

# Preparation and Properties of Branched Polybutylenesuccinate

EUN KYOUNG KIM,<sup>1</sup> JONG SEOK BAE,<sup>1</sup> SEUNG SOON IM,<sup>1</sup> BYOUNG CHUL KIM,<sup>1</sup> YANG KYOO HAN<sup>2</sup>

<sup>1</sup> Division of Chemical Engineering, Hanyang University, 17 Haingdan-dong, Seongdong-ku, Seoul 133-791, Korea

<sup>2</sup> Department of Chemistry, Hanyang University, 17 Haingdan-dong, Seongdong-ku, Seoul 133-791, Korea

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**ABSTRACT:** To obtain long branched polybutylene succinate (PBS), modified PBSs were prepared by introducing a branching agent, trimethylol propane (TMP), to the polycondensation system of succinic acid and 1,4-butanediol. Molecular parameters such as absolute molecular weight and root-mean-square (RMS) radius of the modified PBSs were measured by gel permeation chromatography (GPC) with a multiangle laser light-scattering (MALLS) detector. The RMS radius of TMP05, PBS prepared by incorporating 0.5 wt % TMP during polycondensation, was the smallest of all PBSs tested at the same molecular weight. The notable shear thinning and much reduced loss tangent for TMP05 qualitatively supported the difference in their molecular structures predicted by GPC. The analytical results indicated that introducing 0.5 wt % TMP produced PBS with chain branches long enough to produce molecular entanglements. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1388–1394, 2001

**Key words:** branched structure; polybutylenesuccinate; GPC-MALLS; rheological properties

## INTRODUCTION

The biodegradable aliphatic polyesters attract much attention because they can replace the non-degradable polymers that cause ecological problems. The aliphatic polyesters decompose rather easily, and produce less harmful chemical fragments under natural circumstances. Despite the practical significance, however, the aliphatic polyesters have difficulties in fabrication because of low melt strength and melt viscosity.<sup>1</sup> To solve the problems associated with melt processing, lots of attempts have been made to increase the mo-

lecular weight of the polymer by incorporating a suitable chain-extending agent in the polymerization stage. As recognized, the rheological properties of a molten polymer are influenced not only by molecular weight and molecular weight distribution but branched structures of the polymer. In particular, rheology related with elongation is greatly affected by long-chain branching.<sup>2</sup>

In the past decade numerous researches have been carried out to improve the rheological properties of polyesters. Some have tried to obtain high molecular weight, and some tried to introduce long branches. Branching proved effective in enhancing processability based on elongational flows.<sup>3</sup> To name a few of the processes includes fiber spinning, film blowing, and casting, vacuum forming, and foaming. Branching increases the melt strength and confers ten-

Correspondence to: S. S. Im.

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sion-hardening property on the polymer, which is of help to uniform extension in the polymer processing in which a high degree of orientation is required.

The light-scattering experiment on polymer solutions is one of the basic methods to characterize molecular weight and molecular radius of the polymer. However, some technical difficulties restricted its application to on-line measurements. Recently, the multiangle laser light-scattering detector, which is able to measure light-scattering intensities of various scattering angles at the same time, has been developed. This detector connected with size exclusion chromatography makes it possible to determine absolute molecular weight.<sup>4-7</sup> The existence and extent of long chain branching is mostly estimated from the dimensions of the polymer in solution. A long chain-branched polymer exhibits smaller molecular dimensions than the unbranched one with the same molar mass.<sup>8</sup>

A number of investigations have been made to trace the effect of chain branching on thermal, rheological, and morphological properties. However, few papers have been published so far on the synthesis and characterization of branched polyesters. In fact, it is very difficult to prepare high molecular weight polyesters with branched structures. Further, it is not easy to definitely describe the structure of the branched polyesters because of transesterification during chain branching reaction. The determination of the number of branched points per polymers, mean branch length, branch length distribution, and main chain length between branch points are very difficult jobs to polymer chemists.<sup>9</sup> In this study, the method for obtaining high molecular weight branched polybutylene succinate (PBS) was investigated by introducing trimethylolpropane as a chain-extending agent. The molecular parameters such as molecular weight and mean square radius of gyration were evaluated as well.

## EXPERIMENTAL

### Polymer Synthesis

The reagent grade succinic acid and 1,4-butanediol were used without further purification. As a branching agent and catalyst, trimethylolpropane (TMP) and titanium isopropoxide were used, respectively. Polymerization was accomplished

via two steps—esterification and polycondensation. To begin with, esterification was carried out for the initial composition: 1 mol succinic acid, 1.1 mol 1,4-butanediol, and  $10^{-5}$  mol titanium isopropoxide at atmospheric pressure under nitrogen bleeding in the presence of titanium isopropoxide as a catalyst. Water was distilled off while temperature was raised from 140 to 200°C for 100 min. Then, polycondensation was carried out by introducing 0.1, 0.3, and 0.5 wt % of TMP to the reaction mixture. After premixing at 140°C with nitrogen purging for 30 min, the mixture was heated to 240°C below 1 Torr to complete the condensation reaction.

### Measurement of Thermal Properties

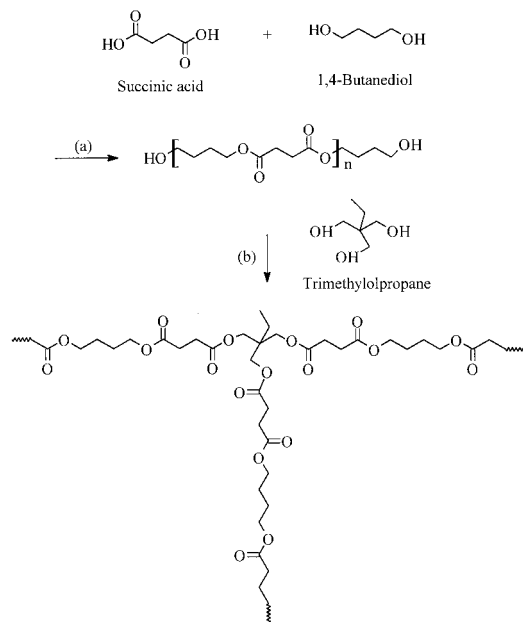
The thermal properties of PBS and modified PBS were measured by Perkin-Elmer DSC 7 in nitrogen atmosphere. DSC was calibrated with indium and zinc prior to measurement. A polymer sample of  $10 \pm 0.1$  mg was heated to 150°C and kept at the temperature for 5 min to remove thermal history. Heating and cooling rate was 10°C/min.

### Molecular Weight Measurement by GPC-MALLS

The molecular weight and the molecular weight distribution of the synthesized polymers were determined by Waters 410 GPC equipped with mixed Shodex K-800 column, using differential refractive index (RI) detector and multiangle laser light-scattering (MALLS) detector. Light scattering was measured at 632.8 nm on a DAWN-F laser photometer, and data were collected and handled by ASTRA software supplied by Wyatt Technology Cooperation. Pure toluene with a known Rayleigh ratio was used to calibrate the system. For a GPC-MALLS eluent, HPLC grade chloroform was used. The solutions were filtered through a 0.2- $\mu$ m Millipore filter. This chromatographic system was operated at 40°C at the flow rate 1.0 mL/min. Molecular weight and mean square radius of the polymer were determined by means of a Debye plot analysis. Refractive index (RI) detector was calibrated by aqueous NaCl solution employing  $dn/dc$ .

### Rheological Measurement

The rheological properties of the molten PBS and modified PBS samples were measured by Rheometric Scientifics rheometer in the parallel plate geometry. The radius of the plates was 25 mm,

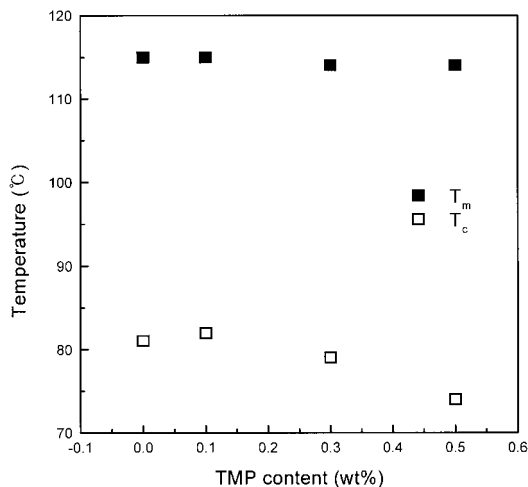


**Figure 1** Structures and synthesis of (a) PBS and (b) branched PBS.

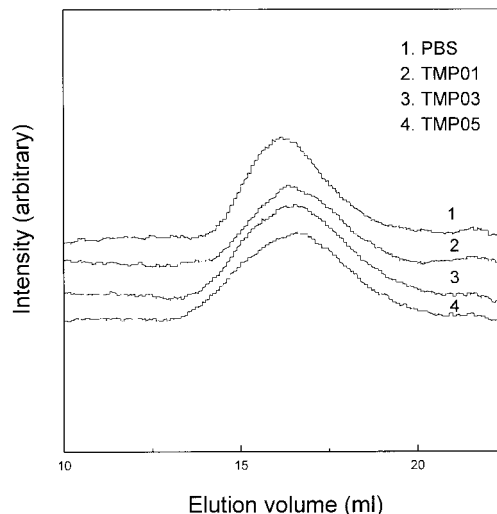
and the gap between plates was 1 mm. The strain amplitude was 0.05.

## RESULTS AND DISCUSSION

A scheme of the structure and reaction of PBS and branched PBS is shown in Figure 1. Figure 2 presents variation of melting temperature ( $T_m$ )



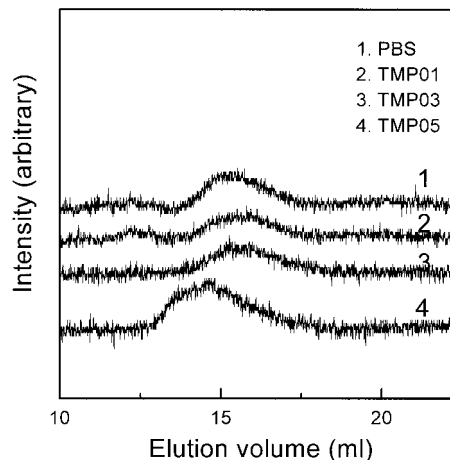
**Figure 2** Variation of melting temperature ( $T_m$ ) and crystallization temperature ( $T_c$ ) with TMP content for PBS and modified PBS samples.



**Figure 3** GPC chromatogram of PBS and modified PBS samples measured by an RI detector.

and crystallization temperature ( $T_c$ ) with the TMP content for PBS and modified PBS samples.  $T_m$  is slightly decreased as the content of modifier is increased. However,  $T_c$  was notably decreased with increasing the modifier content.  $T_c$  of the modified PBS prepared by introducing 0.5 wt % TMP is lower than PBS by about 7°C. The reduction in  $T_m$  and  $T_c$  results from the fact that chain branching reduces molecular regularity and retards crystallization.

Figures 3 and 4 show GPC chromatograms of PBS and modified PBS samples obtained by the RI detector and light-scattering (LS) 90° detector,



**Figure 4** GPC chromatogram of PBS and modified PBS samples measured by an LS 90° detector.

**Table I** Molecular Weight and Its Distribution of PBS and Modified PBS Samples

Code	Composition		$M_n^a$	$M_w^b$	PDI <sup>c</sup>
	PBS	TMP (wt %)			
PBS	100	—	41,000	73,000	1.8
TMP01	100	0.1	39,000	65,000	1.7
TMP03	100	0.3	33,000	80,000	2.4
TMP05	100	0.5	34,000	87,000	2.6

<sup>a</sup> Number-average molecular weight.

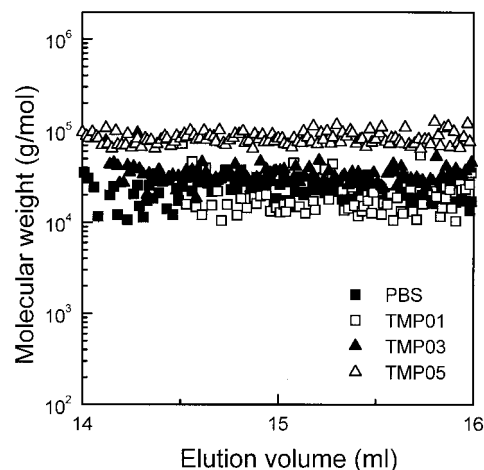
<sup>b</sup> Weight-average molecular weight.

<sup>c</sup> Polydispersity index.

respectively. The results are summarized in Table I. Both figures show a similar tendency except that RI measurements generally give greater elution volume than LS measurements. It is seen that with increasing the introduced TMP content the width of the peak is increased, and the intensity at lower elution volume is increased. This is particularly notable in the TMP05 sample. These results indicate that the molecular weight is notably increased when 0.5 wt % of TMP is introduced during polycondensation of PBS. As numerically given in Table I, the number-average molecular weight ( $M_n$ ) is decreased with TMP content while the weight-average molecular weight ( $M_w$ ) are increased. Hence, the polydispersity index (PDI) is increased with the TMP content.

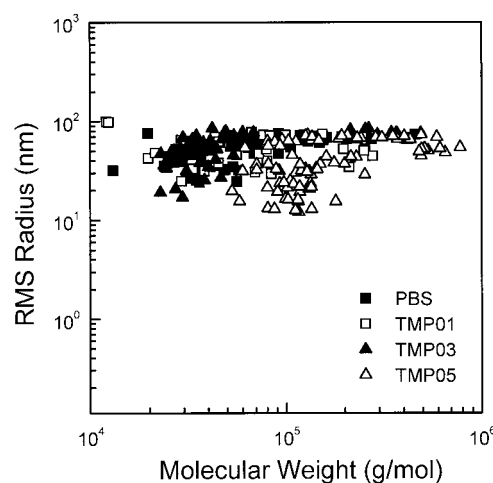
As recognized, in the GPC measurements individual polymer molecules explore the pore systems of the columns to the extent that is allowed by their size, and hence, relative molar mass. Consequently, the elution volume can be a measure of molar size (viz., molecular weight). However, the light scattering gives different molecular weights depending on branched structure even at the identical elution volume, as shown in Figure 5. This can be accounted for by chemical structure of polymer molecules.

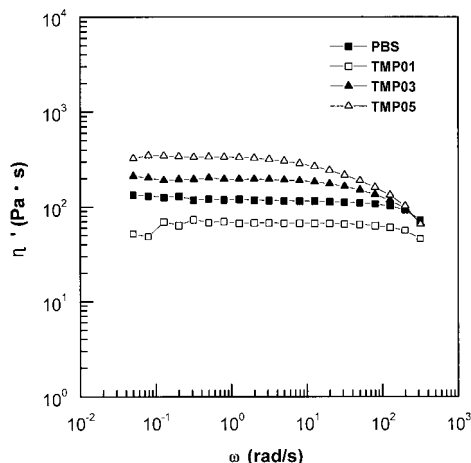
On the whole, branched polymers have a higher average segment density than unbranched ones of the same molecular weight, and hence, have a lower coil volume. In addition, chain branching enhances entanglement of polymer chains, provided that branches are sufficiently longer than the critical molecular weight for producing entanglement. Consequently, long chain branching reduces the hydrodynamic volume.


**Figure 5** Plot of molecular weight against elution volume for PBS and modified PBS samples.

Thus, the fact that TMP05 gives the highest molecular weight among the PBSs at the same elution volume proves that incorporating 0.5 wt % TMP is effective in introducing long branches to PBS. This can be further ascertained by Figure 6, which shows relationship between root-mean-square (RMS) radius and molecular weight for the PBS and modified PBS samples. The RMS radius of TMP05 is the smallest of all PBSs tested at the same molecular weight, verifying that PBS prepared by incorporating 0.5 wt % TMP have some long chain branches.

Figure 7 presents plot of dynamic viscosity of PBS and modified PBS samples at 130°C. In the


**Figure 6** Plot of root-mean-square (RMS) radius against molecular weight for PBS and modified PBS samples.

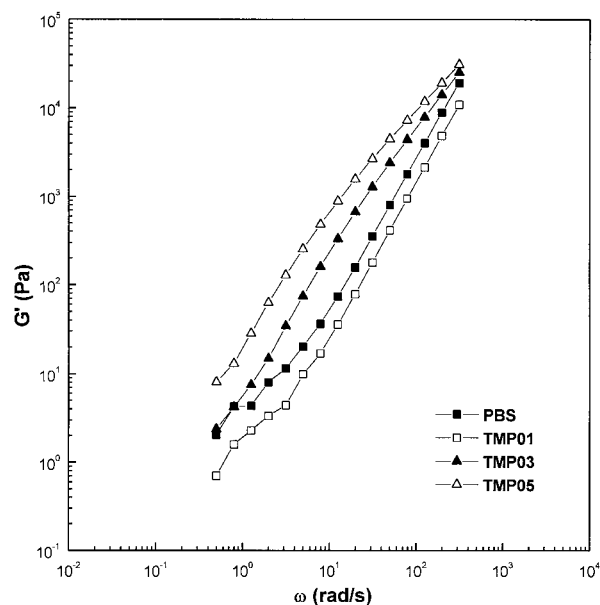


**Figure 7** Plot of dynamic viscosity ( $\eta'$ ) of PBS and modified PBS samples vs. frequency ( $\omega$ ) at 130°C.

viscosity curves, the magnitude of viscosity at very low frequencies is a measure of molecular weight of the polymers. This rheological prediction well coincides with the GPC data. In addition, shear thinning was most pronounced with TMP05. The extent of shear thinning and the onset shear rate for shear thinning is related with two factors; chain branching, and molecular weight distribution.

The branched polymer has a higher average segment density, and long chain branches are helpful to molecular entanglement than the linear polymer of the same molecular weight if they have the same chemical structure. These two factors are opposing each other in influencing rheological properties. At low shear rates polymers with long chain branches would have higher viscosity than linear polymers at the same chemical structure. However, the branched polymer is more prone to be disentangled under shear than the linear polymer due to the small hydrodynamic volume. Further, the former is more compressible than the latter because it possesses more free volume.<sup>10</sup> Thus, shear thinning becomes more noticeable with increasing long chain branch density. Consequently, the branched PBS exhibits higher degree of shear thinning than the linear PBS, as shown in Figure 7. The most notable shear thinning with TMP05 indicates that the modified PBS prepared by incorporating 0.5 wt % TMP has chain branches long enough to produce molecular entanglements.

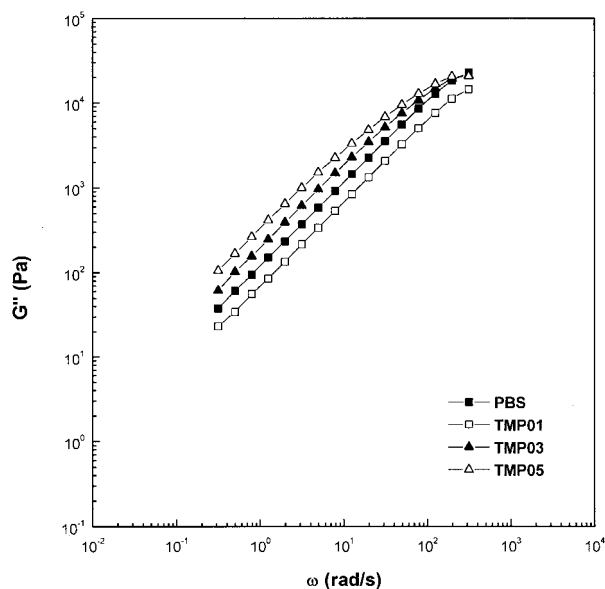
In addition, shear thinning is also affected by molecular weight distribution of polymers. On the



**Figure 8** Plot of storage modulus ( $G'$ ) of PBS and modified PBS samples vs. frequency ( $\omega$ ) at 130°C.

rheological principle, increasing molecular weight distribution increases the extent of shear thinning and the onset shear rate for shear thinning.<sup>11</sup> Hence, shear thinning in Figure 7 includes the effect of molecular weight distribution as well.

Figures 8 and 9 present plots of storage mod-



**Figure 9** Plot of loss modulus ( $G''$ ) of PBS and modified PBS samples vs. frequency ( $\omega$ ) at 130°C.

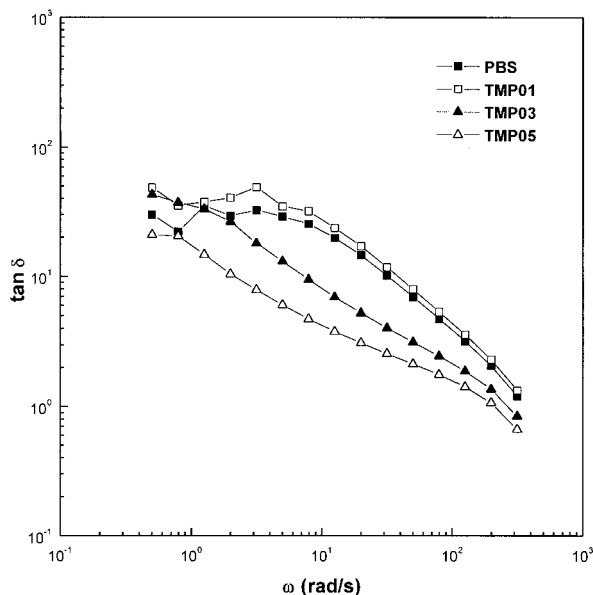


ulus ( $G'$ ) and loss modulus ( $G''$ ) of PBS and modified PBS samples against frequency at 130°C, respectively. TMP05 gives maximum in both modulus curves. Figure 8 reflects that PBS with long chain branches produce a strong contemporary network because of enhanced entangling of molecules. Higher  $G''$  in Figure 9 results from the increased contribution of chain ends of the branched PBS. These effects of chain branching lead to an increase of apparent molecular weight. Consequently, PBS with higher long chain density exhibits more notable solid character, as illustrated in Figure 10.

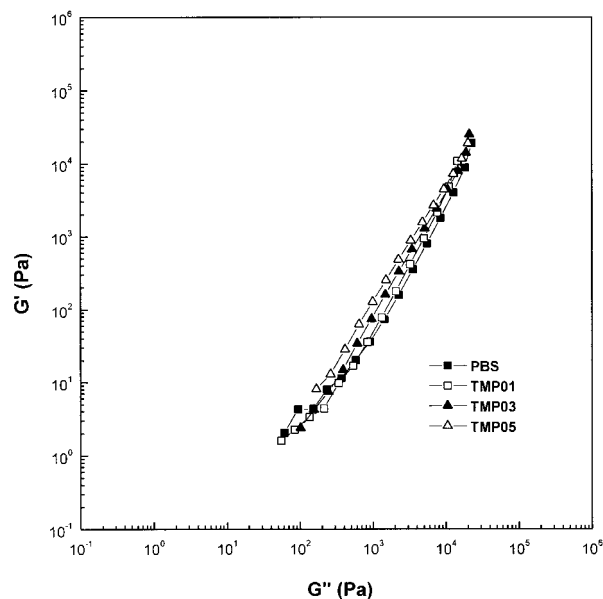
According to Han and John,<sup>12</sup>  $G'$  is related to  $G''$  by eq. (1):

$$\log G' = 2 \log G'' + \log(6/5G_N^0) \quad (1)$$

in which  $5G_N^0 = \rho RT/Me$ ,  $\rho$  is the density,  $R$  is the gas constant,  $T$  is the temperature, and  $Me$  is the entanglement molecular weight, respectively. This equation has been derived from molecular viscoelasticity theory for entangled flexible homopolymers rather than from experimental basis. On both empirical and theoretical bases, most isotropic homogeneous polymer melts and solutions give a slope of 2 on the logarithmic plot of  $G'$  against  $G''$ .<sup>13</sup> In general, heterogeneous polymeric systems such as mesophase and block copolymers



**Figure 10** Variation of loss factor ( $\tan \delta$ ) with frequency for PBS and modified PBS samples at 130°C.



**Figure 11** Plot of storage modulus ( $G'$ ) vs. loss modulus ( $G''$ ) for PBS and modified PBS samples at 130°C.

decrease the slope to below 2 on the logarithmic plot.<sup>14,15</sup> Figure 11 presents plot of  $G'$  against  $G''$  for PBS and modified PBS samples at 130°C. The slope ranges from 1.6 for TMP05 to 1.8 for pure PBS. This suggests that long chain branching makes the melt a little more heterogeneous, which agrees with loss tangent behavior in Figure 10.

## CONCLUSION

The physical properties of long branched PBS prepared by introducing a branching agent to the polycondensation system of succinic acid and 1,4-butanediol were investigated. PBS prepared by incorporating 0.5 wt % TMP during polycondensation gave the smallest RMS radius of all PBSs tested at the same molecular weight. Further, it showed a higher degree of shear thinning and much reduced loss tangent. In general, introducing 0.5 wt % TMP produced PBS with chain branches long enough to form molecular entanglements. This result will be of help in producing highly oriented films or low-density foamed products, whose processes require tension thinning behavior.

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