

# Synthesis and Characterization of Polystyrene Initiated Using Polymeric Peroxide

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**ABSTRACT:** Polymer peroxides were synthesized by copolymerizing *tert*-butyl-3-isopropenylcumylperoxide (D-120) with styrene (St). Exothermic peak at 192.7°C in DSC thermogram indicated that peroxy bonds in D-120 remained intact during the copolymerizing process. The polymeric peroxide was used to initiate polymerization of St. GPC results showed that polystyrene (PS) initiated by the polymeric peroxides was composed of both linear and branched

molecules. In addition, the rheology test showed that PS samples initiated by polymeric peroxide contained branched structure and had lower shear viscosities. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 197–202, 2006

**Key words:** polystyrene; polymeric peroxide; initiator; rheology

## INTRODUCTION

Polystyrene (PS) is a commodity thermoplastic with global sales larger than 10 billion pounds per year. Its many uses include electrical and thermal insulation, packaging, and clear films. The mechanical properties of PS are closely related to its molecular weight. When the weight average molecular weight ( $M_w$ ) is less than 180,000, it is generally too brittle to be useful. The nature of free radical polymerization is such that high polymerization rate and high molecular weight often cannot be obtained simultaneously. Polymerization of styrene (St) can be initiated by heat or peroxides. Usually, monofunctional peroxides such as benzoyl peroxide (BPO) and azobisisobutyronitrile are used to reduce polymerization time or temperature. With these conventional initiators, however, it is not possible to increase the polymerization rate without sacrificing polymer molecular weight.<sup>1</sup> In recent years, difunctional peroxide initiators<sup>2–6</sup> have been proposed for use in continuous bulk polymerization and copolymerization of St. Theoretically, they can initiate polymer growth from two opposite sites in the same fragment, ultimately leading to “double ended PS.” If double-ended PS chains are formed, PS of higher molecular weight can be produced at a higher rate.

It is known that branched polymers, due to their compact molecular structures and low viscosities, are easy to process. Efforts aimed at branching during bulk polymerization include the addition of a small amount of divinyl monomer,<sup>7</sup> vinyl functional initiator,<sup>8</sup> multifunctional initiator,<sup>9</sup> or vinyl functional chain transfer agent<sup>10</sup> into the polymerization mixture. In 1997, Priddy and coworkers<sup>11,12</sup> reported a different approach to make branched PS. In their method, PS with pendant carboxylic and epoxy groups on its backbone was first synthesized and then, through condensation reaction at elevated temperature, branched PS was produced.

*tert*-Butyl-3-isopropenylcumylperoxide (brand name D-120) is a peroxide with a vinyl group. By copolymerizing D-120 with vinyl monomers, Li et al.,<sup>13</sup> Guo et al.,<sup>14</sup> and Shi et al.<sup>15</sup> synthesized polymeric peroxides that have several pendant peroxy bonds in one molecule. The polymeric peroxides can be used to initiate polymerization of other monomers to form graft copolymers at a higher temperature.

In this article, polymeric peroxides synthesized by copolymerizing D-120 with St were used to initiate polymerization of St. The molecular structure and the rheological properties of the products were investigated.

## EXPERIMENTAL

### Materials

St was distilled under reduced pressure before using. D-120 was provided by Kayaku AKZO Co., Japan. It was further purified using methanol to precipitate

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**TABLE I**  
Feed Composition of the Copolymers of St and D-120

|                           | Sample |      |
|---------------------------|--------|------|
|                           | PSD1   | PSD2 |
| D-120 in feed (by weight) | 0.1    | 0.8  |
| St in feed (by weight)    | 0.9    | 0.2  |
| Reaction time (min)       | 30     | 180  |

oligomer and other impurities. The residual methanol was removed by distillation under reduced pressure at 28°C. Benzoyl peroxide (BPO, Beijing Chemical Reagent Factory, People's Republic of China) was recrystallized from a solvent mixture of chloroform and methanol by volume proportion of 40:100 and then dried in a vacuum desiccator at room temperature.

### Copolymerization of St and D-120

St and D-120 of a given proportion (Table I) and BPO (0.3% by molar) were added to an ampoule. After removing oxygen, the ampoule was sealed and immersed in a thermostat at 80°C. Copolymerization was allowed to proceed within the conversion of 10%. The obtained copolymers were precipitated in excessive methanol, filtered, and then purified by dissolving in tetrahydrofuran (THF) and reprecipitating in methanol. At last, the purified products were dried at room temperature under vacuum till the weight was constant.

### Polymerization of St

For polymerization initiated by polymeric peroxide, the initiator was dissolved in St and transferred to ampoules. After flushed with nitrogen for 10 min, the ampoules were sealed and immersed in a thermostat at 115°C for 30, 60, 90, 120, and 150 min, respectively. The products were precipitated, purified, and dried for three times using the same procedure for purifying St and D-120 copolymer. To be used as references, samples of PS initiated thermally and initiated by D-120 were also prepared at 115°C for the same reaction time. Details of some samples reacted for 60 min were tabulated in Table II as examples.

### Characterization

The composition of copolymers of St and D-120 was determined based on <sup>1</sup>H NMR spectra scanned on a Bruker MSL-300 NMR spectrometer with tetramethylsilane as internal standard and CDCl<sub>3</sub> as solvent. The molecular weight and molecular weight distribution of the polymeric peroxides were measured on GPC 1100 (Hewlett-Packard Co., Houston, TX) using THF as eluent at a flow rate of 1.0 mL/min. DSC measure-

**TABLE II**  
Feed Compositions of Polymerization Initiated by Different Methods

|                          | Sample  |         |         |      |
|--------------------------|---------|---------|---------|------|
|                          | BPS1    | BPS2    | DPS     | LPS  |
| Initiator                | PSD1    | PSD2    | D-120   | None |
| Initiator:St (in weight) | 1:8.205 | 1:110.3 | 1:39.8  | —    |
| D-120 unit:St (in molar) | 0.3:100 | 0.3:100 | 0.3:100 | —    |
| Reaction time (min)      | 60      | 60      | 60      | 60   |
| Conversion (%)           | 45.3    | 26.2    | 23.2    | 10.9 |

ments were performed on a Natsch DSC-204 instrument at a heating rate of 10°C/min to detect decomposing temperature of peroxy bonds in polymeric peroxides. A multi-detector GPC (T60A, Viscotek Co., Waldbronn, Germany) equipped with a four-capillary bridge differential viscometer (DV), a right angle laser light scattering (RALLS), and a refractive index detector (RI) was used to analyze the molecular structure of PS products using THF as eluent at a flow rate of 1.0 mL/min. Dynamic frequency sweep test was performed on ARES (Rheometric Scientific) with parallel plates at 140, 160, 180, 200, and 210°C. The span between two plates was 1.7 mm and the diameter of the plates was 25 mm. The strain was set to 1%.

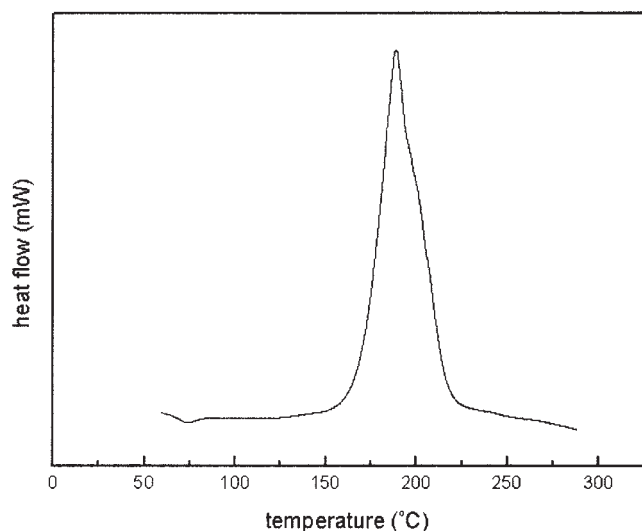
## RESULTS AND DISCUSSION

### Characterization of copolymers of St with D-120

The molecular weight, composition, and sequence structure of the copolymers were listed in Table III. The copolymer composition was obtained from NMR analysis and the mean sequence length was calculated from the reactivity ratios of St and D-120, which were described in our previous article.<sup>14</sup> The more D-120 in the feed, the more D-120 segments in the copolymer, and shorter the mean sequence length of St becomes. Some related discussion was presented in our previous article.<sup>14</sup> Figure 1 is the DSC thermogram of PSD1 with an exothermal peak at 192.7°C resulting from the

**TABLE III**  
Properties of the Copolymers of St and D-120

|  | Sample |       |
|--|--------|-------|
|  | PSD1   | PSD2  |
| Conversion (%)                         | 7.2    | 2.5   |
| $M_n$ ( $10^3$ g/mol)                  | 29.72  | 4.84  |
| $M_w$ ( $10^3$ g/mol)                  | 47.10  | 6.24  |
| Copolymer composition (molar fraction) |        |       |
| D-120                                  | 0.055  | 0.487 |
| St                                     | 0.945  | 0.513 |
| Mean sequence length                   |        |       |
| D-120                                  | 1.02   | 1.70  |
| St                                     | 16.95  | 1.44  |



**Figure 1** DSC thermogram of PSD1 at heating rate of  $10^{\circ}\text{C}/\text{min}$ .

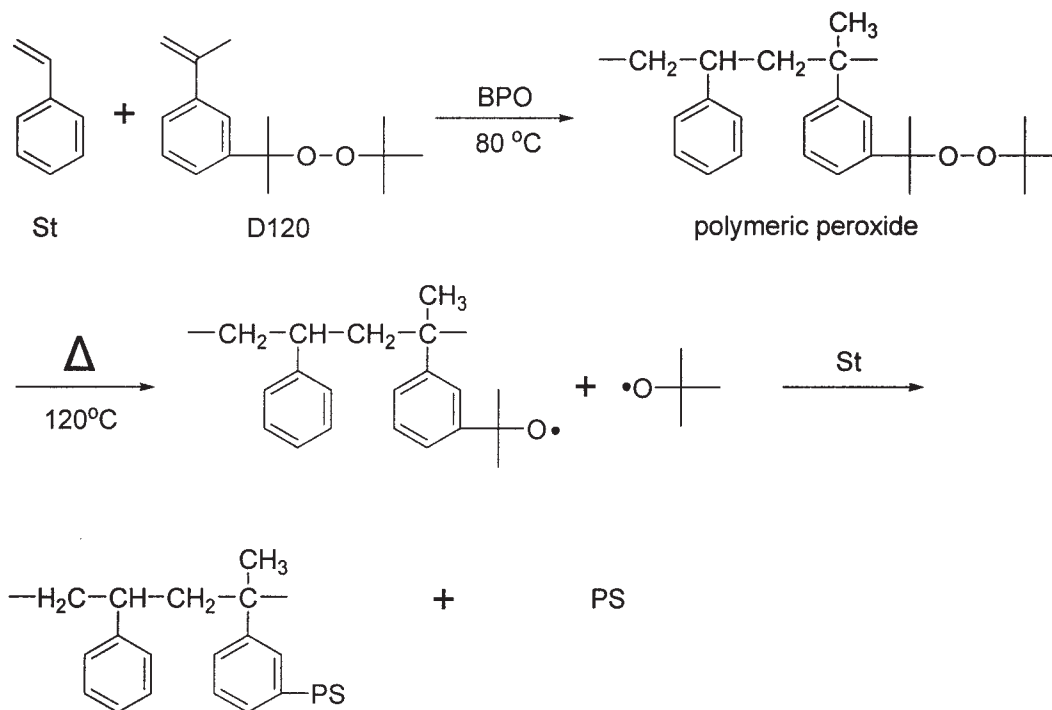
cleavage of peroxy bonds. It implies that the peroxy bonds remain intact during the copolymerization at  $80.0^{\circ}\text{C}$  and the obtained copolymer is a polymeric peroxide. The peroxy bonds surviving from the copolymerization can be used to initiate polymerization at a higher temperature. The scheme of copolymerization of St with D-120 is shown in Figure 2.

### Initiation capability of polymeric peroxides

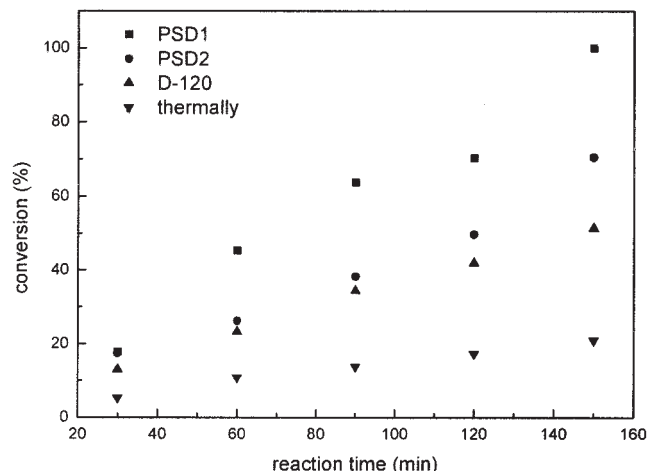
Figures 3 and 4 are plots of reaction time versus St conversion and versus weight average molecular

weight ( $M_w$ ), respectively, for a set of different initiators. The rates of polymerization initiated by polymeric peroxides are higher than that initiated thermally (see Fig. 3), which indicates that the polymeric peroxide does have the ability to initiate polymerization. The polymerization rate of the system initiated by PSD1 is markedly higher than that of the system initiated by PSD2. It is likely caused by the very high peroxy bond concentration in PSD2, which may lead to the loss of radicals resulting from the couple termination of two free radicals on the same chain. Moreover, for the same reaction time, the St conversion of the polymerization initiated by polymeric peroxide is higher than that initiated by D-120. This shows that the polymeric peroxide is a more effective initiator in comparison with D-120. Below  $120^{\circ}\text{C}$ , free radicals of St are mostly terminated through coupling.<sup>16</sup> The free radicals generated from polymeric peroxides, due to their large size, have lower mobility than those from normal initiators, which in turn reduces the possibility of coupling termination and increases the polymerization rate.

It can be seen from Figure 4 that the  $M_w$  of PS from polymerization initiated by polymeric peroxides increases sharply with reaction time, while the  $M_w$  of those from thermally initiated polymerization remains more or less unchanged. This can be attributed to the step-by-step cleavage of the pendant peroxy bonds in polymeric peroxides. The  $M_w$  of PS initiated by D-120 also increases along with the reaction time, which may result from D-120's dual function, i.e., as an initiator and as a monomer to copolymerize with St. Gel for-



**Figure 2** Scheme of the synthesis route using polymeric peroxides.

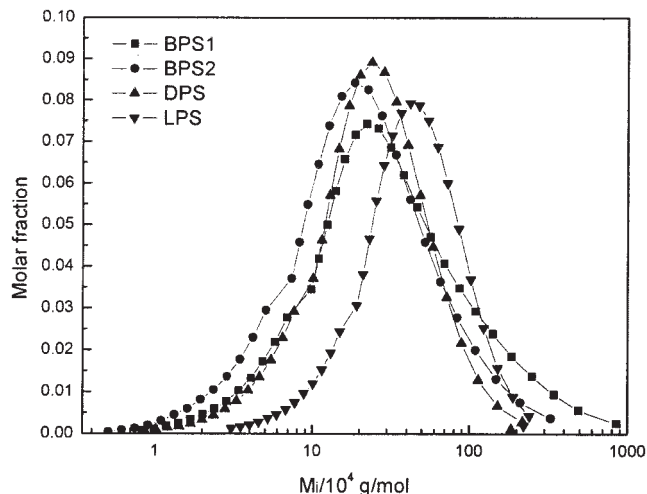


**Figure 3** Conversion versus reaction time plots for the bulk polymerization initiated by PSD1, PSD2, PSD3, and thermally at 115°C.

mation was observed when the reaction time passed 150 min in the system initiated by PSD1 because of the couple termination between the branched chains of different molecules.

### Multi-detectors GPC analysis

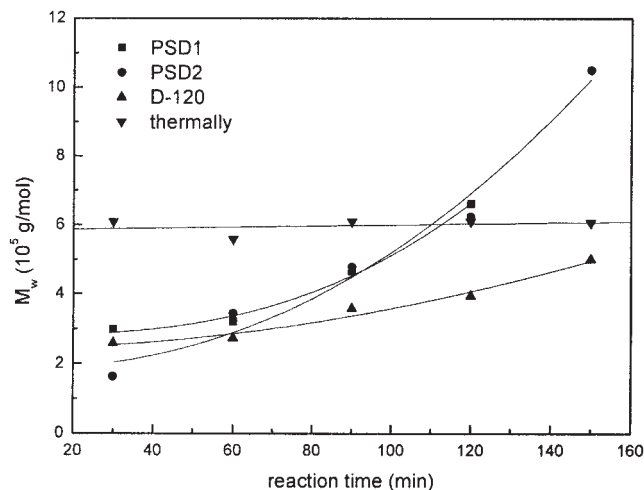
Figure 5 is the molecular weight distribution obtained from the measurement on a multi-detector GPC. It is calculated based on the  $M_i$  (absolute molecular weight)– $V_e$  (eluent volume) diagram from RALLS, and concentration– $V_e$  diagram from RI. It can be seen that the  $M_i$  peak of thermally initiated PS shifts to higher molecular weight when compared with those initiated by initiators. It should be noted that the  $M_i$  distribution of BPS1 is wider and has a significant long



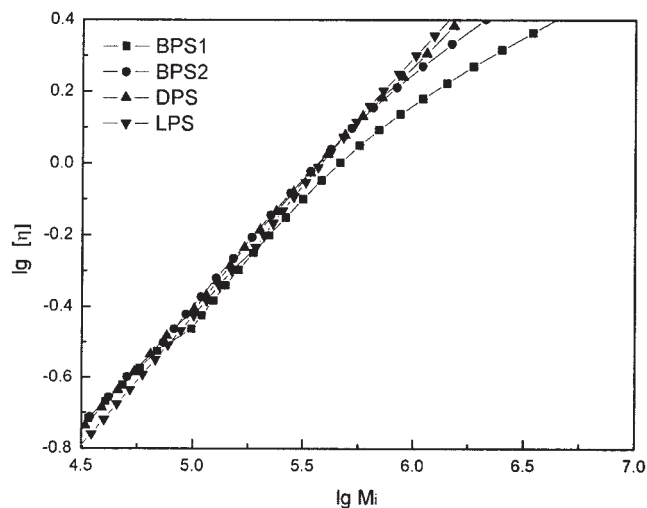
**Figure 5** Molecular weight distribution curves of BPS1, BPS2, DPS, and LPS4.

tail at the high molecular weight region. It indicates the formation of high molecular weight chains via grafting St onto the backbone.

Figure 6 presents the relationship between intrinsic viscosity  $[\eta]$  and  $M_i$ , which are calculated from  $[\eta]$ – $V_e$  diagram obtained from DV, and  $M_i$ – $V_e$  diagram. The slopes of these curves correspond to the  $\alpha$  value of their Mark-Houwink equations. As shown in Figure 6, the slope for the thermally initiated PS is equal to 0.725, which is close to 0.70, the reported value for linear PS.<sup>17</sup> At lower molecular weight region, the intrinsic viscosities of the all samples are equal and their curves overlap, which tells that all samples have linear PS composition. From molecular weight of  $10^{5.5}$  for BPS1 and  $10^6$  for BPS2, curves begin to deviate from the straight line and their slopes decrease. The



**Figure 4** Weight average molecular weight versus reaction time plots for the bulk polymerization of St initiated by PSD1, PSD2, PSD3, and thermally at 115°C.



**Figure 6** Intrinsic viscosity curves of BPS1, BPS2, DPS, and LPS.

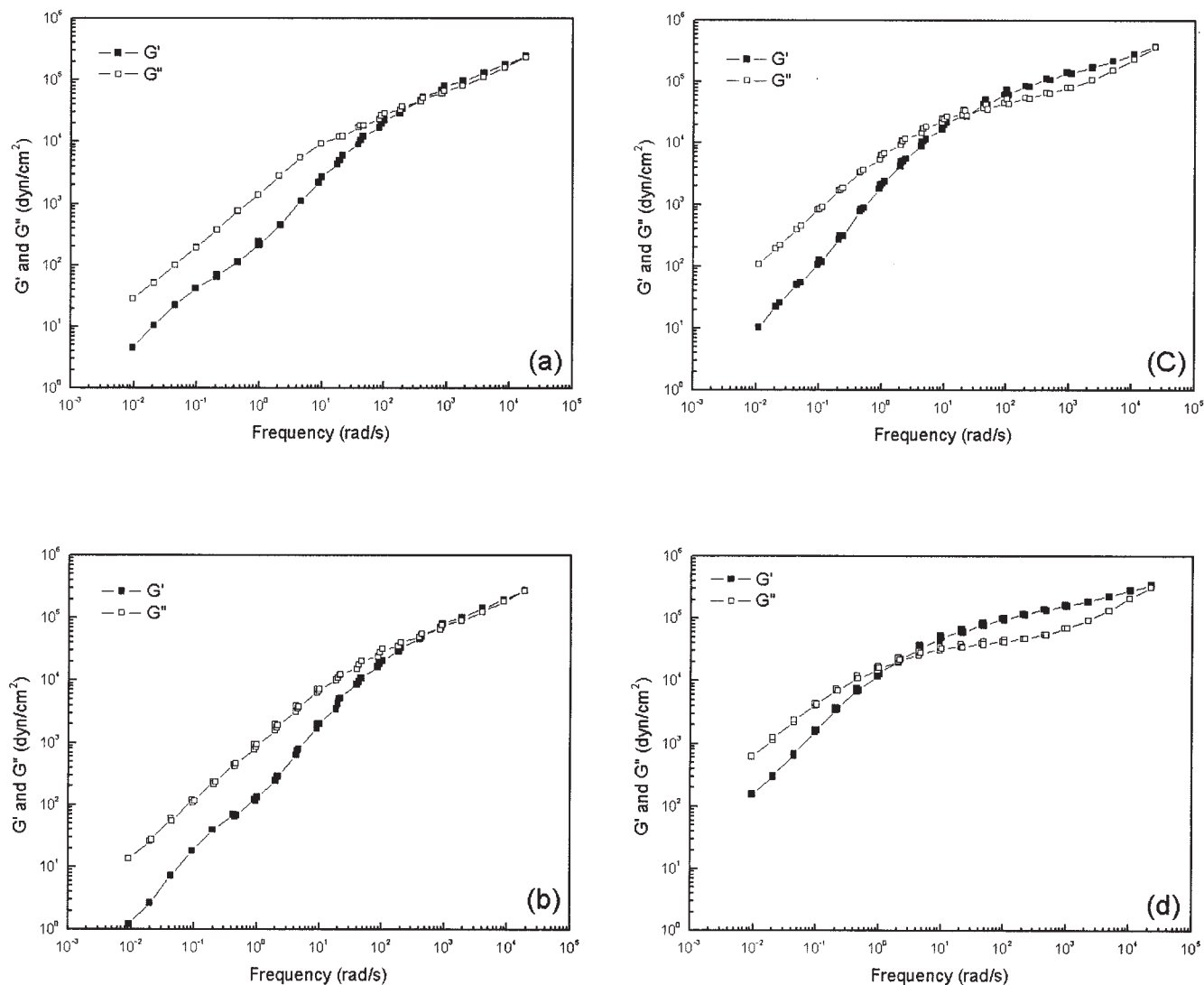


Figure 7 Dynamic frequency sweep diagram of (a) BPS1, (b) BPS2, (c) DPS, and (d) LPS at 180°C.

decrease in intrinsic viscosity is a characteristic of branched polymers when compared with linear polymer of the same molecular weight. Thus, it can be concluded that branched PS is the main component of BPS1 when molecular weight is higher than  $10^{5.5}$ . Together with the integration from Figure 5, the weight ratio of branched PS to linear PS can be calculated, which is about 0.41/0.59 for BPS1. The linear part in BPS1 is the product from the polymerization of St initiated thermally and the polymerization initiated by the small-molecular free radicals produced during decomposition of the polymeric peroxides (see Fig. 1), while the branched PS is from the polymerization initiated by those macromolecular free radicals.

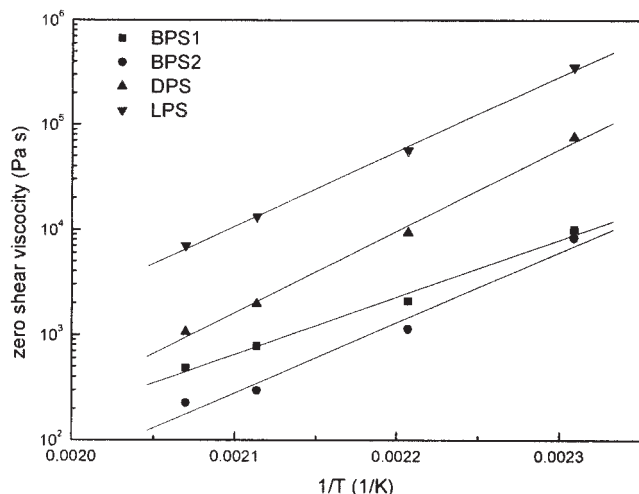
### Rheological properties of PS samples

Figure 7 is the dynamic frequency sweep test diagram at 180°C, which is the time-temperature superposition

from 140 to 210°C. The curve of LPS shows the typical rheological property of linear PS.  $G'$  and  $G''$  increase rapidly with the frequency at the low frequency region, and then increase slowly at the high frequency region. At the low frequency region, there is enough time for the macromolecular chains to disentangle and exhibit viscous behavior. On the contrary, the moduli increase slowly when there is not enough time to relax stress at the high frequency range.<sup>18</sup>

BPS1 and BPS2 behave differently from LPS. In BPS1, the modulus values are much lower and two shoulder-plateaus appear in the diagram. It is because that the branched structure restrains the entanglement between polymer chains. The "shoulder" of  $G'$  at  $10^{-1}$ – $10^0$  rad/s should be attributed to the disentanglement of the linear part of PS initiated thermally and by the small fragments formed during the decomposition of the polymeric peroxide, while the "shoulder" at  $10^2$ – $10^4$  rad/s is due to the retractions of branched





**Figure 8** Plots of zero shear viscosity versus the reciprocal of temperature.

chains. The shape of the curve obtained in our experiment is similar to that reported by Namba et al.<sup>19</sup>

Figure 8 shows the zero shear viscosity at various temperatures. The zero shear viscosities of both BPS1 and BPS2 are lower than that of LPS at every temperature and the amount of decrease is far more than that caused by molecular weight difference. The low viscosities of the two samples can be ascribed to the compact size, smaller radii of gyration, and the less entanglement of the branched molecules. The flow activation energy can be obtained from the slope of the line of the zero shear viscosity versus the reciprocal of temperature. They are 16.37, 18.95, 19.26, and 19.54 KJ/mol for BPS1, BPS2, DPS, and LPS, respectively. BPS1 has the lowest value.

### CONCLUSIONS

By copolymerizing St with D-120, polymeric peroxides were obtained. The peroxy bonds in D-120 remain intact during the copolymerizing process. The polymeric peroxides can be used to initiate polymerization

of St. They have higher initiation efficiency in comparison with pure D-120. The product of polymerization of St initiated by the polymeric peroxide consists of both linear and branched molecules. The linear composition is engendered from both the polymerization of St initiated thermally and the polymerization initiated by the small free radicals produced during decomposition of the polymeric peroxides, while the branched PS are from the polymerization initiated by the macromolecular free radicals. PS samples initiated by polymeric peroxides have lower shear viscosities.

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