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Incorporation of Benzocyclobutene into Polystyrene Allowing Postpolymerizer Chain Extension/Branching

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ABSTRACT: The introduction of long-chain branching in polystyrene has the potential to improve some of the properties of the polymer. However, our attempts to make branched polystyrene in continuous free-radical bulk styrene polymerization processes has led to gel formation and eventual reactor fouling. This paper describes a new approach for introducing long-chain branching into polystyrene which would eliminate the reactor fouling problem. The approach is to place latent functionality on the polymer during polymerization which subsequently reacts to form branches upon thermolysis at temperatures >200 °C. This study focuses on the benzocyclobutene (BCB) moiety as the latent functionality. BCB is incorporated into the polymer chain by initiation with BCB functional peroxides, resulting in chain extension/branching upon heating at 240 °C.

Introduction

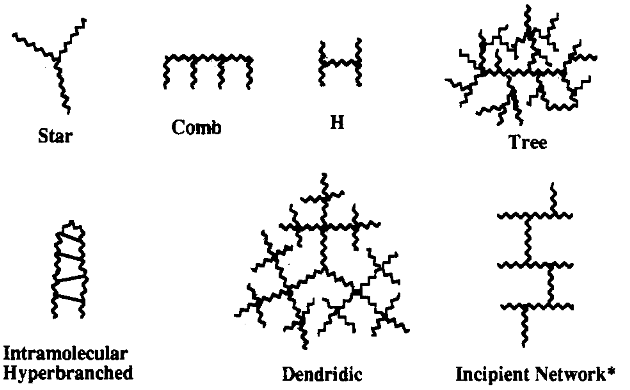
Long-chain branching is found, to some extent, in all commercial free radically produced polymers. Branching takes place during manufacture by chain transfer to polymer and can also take place in the polymer after manufacture by exposure to UV or other forms of radiation.

Chain branching in some polymers is known to improve certain properties and is practiced commercially (e.g., polyethylene and polycarbonate). In polystyrene, many types of branch structures have been synthesized and the effect of branch structure on properties has been studied (Chart 1).

Most of the studies of branched polystyrene have been fundamental in nature and have focused on solution and rheological properties.[1-10]

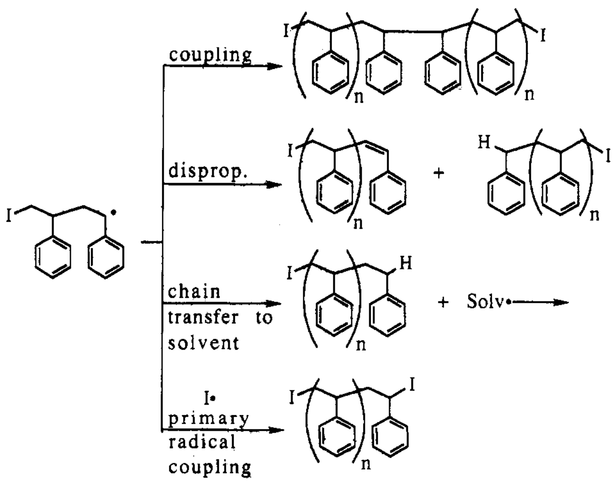
Anionic polymerization has been the polymerization mode most widely used to make and study branched polystyrenes. This is almost certainly because of the ability to control the termination step which is required for making many of the branch architectures shown in Chart 1. However, all large-scale polystyrene production plants utilize free-radical polymerization chemistry. This is likely due to the cost associated with monomer purification needed for the anionic chemistry.[11] For branched polystyrene made using only free-radical polymerization chemistry, the type of branch architecture that is possible is limited, in general, to incipient network. This limitation is due to the complexity of the termination processes (occurring simultaneously with initiation and propagation) taking place during free-radical styrene polymerization (Scheme 1).

Chart 1. Several Possible Polystyrene Branch Architectures[a]



[a] Asterisk indicates the name suggested by B. Meister of Dow Chemical Co.

Scheme 1. Multiple Termination Processes Taking Place during Free-Radical Styrene Polymerization



Background

The most economical process to manufacture polystyrene is by continuous free-radical bulk styrene polymerization (CFRBSP).[11] In general, three reactor types are used for CFRBSP (Figure 1). These three reactor types are characterized as being either plug-flow or backmixed. Continuous plug-flow reactors (CPFR) typically have excellent radial mixing but virtually no backmixing, unless they are recirculated. These reactors are usually described as stratified agitated tower reactors. Continuous stirred tank reactors (CSTR), on the other hand, have high degrees of backmixing. They are usually single staged and operated isothermally and at constant monomer conversion. CPFR-type reactors, on the other hand, are mul-

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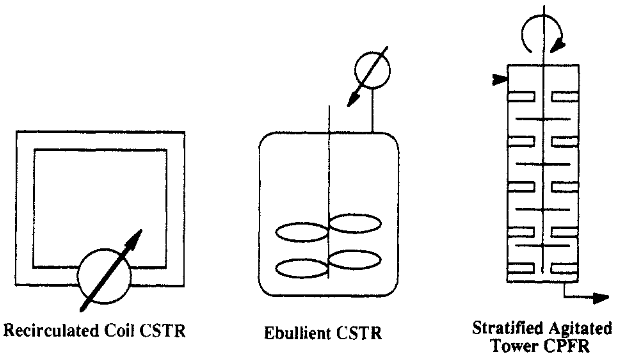
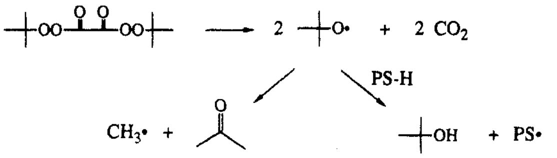


Figure 1. Three reactor configurations utilized for CFRBSP.

Scheme 2. Formation of *tert*-Butoxy Radicals and Subsequent H-Abstraction



tistaged, having a temperature profile of typically 100–170 °C. Two general configurations of CSTR reactors are utilized commercially, i.e., recirculated coil and ebullient.

Typically, a few percent by weight of a chain-transfer (CT) solvent (e.g., ethylbenzene) is utilized during CFRBSP. The addition of CT solvent to the polymerization decreases the polymer molecular weight and overall plant capacity but is essential to keep the polymerizer from becoming eventually plugged with gels and insoluble cross-linked polymer. The mechanism of buildup when running a CFRBSP without a CT solvent is likely chain transfer to polymer.

Peroxide initiators typically utilized for the manufacture of polystyrene from *tert*-butoxy radicals.[12] These radicals have a strong propensity to abstract H-atoms. This propensity has found utility when making high-impact PS. For example, the use of initiators which generate *tert*-butoxy radicals increases the level of grafting of PS onto polybutadiene rubber. The increase in grafting is generally thought to be due to allylic H-abstraction from the rubber backbone by *tert*-butoxy radicals.[13] This raises questions regarding the extent of H-abstraction from the PS backbone during polymerization; i.e., the use of initiators that generate potent H-abstracting radicals may increase the extent of long-chain branching during polystyrene manufacture. This question has been investigated by decomposing bis(*tert*-butylperoxy)oxalate in benzene solutions of polystyrene.[14,15] Bis(*tert*-butylperoxy)oxalate decomposes upon heating to form two *tert*-butoxy radicals and carbon dioxide. Once the *tert*-butoxy radicals are formed, they either abstract a H-atom or decompose to form acetone and a methyl radical (Scheme 2).

The extent of H-abstraction was determined by measuring the ratio of *tert*-butyl alcohol (TBA)/acetone produced. Using cumene as a model for PS, a high level of H-abstraction was observed. However, PS showed a very low level of H-abstraction which decreased further as the degree of polymerization of the PS was increased (Figure 2). This is because the coil conformation of the PS chains restricts access of the *tert*-butoxy radicals to the labile tertiary benzylic H-atoms on the PS backbone.

The long-chain branching that takes place during polystyrene manufacture in CFRBSP reactors is extremely small. However, manufacturers of polystyrene for film applications, for which gel particles are a big problem, constantly monitor the product for gels. If the level of gels gets too high, the polymerizer must be cleaned to remove the coating of gel on the reactor walls. The mechanism of gel formation is not certain, but it is believed that a polymer layer forms on metal surfaces inside the polymerizer.[16] The layer is dynamic, but the polymer chains that are in the layer are exposed to a free-radical environment for a longer period of time than polymer chains in solution. The longer polystyrene is exposed to free radicals, the more backbone H-abstraction can take place. Also, the concentration of polystyrene in the absorbed layer is very high. Thus, the "gel" effect (Trommsdorff effect)[17] may contribute to increased molecular weight growth in the layer. In any event, the layer of polymer chains ends up becoming more branched and higher in molecular weight than other chains. This effect not only can lead to the formation of gels but can eventually result in reactor plugging if not controlled.

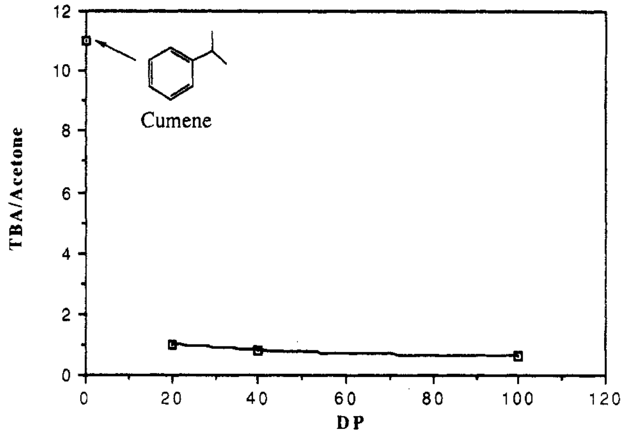
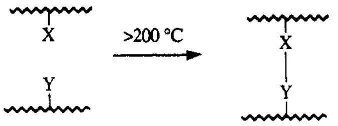


Figure 2. H-abstraction by *tert*-butoxy radicals as a function of the degree of polymerization of polystyrene.

Scheme 3. General Approach to Postpolymerizer Branching



The approaches to branching during free-radical polymerization that have been reported include the addition of a small amount of divinyl monomer,[18,19] vinyl functional initiator,[20] polyfunctional initator,[21] or vinyl functional chain-transfer agent[22] to the polymerization mixture. We have investigated these approaches, except the use of vinyl chain-transfer agent, in CFRBSP for extended periods of time and found that they all lead to gels and eventual reactor fouling after a few days of continuous operation, even in the presence of a chain-transfer solvent. Kirkpatrick and Meister have developed equations[23] to predict the gel potential in CFRBSP using vinyl functional chain-transfer agents. These equations predict that gels would form.

Approach to Branching without Polymerizer Fouling

An approach to branched polystyrene that would eliminate the reactor fouling problem is to accomplish the branching after the polymer exits the polymerization reactor. The concept is to incorporate latent functional groups into the polymer backbone during the polymerization which subsequently couple to make branch points after the polymer exits the polymerizer (Scheme 3). The requirement is that the functional groups be inert at polymerization temperatures (100–170 °C); then during the devolatilization step in which the polymer is heated to 240 °C, the groups must efficiently couple in the viscous polymer melt.

A latent functional group that should meet the above criteria is a benzocyclobutene (BCB) moiety.[24] The BCB functional groups can be incorporated into polystyrene using a BCB functional polymerization initiator.[25,26] On the basis of previous work, at 240 °C, the half-life for decomposition of the BCB functionality is estimated to be about 5 min.[27]

Experimental Section

Materials. The materials used during this study along with the corresponding purities and sources are summarized in the following table:

material	grade/purity	source
styrene	99.70%	Dow Chemical Co.
4-phenylazomaleinanil (PAM)	97%	Aldrich
diphenyl oxide	refined	Dow Chemical Co.
toluene	HPLC	Fischer
methanol	HPLC	Fischer
benzoyl peroxide (BPO)	97%	Aldrich
benzocyclobutenoyl peroxide (BCBPO)	90–95%	ATOCHEM

Ampule Polymerizations. Ampule polymerizations were carried out in glass ampules (7 mm o.d. × 5 mm i.d.). The styrene initiator solutions were placed in ampules, frozen in dry ice, and sealed under vacuum (<5 Torr) using the freeze–thaw technique to exclude air. After 2 h in a hot oil bath at 80 °C, the polymer solutions were removed from the ampules. A portion of the solution was used to gravimetrically determine monomer conversion by devolatilization in a vacuum oven. Residual monomer was removed by dissolving the syrups in toluene and precipitating the polymer by the addition of three volumes of methanol. The precipitation procedure was repeated to ensure that all unchanged monomers were removed. The doubly precipitated polymers were dried overnight in a vacuum oven at 60–70 °C.

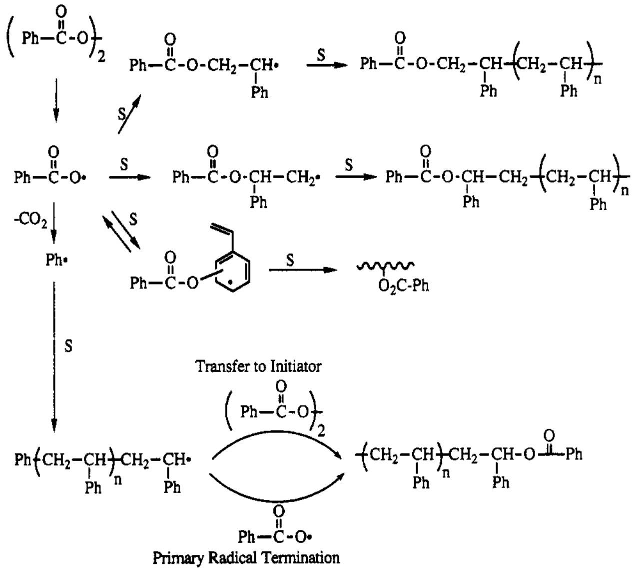
Thermolyses. The dried polymer samples were sealed at reduced pressure (<5 Torr) in glass ampules. The ampules were placed in an oven heated at 240 °C for 2 h. The polymers were removed from the ampules and analyzed by gel permeation chromatography (GPC) and by a low-angle light scattering detector equipped GPC (GPC/LALLS).

GPC/LALLS. GPC/LALLS measurements were done using a modular liquid chromatographic system consisting of a Waters M-6000 pump, Valco air-actuated manual injection valve, Waters 410 differential refractive index detector, and Chromatix KMX-6 low-angle laser light scattering detector. HPLC-grade tetrahydrofuran was used as the eluent at a flow rate of 1 mL/min. Samples were dissolved in tetrahydrofuran and analyzed using three 7.5 × 300 mm Polymer Laboratories mixed-bed columns (two-μm Mixed B, one 5 10-μm Mixed C). Narrow molecular weight distribution polystyrene standards were used to calculate the apparent weight-average molecular weights using data obtained from the refractive index detector alone.

Data acquisition was done using the Polymer Laboratories Caliber GPC/SEC data system; light scattering software written in-house was used to calculate absolute molecular weights and long-chain branching levels. Long-chain branching per 1000 carbon backbone atoms was calculated for the samples for both one-point and two-point branching using the weight-average model for a randomly branched polymer developed by Zimm and Stockmayer.[28] The 2000 ppm benzoyl peroxide (BPO) initiated sample was used as the linear polymer for branching calculations.

BCB Functionality Tagged with Dye. To permit ready UV/vis detection of the polymer for GPC analysis, the polymer was derivatized with 4-phenylazomaleinanil (PAM). The polymer was dissolved to 5% w/w in diphenyl oxide containing 500 ppm of the PAM. The polymer in the dye solution was heated in REACTIVIALS on a hot plate at 240 °C for 5 min. The samples were removed and allowed to cool at ambient temperature. Methanol was added to precipitate the polymer. The polymer was removed and allowed to air dry overnight. The samples were analyzed using a GPC equipped with a diode-array detector, and UV/vis spectra were collected every few milliseconds during the analyses. Polystyrene has no absorbance above 280 nm. However, examination of the UV/vis spectra (Figure 8) of the PAM-tagged polymers revealed absorbance maxima at 320 and 450 nm. Thus the samples were reanalyzed with signals collected at 260, 320, and 450 nm.

Scheme 4. Summary of the Chemistry Taking Place during Polymerization of Styrene Using Benzoyl Peroxide Initiator (S = Styrene)



Results and Discussion

The chemistry of initiation of styrene polymerization using benzoyl peroxide (BPO) is quite complex.[29–31] Most initiators add only to the tail position of styrene to form initiating radicals. Benzoyloxy radicals, however, are so reactive toward styrene that they add to the phenyl ring, the head position, and the tail position of styrene in the relative amounts of 15, 5, and 85%, respectively (Scheme 4).

By analogy to initiation using BPO, initiation using benzocyclobutenoyl peroxide (BCBPO) is expected to result in the placement of a BCB functionality mainly on chain ends.

The criteria for a useful latent group are as follows: (1) the latent group must be inert to the polymerization conditions surviving the polymerization intact, and (2) once the polymer is made, the latent groups must react with each other upon heating, leading to chain extension/branching. The BCB moiety should meet these criteria because it is stable at temperatures <180 °C, opening readily at higher temperatures reacting with itself to form a stable linkage.[24] Scheme 5 shows how BCBPO-initiated polystyrene can theoretically lead to chain extension/branching during subsequent heat treatment.

BCBPO (1-h half-life = 93 °C) was used to initiate styrene polymerization. Loadings of 500, 1000, and 2000 ppm BCBPO were used, and the polymerization was carried out over 2 h at 80 °C. As expected, the M_w of the polymers obtained decreases, and conversion increases, with increasing initiator loading (Figure 3).

At 80 °C the amount of styrene conversion achieved by spontaneous initiation is about 1%. As the level of BCBPO changes, both the relative amount of polystyrene initiated by the spontaneous mechanism and the molecular weight of the polystyrene are changing. To keep these two factors relatively constant, mixtures of BPO and BCBPO totaling 2000 ppm (w/w) were used to initiate polymerization (Table 1).

Scheme 5. Incipient Network Formation *via* Chain Extension/Branching Resulting from Coupling of Latent BCB Moieties Attached to Polystyrene

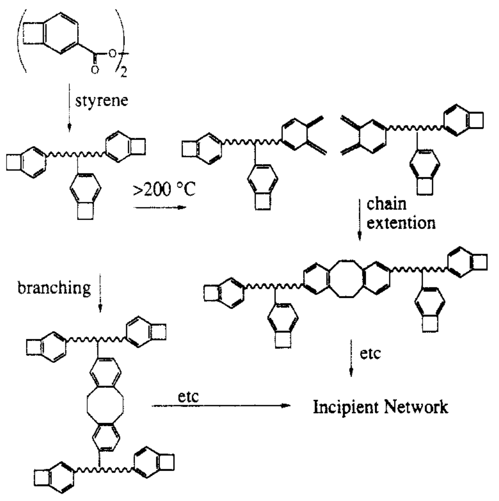


Table 1. M_w Measured Using GPC before and after Heating and GPC/LALLS after Heating Polystyrene Initiated with Various Mixtures of BCBPO and BPO[a]

	M_w/1000		
BCBPO (wt frac of total initiator)	GPC before heating	GPC after thermolysis	GPC/LALLS after thermolysis
0.00	162	149	157
0.25	159	190	201
0.50	149	254	271
0.75	142	413	486
1.00	146	645	873

[a] The total initiator loading in all polymerizations was 2000 ppm (w/w).

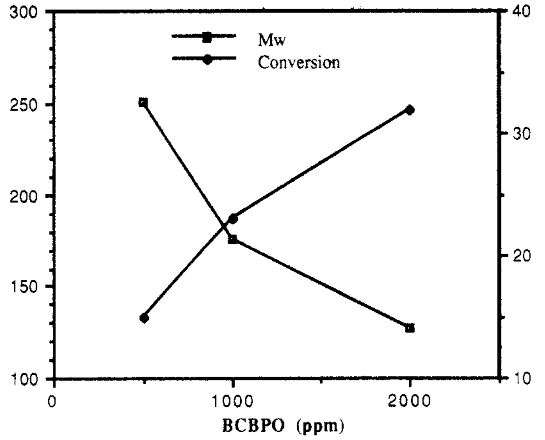


Figure 3. Effect of BCBPO initiator concentration on conversion and M_w for styrene.

The molecular weight determined using GPC/LALLS is the correct molecular weight. The molecular weight obtained by the GPC equipped with a mass detector is lower because the columns were calibrated using linear polystyrene standards. Since branching reduces the hydrodynamic volume for a given molecular weight, the extent of the difference between the molecular weights determined using the two techniques is proportional to the extent of branching.

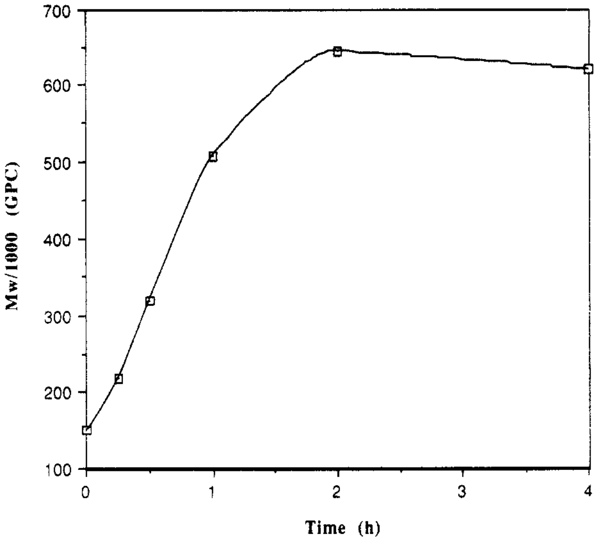


Figure 4. Increase of M_w (GPC) upon thermolysis at 240 °C of polystyrene initiated using 2000 ppm of BCBPO.

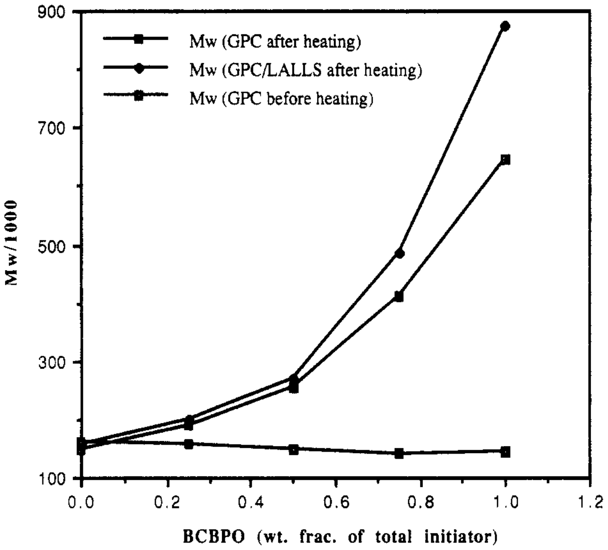


Figure 5. M_w by GPC and GPC/LALLS of polystyrene vs weight fraction of BCBPO in the BCBPO/BPO initiator mixture before and after heating for 2 h at 240 °C.

Thermolysis at 240 °C of the polystyrene sample initiated using 2000 ppm of BCBPO showed a continued molecular weight increase up to 2 h of heating, after which the molecular weight began to slowly decrease (Figure 4). Thus, 2 h at 240 °C was chosen for the thermolysis conditions for the rest of the study. As mentioned previously, the predicted half-life of the BCB functionality at 240 °C is about 5 min. The continued M_w increase over 2 h during thermolysis at 240 °C is likely due to diffusion constraints, since the BCB groups are anchored to the viscous polymer.

The M_w after thermolysis increases exponentially with the weight fraction of BCBPO in the initiator mixture (Figure 5). The GPC curves show the growth of a high molecular weight shoulder as the level of BCBPO increases in the initiator mixture (Figure 6).

Using the method described by Dickie and Koopmans,[32] the level of long-chain branching (LCB) in the samples was calculated. The calculation gives the level of LCB/1000 backbone carbon atoms. For polystyrene, this would be 500 repeat units having a molecular weight of 52 000. The polymers before heating had number-average molecular weights (M_n) in the range of 85 000–90 000, or they contained an average of 820–865 repeat units/chain. A problem with applying the Dickie and Koopmans calculation to BCB functional polystyrene is that the mode of BCB self-condensation is complex (Scheme 6). BCB can react with itself to generate either one or multiple connections. The number of LCB/1000C given by the calculation is dependent upon the ratio of the two pathways (Figure 7). Another factor affecting the branch structure

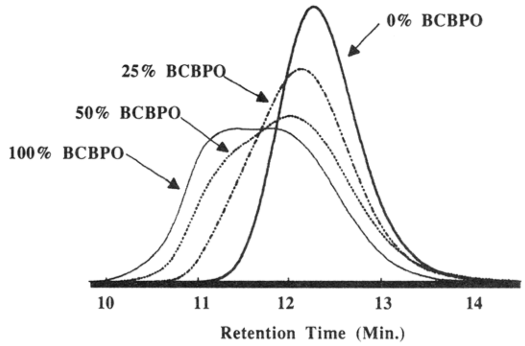


Figure 6. Overlay of the GPC curves obtained upon thermolysis of BCBPO/BPO initiated polystyrenes at 240 °C. Peak areas are normalized.

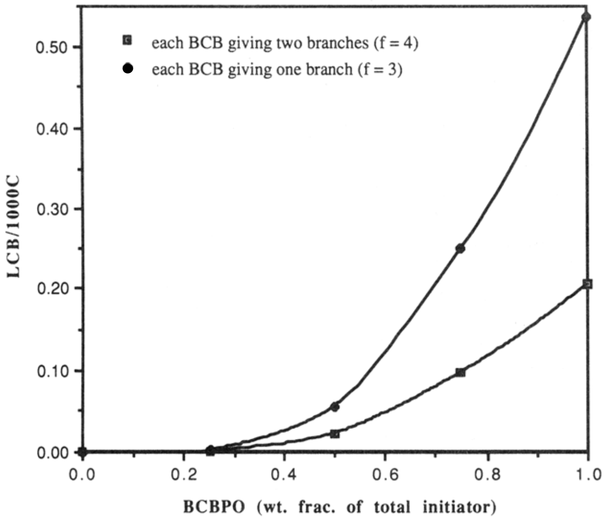
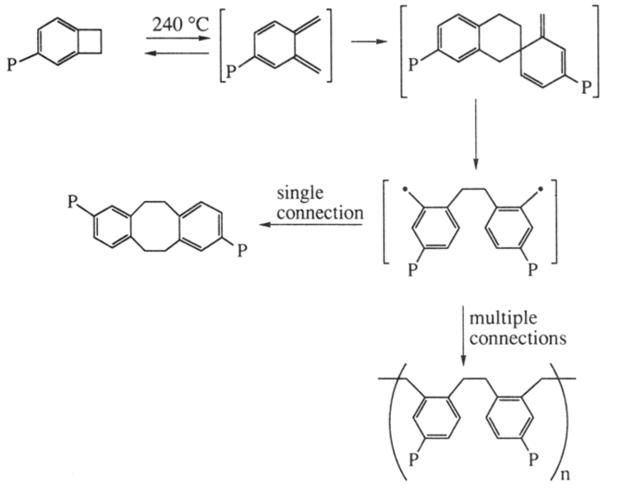


Figure 7. Calculated LCB/1000 backbone carbon atoms vs amount of BCBPO in the BCBPO/BPO initiator mixture.

Scheme 6. Possible Pathways for Coupling of BCB Functionalities



is the ratio of pendant to end-group functionality. For BCB functional polystyrene, the LCB/1000C vs BCBPO used for initiation is likely somewhere between the two curves (single vs double connections/BCB function) shown in Figure 7.

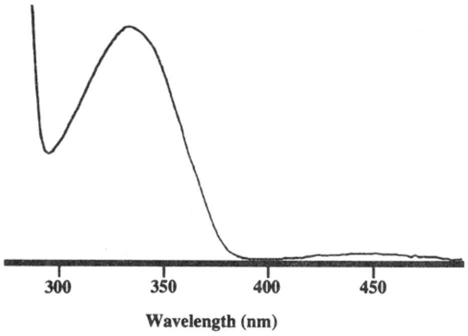


Figure 8. UV/vis spectrum of polystyrene initiated using 2000 ppm of BCBPO after reaction with PAM in solution at 240 °C.

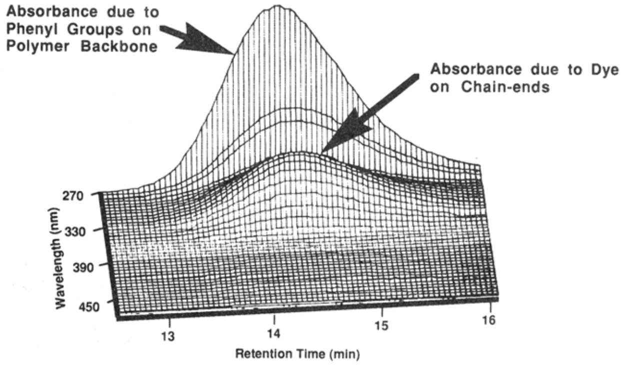
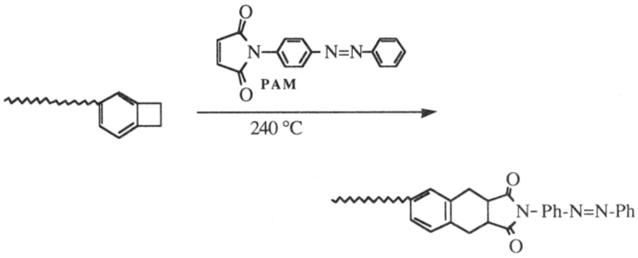


Figure 9. Three-dimensional plot of the GPC–UV/vis data for polystyrene, initiated using 2000 ppm of BCBPO followed by heating with PAM.

Scheme 7. Reaction Used to Tag BCBPO-Initiated Polystyrene for GPC–UV/Vis Analysis to Confirm Point of Attachment of BCB Groups to the Polymer



To demonstrate that, using BCBPO, BCB moieties are incorporated mainly on chain ends, the polystyrene generated using 2000 ppm of BCBPO as initiator was heated in a solution of 4-phenylazomaleimanil (PAM) at 240 °C (Scheme 7). The location of a chromophore on chain ends vs pendant is readily distinguished using GPC–UV/vis as described previously.[33,34] For electronic reasons BCB shows a strong preference for reaction with maleimide as opposed to self-reaction. This selectivity permitted the conversion of BCB groups to strongly absorbing chromophores without a change in molecular weight by heating a solution of the polymer containing excess PAM at 240 °C. A solution of polystyrene containing high loadings of BCB functionality quickly gelled upon heating at 240 °C when PAM was absent.

Figure 8 shows the UV/vis spectrum of the polymer having absorbance maxima at 330 and 450 nm due to tagging with PAM. Figure 9 shows a GPC–UV/vis three-dimensional plot (wavelength vs retention time vs absorbance). It may be noted that the absorbance maximum due to the BCB/PAM adduct (330 nm) is at a longer retention time than the absorbance maximum due to the phenyl groups (260 nm). This offset is more readily visualized by an overlay of the GPC curves collected at 260 and 320 nm of the BCBPO-initiated polystyrene (Figure 10).

The offset of the GPC curve observed at 260 nm with respect to the 320-nm GPC curve shows that most of the BCB groups are located on chain ends. The offset of the 320-nm GPC curve to the low molecular weight side of the

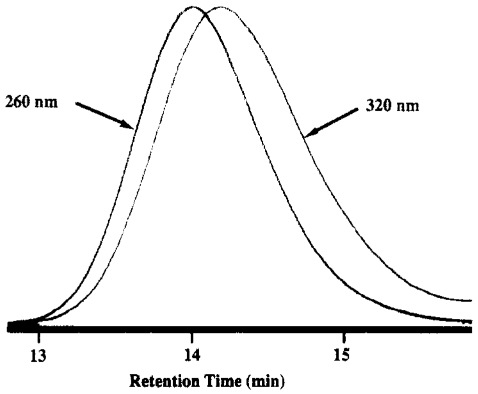


Figure 10. Overlay of the 260- and 320-nm GPC curves collected for BCBPO-initiated polystyrene.

260-nm GPC curve is due to the population of chain ends increasing as molecular weight decreases or the population of moieties giving the 320-nm response (BCB/PAM adduct) increases relative to the moieties giving the 260-nm response (phenyl groups), as molecular weight decreases.

Conclusions

BCB can be incorporated into polystyrene using BCBPO to initiate styrene polymerization. Most of the BCB moieties end up attached to chain ends. The BCB groups attached to polystyrene are latent functional groups. The groups survive the polymerization conditions intact. Upon subsequent thermolysis of the polymer at 240 °C they undergo cycloaddition coupling reactions which results in chain extention/branching. This approach to making branched polystyrene should allow the manufacture of branched polystyrene in CFRBSP processes without gel formation and reactor fouling.

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