Approaches to Branched Polystyrene Using Bulk Free-Radical Polymerization

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ABSTRACT: Preparation of branched polystyrene using continuous bulk styrene polymerization is extremely difficult due to gel formation and can even lead to reactor plugging. This investigation explores the concept of post-polymerizer branching by placing latent functional groups along the polymer backbone which couple during high-temperature devolatilization of the polymerizer effluent. The latent functional monomer pair investigated is glycidyl methacrylate and acrylic acid. The key to producing a branched polystyrene that is thermally stable is to add one of the latent functional monomers in large excess, making the other monomer the limiting reagent. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 683–687, 1997

INTRODUCTION

Due to the complexity of free-radical styrene polymerization (e.g., multiple termination pathways),[1] it is extremely challenging to introduce branching into polystyrene during the polymerization without also making insoluble gels. Recently, we described a method to chain-extend and -branch polystyrene made by bulk free-radical polymerization.[2] Latent functional groups (benzocyclobutene [BCB]) were placed primarily on the ends of the polymer chains by initiating the polymerization using benzocyclobutenoylperoxide (BCBPO). Some of the BCB groups also end up pendant to the polystyrene chain due to side reactions of the initiator. The BCB groups are subsequently coupled when the polymer is heated to temperatures > 180°C (Scheme 1).

The BCB functional polystyrenes made via bulk styrene polymerization were freed of unreacted monomer by multiple precipitations. The monomer-free polymers rapidly increased in molecular weight when heated at 240°C as shown in Figure 1.

However, when we scaled this chemistry up to a bulk free-radical pilot plant where the polymer syrup from the polymerizer was continuously freed of the unreacted monomer by vacuum extrusion, very little chain extension/branching took place. The main difference between the pilot plant experiments and the early ampule studies was the method of freeing the polymer of the unreacted monomer; i.e., precipitation vs. continuous vacuum extrusion. Continuous vacuum extrusion does not remove all of the monomer, typically leaving about 200–600 ppm residual styrene. Since BCB is a diene in its ring-opened form, it will cycloadd to dienophiles such as styrene. Since styrene is a small molecule, it can readily diffuse through the molten polystyrene and intercept the ring-opened BCB moieties before they can couple with themselves. These findings led us to investigate other chemistries for post-polymerizer coupling of polystyrene that would not be affected by the level of residual styrene.
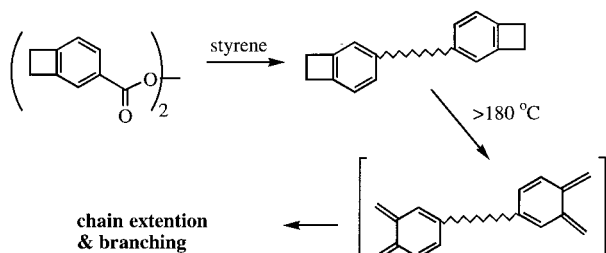
EXPERIMENTAL

Materials

Acrylic acid (AA) and glycidyl methacrylate (GMA) were purchased from Aldrich. Styrene (3

Scheme 1   Use of a BCB functional initiator to introduce branching into polystyrene.

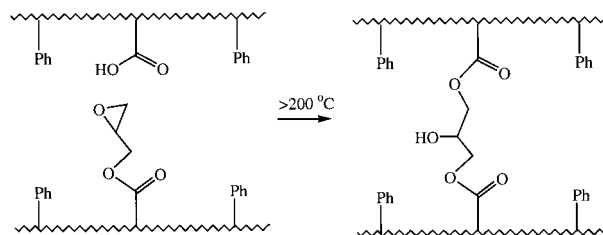**Scheme 2**   Copolymerization of AA and GMA with styrene to achieve post-polymerizer branching.

ppm *t*-butylcatechol) and ethylbenzene (EB) were obtained from Dow. 1,1-Bis(*t*-butylperoxy)cyclohexane (BBPC) was obtained from Akzo-Nobel. All materials were used as received.

Ampule Polymerizations

Ampule polymerizations were carried out in glass ampules (9 mm o.d. × 5 mm i.d. × 30 cm). Solutions containing styrene, EB, AA, GMA, and BBPC were placed in ampules, frozen in dry ice, and sealed under vacuum (< 1 mmHg) using the freeze–thaw technique to exclude air. After the desired thermal treatment, the partial polymer syrup was removed from the tubes. A portion of the syrup was used to gravimetrically determine monomer conversion by devolatilization in a vacuum oven. Once the concentration of polymer was known, a portion of the syrup was dissolved to 0.25% w/w polystyrene in tetrahydrofuran for molecular weight analysis by gel permeation chromatography (GPC). The remainder of the syrup was utilized for vacuum thermolysis studies.

Lab Reactor Polymerizations

Larger-scale polymerizations were carried out using an electrically heated kettle having a volume of 2 L. The agitator was a hollow auger as previously described.[3] The reactor was charged with 1200 g of styrene containing EB, 500 ppm BBPC, GMA, and AA and then pressurized to 20 psi with nitrogen. The reactor contents were heated to 100°C over 50 min and then to 160°C at a rate of 12°C/h. Samples of the reactor contents were collected periodically and the % w/w and molecular weight of polystyrene in the polymerization mixture determined.

Vacuum Thermolyses

About 0.5 g of prepolymer syrup was placed in a small aluminum weigh pan which was then placed in a vacuum oven heated at 230°C. After the desired time, the polymers were removed from the oven and analyzed by GPC and GPC–low-angle laser light scattering (GPC–LALLS).
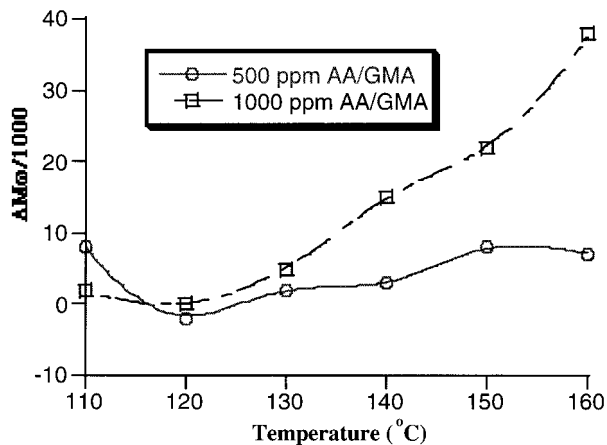
GPC and GPC–LALLS

GPC and GPC–LALLS measurements were performed as previously described.[2]

RESULTS AND DISCUSSION

Acrylic acid (AA) and glycidyl methacrylate (GMA) are readily available commercial monomers and it is well known that carboxylic acids add rapidly to epoxides at high temperatures. Thus, we chose to investigate the AA/GMA combination to achieve post-polymerizer branching in polystyrene (Scheme 2).
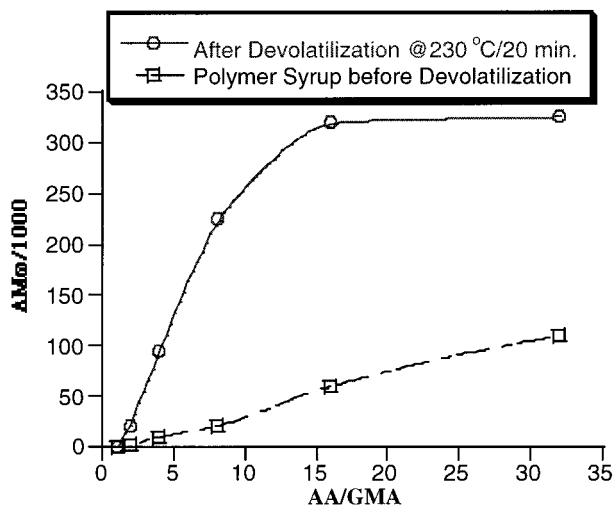
To determine if any reaction took place during the polymerization, styrene containing 20% w/w EB and 500 ppm of BBPC was polymerized in

Figure 1 M_w before and after heating (2 h at 240°C) BCBPO-initiated polystyrene vs. the amount of BCBPO in the monomer feed.[2]
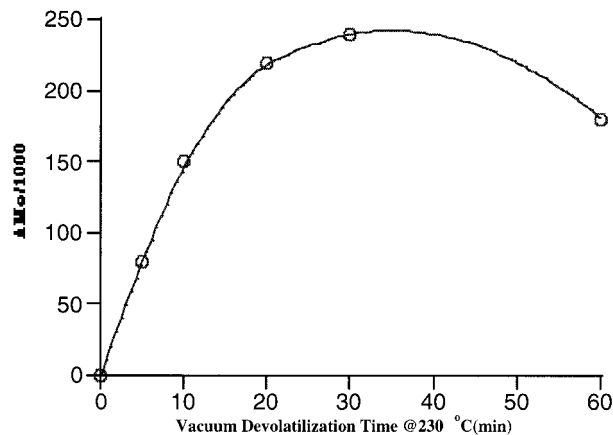
Figure 2 Change in M_w at various temperatures during the polymerization of styrene with 500 and 1000 ppm loadings of a 1 : 1 molar mixture of AA and GMA.

Figure 4 Change in M_w during the devolatilization of polystyrene (made by adding 1600 ppm AA and 200 ppm GMA to the polymerization feed) at 230°C.

glass ampules with a 1 : 1 molar mixture of AA and GMA at the 500 and 1000 ppm levels. The sealed ampules were heated from 100 to 160°C at 10°C/h. An ampule was removed from the oil bath each hour and the molecular weight measured using GPC. The temperature range at which a significant change in M_w relative to the polystyrene control began to appear was around 130°C for the polymerization containing 1000 ppm of the 1 : 1 AA : GMA mixture (Fig. 2). The M_w of the polystyrene produced from the 500 ppm loading remained relatively constant.

Upon heating the polymers made from these

experiments to 230°C in a vacuum oven for 20 min, the polymers made using the 1000 ppm AA/GMA solution became partially insoluble. The polystyrene samples made using only 500 ppm of the AA/GMA solution remained soluble, allowing molecular weight measurement by GPC.

A potential problem with using a 1 : 1 molar mixture of comonomers is that it is highly unlikely that all the functional groups in the polymer matrix are able to diffuse to each other for bimolecular reaction. To achieve a polymer which is thermally stable during fabrication, one of the latent functional groups must be completely reacted. To accomplish this, one latent functional monomer must be used in excess and the other as the limiting reagent. We decided to make GMA the lim-
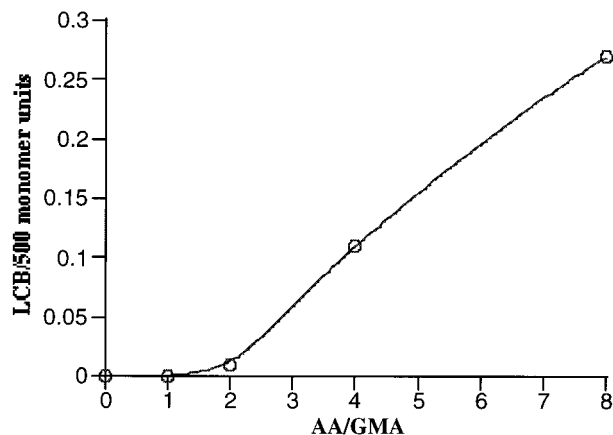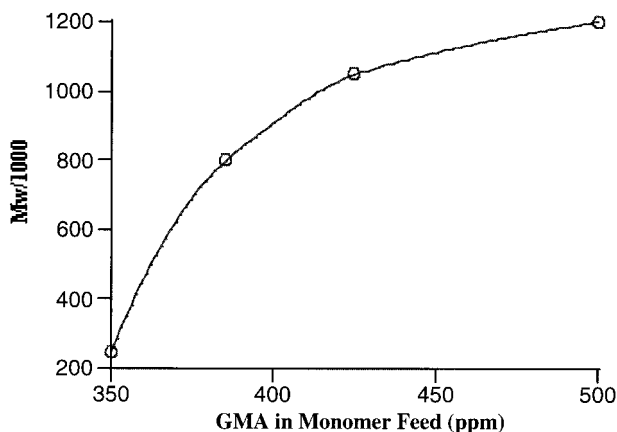

Figure 3 Change in molecular weight for polystyrene prepared with various molar ratios of AA/GMA. The GMA level is constant at 200 ppm in all cases.

Figure 5 LCB/500 monomer units for polystyrene prepared with various molar ratios of AA/GMA. The GMA level is constant at 200 ppm in all cases.

Figure 6 Effect of GMA loading on M_w at 40% w/w EB level (from Table I).

iting reagent because it is the more costly of the two monomers and because the reactivity of the epoxide group makes GMA more susceptible to unwanted side reactions (e.g., reaction with mold-release agents such as stearic acid).

We then focused on determining the appropriate GMA level and how much AA was necessary to react most of the epoxide functionalities and still obtain a soluble polymer. Figure 3 shows that a fairly significant increase in M_w had occurred during polymerization with 1000 ppm of 1 : 1 AA/GMA. The 500 ppm 1 : 1 AA/GMA polymerization showed less of an increase, so we decided to begin with the GMA level present in that mixture (330 ppm). Another set of isothermal styrene polymerizations were performed in which the GMA level was held constant at 330 ppm and the AA increased. Beginning at a 4 : 1 molar ratio of AA/GMA (670 ppm AA and 330 ppm GMA), the polymers became insoluble after vacuum devolatilization for 20 min at 230°C. The level of GMA was then decreased to 200 ppm and a similar set of polymerizations run. This time, even at high molar ratios of AA/GMA, all the devolatilized polymers were soluble.

An M_w increase of about 300,000 occurred at high AA/GMA ratios (Fig. 3). It appears that the M_w increase reaches a plateau at around a 16 : 1 molar ratio of AA/GMA (1600 ppm AA and 200 ppm GMA).

To determine the optimum time needed to reach the maximum M_w increase during vacuum devolatilization at 230°C, the polymer syrup from the 16 : 1 AA/GMA polymerization was devolatilized for different time intervals. The results are

shown in Figure 4. Twenty to thirty minutes at 230°C appeared to be sufficient for obtaining the maximum molecular weight increase. After 30 min, thermal degradation of the polymer begins to occur which decreases the polymer M_w.

The polystyrene samples were analyzed by GPC–LALLS analysis and the amount of long-chain branching (LCB) calculated using the method described by Dickie and Koopmans.[4] The calculation gives the level of LCB/500 monomer units. As expected, LCB increased as the AA/GMA molar ratio (Fig. 5) was increased. In fact, the 16 : 1 AA/GMA polymer sample contained extremely high molecular weight fractions which exceeded the linearity of GPC columns (10 million). Based on the LCB value for the 8 : 1 AA/GMA, approximately one out of every two polystyrene chains would have a branch point.

Lab Reactor Experiments

Next, a set of experiments were run varying the level of EB and GMA but keeping the polymerization conditions and AA : GMA mol ratio constant at 16 : 1. The GPC-LALLS data (Table I) show that final M_w increases with GMA concentration (Fig. 6) and that the degree of LCB is linear with GMA concentration at a constant EB level (Fig. 7).

CONCLUSIONS

Copolymerization of small amounts of latent functional monomers into polystyrene provides a way
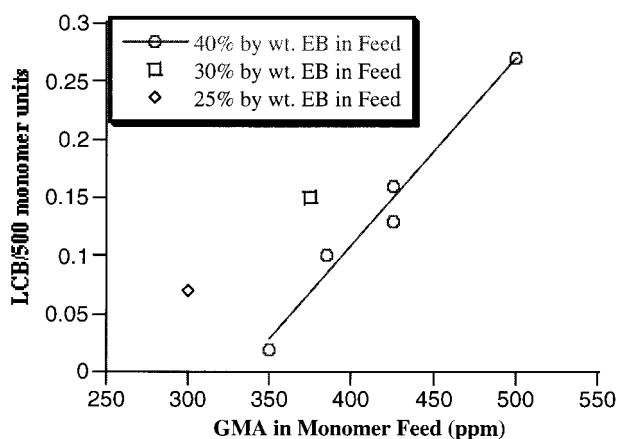
Figure 7 LCB/500 monomer units vs. GMA loading (from Table I).

Table I Summary of GPC and GPC–LALLS Analyses—All Polymerizations Performed Using Identical Temperature Profile and Initiator (500 ppm BBPC)

Sample No.	% EB (w/w)	GMA (ppm)	Predevolatilization GPC (M_w/1000)	Polymer GPC (M_w/1000)	Polymer LALLS (M_w/1000)	LALLS (M_w/M_n)	MFR (Cond G)	LCB/500
1	40	350	114	205	246	3.6	24	0.02
2	40	500	156	477	1220	8.1	2.1	0.27
3	40	425	136	463	1020	8.3	5.1	0.13
4	40	425	169	472	1040	8.2	5	0.15
5	30	375	230	551	1130	6.8	1.2	0.15
6	25	300	227	504	849	5.8	2	0.07
7	40	390	170	451	811	6.5	2.4	0.10

to make randomly branched polystyrene using bulk free-radical polymerization. The branching reaction takes place after the polymerization during high-temperature devolatilization. To produce a polystyrene having a stable branch density, one of the latent functional monomers must be used in excess over the other so that the monomer acting as the limiting reagent becomes almost completely reacted during devolatilization.

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