.2.0]octa-1,3,5-trien-3-yl)-1,1',3,3'-tetramethyl).

These monomers can also be thermally polymerized by Diels-Alder chemistry to form high performance resins useful in microelectronics, structural composites, and to modify thermoplastics.^{1–3} One special commercial application of DVS-*bis* BCB oligomers is for thin-film coatings in microelectronics.^{12–14} A recent report describes the use of BCB functionalized peroxides to polymerize styrene with BCB latent functional groups, which could later be thermolyzed to form branches.¹⁵

Syndiotactic polystyrene (SPS) is a semicrystalline polymer with a melting point of 270°C.^{16,17} This material begins to decompose at approximately 300°C with loss of molecular weight and the formation of styrene monomer. Although SPS

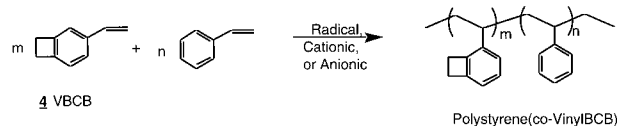


Figure 2 Styrenic copolymers with BCB functionality.

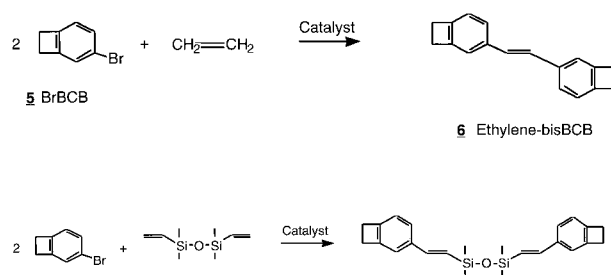


Figure 3 Preparation of *bis* BCB monomers.

can be melt devolatilized, further processing without vacuum may generate more monomer. Molecular weight degradation can also occur at temperatures above 300°C. The general thermal decomposition mechanism for atactic polystyrene (APS) is first chain scission followed by some depolymerization.^{18,19} We expect that similar reactions occur for SPS.

APS is susceptible to thermal degradation because of the relatively labile benzylic hydrogen and subsequent relative stability of the benzyl radical (activation energy of about 10 kcal/mol). Chain transfer via hydrogen abstraction can lead to chain scission (Fig. 4). Once a radical is formed, a chain depolymerization reaction can lead to formation of styrene monomer as shown below (Fig. 5). If the hydrogen abstraction (Fig. 4) occurs at the end of the chain, monomer formation can occur directly from the polymer radical. Carbon-carbon bond breakage is less likely because of its high (65 kcal/mol) dissociation energy.²⁰

The relatively low ceiling temperature (T_c , the temperature at which monomer formation and consumption are equal) of 230°C for APS is fairly close to most of its processing temperatures of

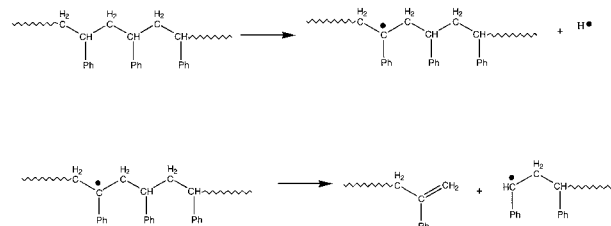


Figure 4 Chain transfer via hydrogen abstraction leads to chain scission in polystyrene.

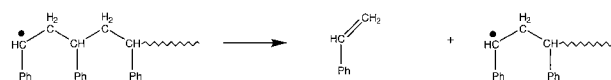


Figure 5 Formation of styrene monomer by chain depolymerization reaction of polystyrene.

180–220°C. Thus processing of APS will lead to formation of styrene monomer and molecular weight loss.

One approach to controlling this buildup of styrene and molecular weight loss during processing of SPS or APS is to add a compound that will react with styrene and/or with polymer decomposition fragments at the processing conditions. This report describes the use of additives containing BCB moieties during SPS and APS processing. Evaluation was made by repeated passes of SPS through a twin screw extruder followed by measurement of residual monomer and molecular weight distributions. APS was processed for various times in a Brabender mixer. The addition of BCB functionalized materials to polystyrene that is being processed at high temperatures could serve two roles: 1. to scavenge residual styrene; and 2. to crosslink the polystyrene to counter the molecular weight loss.

EXPERIMENTAL

The BCB monomers were prepared using the palladium-catalyzed Heck vinylation reaction.^{11,21–26} Monomer **4** (liquid) was prepared via the Pd-catalyzed reaction of BrBCB, **5**, with ethylene. Monomer **6** (mp 132°C) was prepared via the Pd-catalyzed reaction of BrBCB, **5**, with ethylene, followed by addition of a second mol of BrBCB. Monomer **7** (oil) was prepared by the palladium-catalyzed reaction of BrBCB **5** with 1,2-divinyl-1,1,2,2-tetramethyldisiloxane.

The poly(styrene-*co*-4-vinyl-benzocyclobutene) was prepared by cationic polymerization of vinyl-BCB and styrene using TiCl₄ as catalyst and ethylene dichloride as solvent. The polystyrene oligomer sample was prepared by cationic polymerization of styrene under identical conditions to the copolymer. The control polystyrene was Dow STYRON™ 663 which has an M_w of 305,000 and an M_w/M_n ratio of 2.4.

SPS was produced in a pilot plant at The Dow Chemical Company using a titanium catalyst. Extraction with methylethyl ketone and also analysis by ¹³C-nuclear magnetic resonance spectroscopy showed that the SPS contains more than 97% syndiotactic polymer.

Thermal stability studies of APS were conducted using a Brabender torque rheometer operated at 60 rpm and at 220°C. Blends were prepared by tumble blending the polystyrene pellets and additives. At periodic times, the agitator was

stopped and samples were removed for molecular weight and residual styrene content determinations.

SPS- and BCB-containing compounds were tumble blended then compounded in a 0.8-inch diameter Welding Engineers twin screw extruder using barrel temperatures of 260 to 318°C and a screw speed of 200 rpm. The exiting strand was water cooled and pelletized. The pellets were then analyzed for residual styrene and for molecular weight distribution.

Residual styrene monomer was determined on the SPS pellets by headspace gas chromatography. SPS (0.5 g) was dissolved in 5 mL *o*-dichlorobenzene at 140°C, then the headspace was sampled into a Hewlett-Packard 5890 gas chromatograph equipped with a Hewlett-Packard 19395A headspace sampler and a capillary column [25-m methyl phenyl (5%) silicone, 0.32-mm inner diameter, 5.0-micron film thickness], and a Hewlett-Packard 3393 integrator. For five samples at 1000 ppm styrene, two standard deviations (2σ) is ± 125 ppm; at 500 ppm, 2σ is ± 55 ppm; and at 100 ppm, 2σ is ± 35 ppm. Molecular weight was determined by high temperature size exclusion chromatography in 1, 2, 4-trichlorobenzene. For a sample with $M_n = 140,000$ and $M_w = 294,000$, 2σ for M_n is +8300 and 2σ for M_w is 10,900.

RESULTS AND DISCUSSION

Extrusion of SPS (High Styrene Content, High Molecular Weight) with *bis*-BCB Materials

Powdered SPS was tumble mixed with styrene-*co*-4-vinyl-BCB polymer to form a 2 wt % blend, corresponding to 0.5 wt % BCB in the blend. SPS was also mixed with ethylene-*bis*-BCB to form a 1 wt % blend. These blends were extruded then analyzed for residual styrene and for molecular weight distribution. The results are shown in Table I.

Upon extrusion, the SPS control lost molecular weight. With 2% styrene-BCB copolymer or 1% ethylene *bis*-BCB, the molecular weight loss was not as great. When SPS having high residual styrene level (27,100 ppm) is extruded, much monomer is devolatilized through the extruder vent. The loss of monomer by devolatilization is greater than the formation of monomer. No differences were seen in the residual styrene between the control and the SPS with the BCB additives. The starting residual styrene concen-

Table I Molecular Weights and Residuals for Syndiotactic Polystyrene (SPS) Powder Extruded with BCB Compounds

	Starting SPS Powder, Not Extruded	SPS Extruded 1×	SPS + 2% Styrene-BCB Copolymer, Extruded 1×	SPS + 1% Et- <i>bis</i> BCB, extruded 1×
$M_p \times 10^{-3}$	704	357	445	438
$M_n \times 10^{-3}$	339	189	226	225
$M_w \times 10^{-3}$	960	417	505	495
$M_z \times 10^{-3}$	2023	715	868	850
M_w/M_n	2.83	2.20	2.23	2.02
M_z/M_w	2.11	1.72	1.72	1.72
Styrene (ppm)	27,100	9100	9570	8000
Toluene (ppm)	40	110	80	80
Ethylbenzene (ppm)	140	70	90	90

tration, however, was very high, and any effect by the BCB compounds was probably hidden. The next experiments were done using SPS containing approximately 500 ppm styrene.

Extrusion of SPS Pellets (Low Styrene Content, Low Molecular Weight) with *bis*-BCB Materials

The ethylene-linked *bis*-BCB and divinyl disiloxane-*bis*-BCB were added to 1000 g of SPS pellets ($M_w = 390,000$ and 500 ppm styrene) at levels of 1 and 2 wt %. The polymer and additive were thoroughly shaken by hand in a polyethylene bag to blend, then the coated pellets were fed into the extruder with a vibrating feeder. Extrusion was done on the Camile 3000-controlled 0.8" Welding Engineers extruder. This machine has a twin screw counter-rotating non-intermeshing design and is vented near the die. Barrel temperatures ranged from 270°C at the feed end to 295°C at the die. The melt temperature of the extrudate measured with a hand-held thermocouple probe was 310°C. The screw speed was maintained at 200 rpm, and rates of approximately 10 lbs./h were used. In all cases, the maximum feeding rate at which no plugging in the vent occurred was used. The strand was passed through a water bath to cool, then pelletized with a Conair Jetro Model 304 rotary cutter. The rate was determined by dividing the weight of pellets collected by the time. No attempt was made to control crystallization of the extrudate.

Shown in Figure 6 are the residual styrene in SPS extruded with BCB compounds. With 2% Et *bis*-BCB, the residual styrene after one pass through the extruder was 310 ppm, compared

with 640 ppm for the control. After further passes through the extruder, the concentration of residual styrene increased similar to the control, suggesting that most of the Et *bis*-BCB had reacted during the first pass. Et *bis*-BCB at the 1% level had little effect on the residual styrene. Results were similar with the divinyl disiloxane-*bis*-BCB. Compared with a control, the divinyl disiloxane-*bis*-BCB blends had less residual styrene after one pass through the extruder; additional passes resulted in increases in residual styrene as though no additives were present. Similar to the Et *bis*-BCB, the divinyl disiloxane-*bis*-BCB effect was greater at 2% loading than at 1% loading.

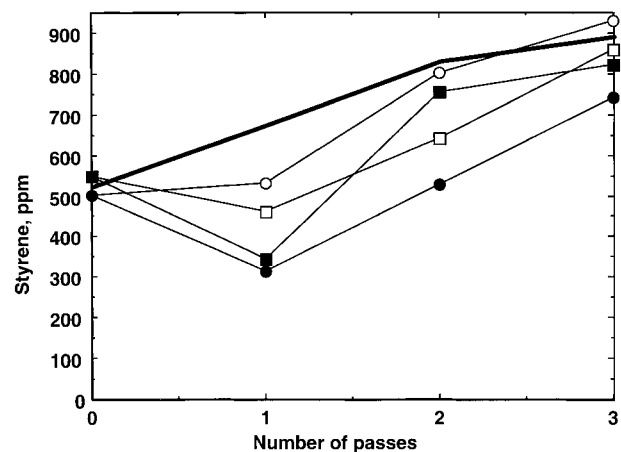


Figure 6 Residual styrene in SPS after repeated extrusions with ethylene-*bis* benzocyclobutene and with divinyl disiloxane-*bis*-BCB (dark line, control; open circle, 1% ethylene-*bis* BCB; filled circle, 2% ethylene-*bis* BCB; open square, 1% divinyl disiloxane-*bis* BCB; filled square, 2% divinyl disiloxane-*bis* BCB).

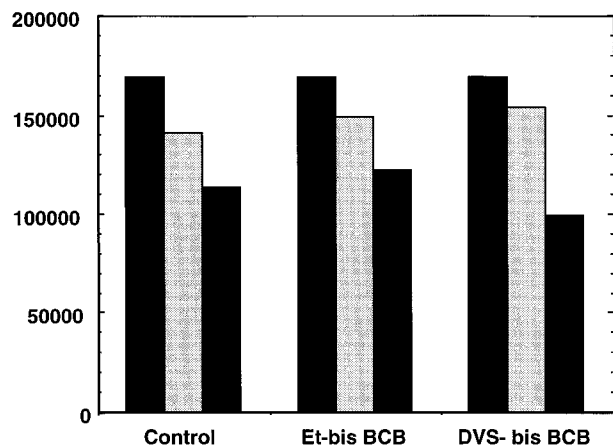


Figure 7 Number average molecular weight, M_n , of SPS after extrusion with 2% ethylene-*bis*BCB and 2% divinylsilyl-*bis*-BCB. (The first bar of each set represents no passes through the extruder, the second bar of each set represents one pass through the extruder, and the third bar of each set represents three passes through the extruder.).

In addition to lowering the residual styrene level, this additive also affected the molecular weight (Figs. 7–10). After three extrusions, the control had a 35% drop in M_n whereas the SPS-2% Et *bis*-BCB blend had a 30% drop. Compared with a control, which had a 35% decrease in M_w after three extrusions, the SPS with 2% BCB had only a 25% drop in M_w . Whereas the control

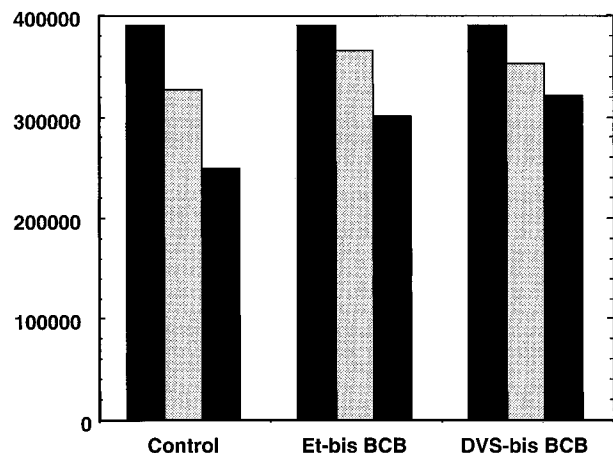


Figure 8 Weight average molecular weight, M_w , of SPS after extrusion with 2% ethylene-*bis*-BCB and 2% divinylsilyl-*bis*-BCB. (The first bar of each set represents no passes through the extruder, the second bar of each set represents one pass through the extruder, and the third bar of each set represents three passes through the extruder.).

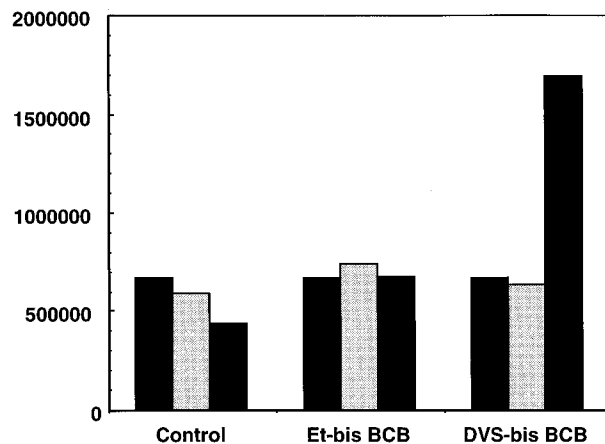


Figure 9 Z-average molecular weight, M_z , of SPS after extrusion with 2% ethylene-*bis*-BCB and 2% divinylsilyl-*bis*-BCB. (The first bar of each set represents no passes through the extruder, the second bar of each set represents one pass through the extruder, and the third bar of each set represents three passes through the extruder.).

had a 35% drop in M_z , the SPS with 2% Et *bis*-BCB showed no change. For M_{z+1} , the control had a 30% drop after three extrusions whereas the 2% Et *bis*-BCB blend showed a 35% increase.

With DVS-*bis*-BCB, the effect on SPS molecular weight was even more dramatic: After three passes, M_n decreased by 40%, but M_w dropped by only 20%, and M_z and M_{z+1} increased by 150 and 500%, respectively.

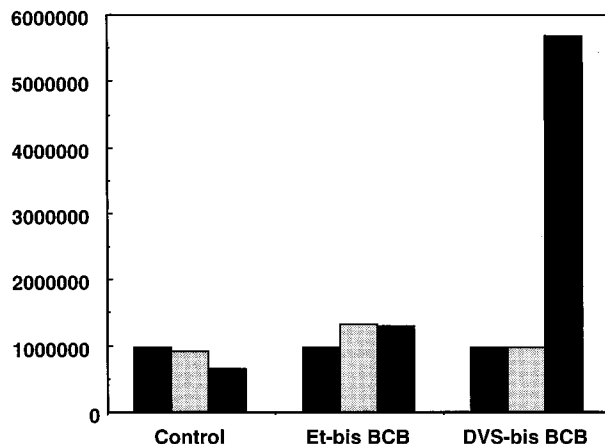


Figure 10 Z + 1-average molecular weight, M_{z+1} , of SPS after extrusion with 2% ethylene-*bis*-BCB and 2% divinylsilyl-*bis*-BCB. (The first bar of each set represents no passes through the extruder, the second bar of each set represents one pass through the extruder, and the third set represents three passes through the extruder.).

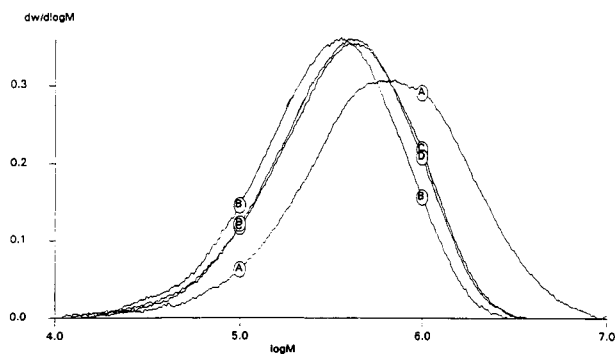


Figure 11 Molecular weight distribution of syndiotactic polystyrene extruded with BCB compounds. A, starting SPS powder, no extruded, $M_w = 960,000$; B, SPS extruded 1 time, $M_w = 417,000$; C, SPS + 2% BCB-PS extruded 1 time, $M_w = 505,000$; D, SPS + 1% BCB-Et-BCB extruded 1 time, $M_w = 495,000$.

The chromatograms (Fig. 11) clearly show high molecular weight tails produced upon extruding SPS with these bifunctional BCB compounds, especially in the case of the divinyl disiloxane-linked BCB.

APS

APS is processed at 180 to 220°C (extrusion, injection molding, etc.) and this heat treatment occurs for 1 to 60 min, depending on the exact process being used. Average time for injection-molding conditions are 5 min. A temperature of 220°C was chosen for this experiment because it represents the maximum temperature of most processes for polystyrene and it is below the T_c .

Figure 12 shows the effect of various additives

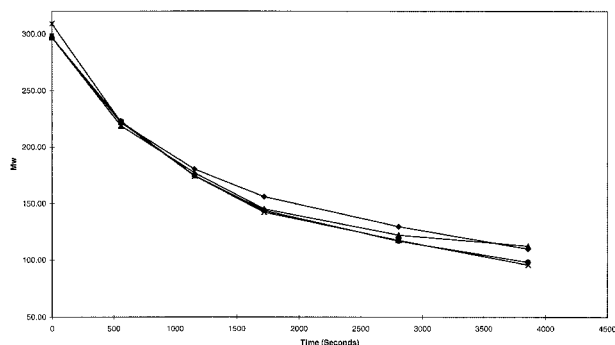


Figure 12 Effect of BCB additives on weight average molecular weight of polystyrene versus mixing time at 220°C. Filled diamond, 2% BCB-PS; filled circle, 2% oligomers; filled triangle, 0.6% BCB-Et-BCB; X, PS 665 only.

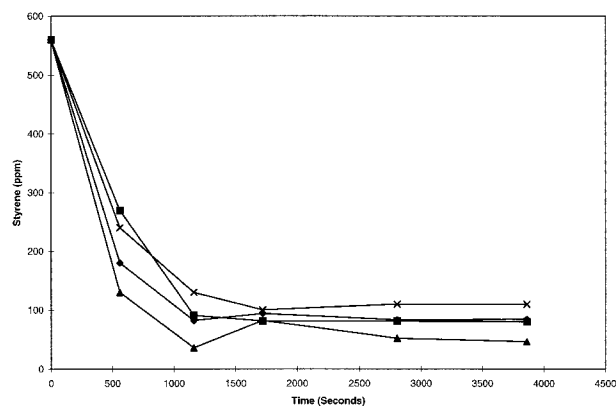


Figure 13 Effect of BCB additives on residual styrene in polystyrene versus mixing time at 220°C. Filled diamond, 2% BCB-PS; filled square, 2% oligomers; filled triangle, 0.6% BCB-Et-BCB; X, PS 665 only.

on the molecular weight of polystyrene maintained at 220°C for up to 1 h. As expected, there is a continuous decrease in molecular weight with time at temperature. Both of the BCB additives gave less of a decrease than the control or the control with added oligomers. A portion of the degradation could be due to catalysis of the thermal reaction by O_2 which may have been inadvertently present in the mixing chamber.

Figure 13 shows the effect of the same BCB additives on the residual styrene levels that are present in the polystyrene samples. The control polystyrene sample loses residual styrene monomer because of devolatilization through the vent. However, with the BCB additives, the amount of styrene that was present in the polymer upon thermal treatment is lower than the control. The addition of BCB compounds at the 0.5 wt % BCB content (2% BCB-PS) gives a 30–50% reduction in the styrene levels compared with the control samples.

Note that at the temperatures tested, there is not a gradual decline in the styrene levels fol-

Table II Effect of Temperature on Half Life of BCB Functionality

Temperature (°C)	$t^{1/2}$ (min)
200	124
220	21
250	2
275	0.3
300	0.06

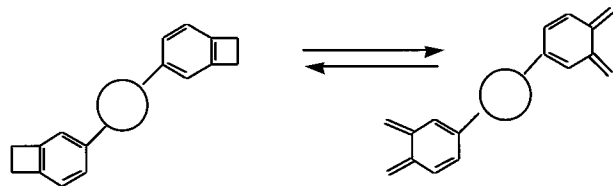


Figure 14 Ring opening of BCB derivatives upon thermal treatment.

lowed by an increase in styrene. This behavior would be expected if the BCB moiety was completely consumed. The data in Table II indicate that the half life of BCB at 220°C is approximately 20 min. Thus, the use of BCB styrene scavengers is effective at most temperatures used for processing polystyrene.

Possible Mechanisms

BCB materials will ring open under thermal treatment to give the *o*-quinodimethane species as shown in Figure 14. The circle in Figure 14 represents any group used to link the BCB units together. The half life for this reaction at 200°C is approximately 2 h whereas at 300°C it is approximately 4 s.

Once this ring opening has occurred, the material can react in several ways with the thermal decomposition products, as shown in Figure 15. The reactions show only one of the BCB rings that are present in the additives. Reaction with any radicals generated could produce the stabilized benzylic radical which could then continue to couple or terminate with another radical. This reaction would prevent depolymerization and the re-

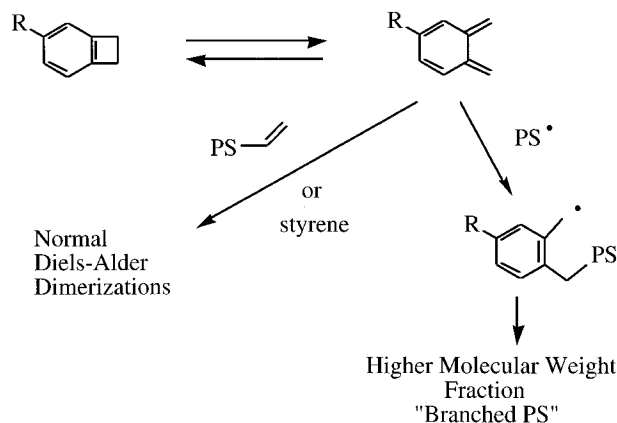


Figure 15 Reaction of benzocyclobutenes with radicals or olefins.

sulting generation of monomer. The second possible pathway involves a simple Diels-Alder reaction and is the most likely mechanism for removal of styrene from the system. The self-coupling Diels-Alder reaction between two BCB moieties is possible, but we believe it is unlikely because of the low concentration of BCB moieties in the system. Ring-opened BCB has a very short lifetime. If it does not find styrenic radicals, styrene monomers, or other species to react with, it will condense back to its original state.

CONCLUDING REMARKS

1. Ethylene-*bis* benzocyclobutene and divinyl disiloxane-*bis* benzocyclobutene, when extruded with SPS at the 2% level, caused a substantial decrease in residual styrene, whereas the level of styrene in controls increased. Et-*bis* BCB and DVS-*bis* BCB at the 1% level had less of an effect on the styrene level.
2. Ethylene-*bis* benzocyclobutene and divinyl disiloxane-*bis* benzocyclobutene, when extruded with SPS, resulted in high molecular weight fractions. The result with the divinyl disiloxane-*bis* BCB was especially dramatic.
3. Et-*bis* BCB and DVS-*bis* BCB may find utility as an additive in atactic and syndiotactic polystyrenes during processing to minimize loss of molecular weight and buildup of styrene.

The authors thank Greg Kormelink, Phil Kuch, and Rose Nelson for analytical measurements.

REFERENCES

1. Kirchhoff, R. A. U.S. Pat. 4,540,763, 1985.
2. Kirchhoff, R. A.; Carriere, C. J.; Bruza, K. J.; Rondan, N. G.; Sammler, R. L. *J Macromol Sci Chem* 1991, A28, 1079.
3. Hahn, S. F.; Martin, S. J.; McKelvy, M. L.; Patrick, D. W. *Macromolecules* 1993, 26, 3870.
4. Kirchhoff, R. A.; Bruza, K. A. *Prog Polym Sci* 1993, 18, 85.
5. Wong, P. K. U.S. Pat. 4,698,394, 1987.
6. Wong, P. K. U.S. Pat. 4,798,990, 1987.
7. Wong, P. K. U.S. Pat. 4,722,974, 1988.
8. Wong, P. K. U.S. Pat. 4,687,815, 1987.
9. Pabon, R. A.; DeVries, R. A. U.S. Pat. 5,310,809, 1994.

- Campbell, R. E.; DeVries, R. A. U.S. Pat. 5,077,367, 1991.
- Kirchhoff, R. A.; Schrock, A. K.; Hahn, S. F. U.S. Pat. 4,783,514, 1988.
- Burdeaux, D. C.; Townsend, P. H.; Hahn, S. F.; Thomsen, M.; Gilpin, J. A.; McGee, R.; Carr, J. N. Proc NEPCON West, 1989, 927.
- Burdeaux, D.; Townsend, P.; Carr, J.; Garrou, P. J Electron Mater 1990, 19, 1357.
- Townsend, P. H.; Burdeaux, D. C.; Hahn, S. F.; Thomsen, M.; Carr, J. N. Proc MRS, 1989, 154, 47.
- DeLassus, S. L.; Howell, B. A.; Cummings, C. J.; Dais, V. A.; Nelson, R. M.; Priddy, D. B. Macromolecules 1994, 27, 1307.
- Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. Macromolecules 1986, 19, 2464.
- Pasztor, A. J.; Landes, B. G.; Karjala, P. J. Thermochim Acta 1991, 177, 187.
- Maecker, N. L.; Armentrout, D. N. In Encyclopedia of Polymer Science and Engineering; John Wiley & Sons: New York, 1989; Vol. 16.
- Winkler, R. E. Ph.D. Dissertation, 1989, University Microfilms International Order Number 9011320.
- Stivala, S. S.; Kimura, J.; Gabbay, S. M. In Degradation and Stabilization of Polyolefins; Allen, N. S., Ed.; Applied Science: London, Chapter 3.
- Heck, R. F. Org React 1980, 27, 345.
- Heck, R. F. U.S. Pat. 3,922,299, 1975.
- DeVries, R. A.; Frick, H. R. U.S. Pat. 5,136,069, 1992.
- DeVries, R. A.; Ash, M. L.; Frick, H. R. U.S. Pat. 5,138,081, 1992.
- DeVries, R. A.; Frick, H. R. U.S. Pat. 5, 243,068, 1993.
- DeVries, R. A.; Schmidt, G. F.; Frick, H. R. U.S. Pat. 5,264,646, 1993.