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EFFECTS OF BRANCHING ON MELT-PREPARED POLY(PHENYLENE SULFIDE)

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ABSTRACT

Poly(phenylene sulfide), made via the melt polymerization of *p*-diiodobenzene and sulfur, has been prepared with added branching species at levels up to 1.0 mol%. Effects of increasing branching on the thermal characteristics were seen to be quite large for even 0.25 mol% brancher. Both the T_m and the apparent rate of crystallization, as judged by the undercooling for melt crystallization, T_m minus the crystallization upon cooling from the melt, decreased rapidly with increasing brancher level. Melt rheology also confirmed the large increase in melt elasticity in this system with increasing branching level, even at the moderate melt viscosities of the polymers of this work. Melt elasticity for polymers with 0.5 mol% brancher or above was sufficiently high to preclude rheological testing.

INTRODUCTION

Poly(phenylene sulfide) (PPS) has found numerous applications owing to its excellent combination of chemical resistance and thermal properties. We recently reported a new melt phase polymerization process for the preparation of PPS involving the reaction of *p*-diiodobenzene and sulfur [1–3] (Fig. 1) and some of the characteristics of the resultant polymer. In the course of that work we reported that almost all samples of PPS were noted to increase in melt viscosity with time in the melt rheology test. Evidence was not presented at that time as to whether chain extension and/or branching reactions were the cause of the melt viscosity increase. As part of the information necessary to determine the cause of the melt viscosity increase and to assess the qualitative degree of any branching observed, it was necessary to prepare a series of branched samples with at least a known relative degree of branching. This work reports our efforts to this end.

EXPERIMENTAL

1,2,4-Triiodobenzene was prepared via vapor-phase oxyiodination of *p*-diiodobenzene [4] over a zeolite catalyst and was purified by vacuum distillation. Composition was verified by GC/MS. Tris(*p*-bromophenyl) amine was purchased from Aldrich and used as received. 4-Iodobiphenyl was similarly prepared via oxyiodination of biphenyl.

Melt preparations of the polymers were conducted as previously reported [2]. It should be noted that the vapor pressure of *p*-diiodobenzene at 230°C, the initial bath temperature of the reaction, was measured by us to be about 220 torr. There was, therefore, some codistillation of *p*-diiodobenzene along with the iodine reaction by-product. This codistillation was minimized by the Vigreaux take-off column. The mole percent brancher was calculated based on the amount of sulfur present in the mixture, assuming no loss of branching agent. 4-Iodobiphenyl was employed as a terminator at a calculated level for a nominal 250 *DP* polymer, assuming complete termination of the chains via biphenyl groups.

Percents carbon, hydrogen, sulfur, and iodine in the final products were determined by standard combustion analysis methods. Differential scanning calorimetry (DSC) was measured on a DuPont 9900 Thermal Analyzer at a scan rate of 20°C/min by using a sample that had been previously melted at 320°C for 2 minutes and then quenched on a metal block cooled in dry ice. Melt stability versus time and complex viscosity were determined using a Rheometrics Mechanical Spectrometer at 300°C oven temperature by taking measurements over a period of about 35 minutes at a shear rate of 25 radians/s. Extrapolation of the plot of the log of the melt viscosity versus linear time was used to determine the intercept, which was taken as the melt viscosity at zero testing time. The complex viscosity yielded the loss modulus, G'', and the storage modulus, G', from which $(\tan \delta)^2$ was calculated.

RESULTS AND DISCUSSION

The first and most obvious approach to generating a series of samples for testing branching behavior was to use 1,2,4-triiodobenzene (TIB) as the branching agent. When this was attempted using a range of from 0.5 to 2.0 mol% TIB, the DSC results did not appear consistent either within both sets of unterminated runs (employing different *p*-diiodobenzene excesses during the reaction) or within the set of terminated runs (Table 1). A part of the reason was no doubt the large variation in T_g seen in any one series of samples. There does appear to be a general trend to lower the crystalline melting point, T_m, with increased brancher added, but the data were clearly not good enough to draw any solid conclusions. Additionally, the melt viscosities of the unterminated and the terminated series do not appear consistent.

TABLE 1. Effect of 1,2,4-Triiodobenzene (TIB) on DSC Properties of PPS

Sample	TIB, mol%	T_g, °C	T_{ch}, °C	T_{cc}, °C	T_m, °C	MV[a]	$(\tan\delta)^2$[b]
1	0.0	84	151	197	274	165	3.40
2	0.5	81	148	198	271	119	25.00
3	1.0	72	129	198	269	Too thin	–
4	2.0	78	145	176	263	Too thin	–
(24.5% excess)[c]							
5	0.0	91	180	161	268	72,300	0.06
6	0.5	93	180	166	260	104,000	0.15
7	1.0	87	162	176	267	6,610	0.18
8	2.0	91	175	157	252	>1,000,000	–
(20.8% excess)[c]							
9	0.0	86	161	172	272	2,570	0.78
10	0.5	92	190		257	92,800	0.17
11	1.0	73	137	200	269	Too thin	–
12	2.0	85	167	167	261	17,100	0.05
13	2.0	84	158	188	264	895	0.84
(20.8% excess)[c] (terminated)							

[a] Melt viscosity in poise at 300°C.

[b] Tan δ = loss modulus/storage modulus.

[c] Excess *p*-diiodobenzene used in preparations.

Tris(*p*-bromophenyl)amine as a branching agent, when employed in terminated PPS preparations (Table 2), gave DSC data that appeared consistent. The T_gs of the samples all fell within a narrow range with only a very slight upward trend with increasing branching. This effect may be a result of the increased branching rather than the disulfide level of the polymer, but elemental analysis does not support any substantial differences. The T_m was seen to be a strong function of the branching level (Fig. 1) with 1.0 mol% being sufficient disruption to the chains to eliminate the second cycle melting transition. Neither was there a detectable crystallization on cooling or heating at that level of brancher. Thus, even a 1 mol% branching level in this system interferes very effectively with the ability to crystallize in the time scale of the DSC experiment. The crystallization upon cooling from the melt, T_{cc}, also showed a large decrease with increasing brancher level (Fig. 2), although the scatter in the data is a bit higher than seen for the T_m. When the crystallization upon heating from the glass, T_{ch}, was examined, the results were complicated by the fact that the 0.5 and 0.75 mol% samples each showed two peaks on heating from the glass (Fig. 3). This complicated the determination of the quantity $T_{cc} - T_{ch}$, which would be a measure of the relative crystallization rates. Instead, one can determine $T_m - T_{cc}$ (the degree of undercooling for melt crystallization) as another way of looking at the relative crystallization rate. These data (Fig. 4) were more scattered than the T_{cc} data but still appeared to be a good enough correlation to state that the crystallization rate was slowed considerably by an

TABLE 2. Effect of Tris(*p*-bromophenyl)amine on DSC Properties of PPS

Sample	Brancher, mol%	T_g, °C	T_{ch}, °C[a]	$H_{T_{ch}}$, cal/deg[b]	T_{cc}, °C[c]	$H_{T_{cc}}$, cal/deg[d]	T_m, °C	H_f, cal/deg[e]	$T_m - T_{cc}$, °C
1	0.0	88	158	8.86	192	10.67	279	10.67	87
2	0.25	90	167	9.20	184	10.21	276	9.79	92
3	0.50	88	172	7.19	158	5.69	268	9.03	110
			147	1.43					
4	0.75	90	175	3.81	147	2.47	260	7.52	113
			144	2.87					
5	1.00	91	—[f]	—	—	—	—	—	—

[a] Crystallization upon heating from the glass.

[b] Heat release for T_{ch} transition.

[c] Crystallization upon cooling from the melt.

[d] Heat released for T_{cc} transition.

[e] Heat of fusion at T_m.

[f] None detected.

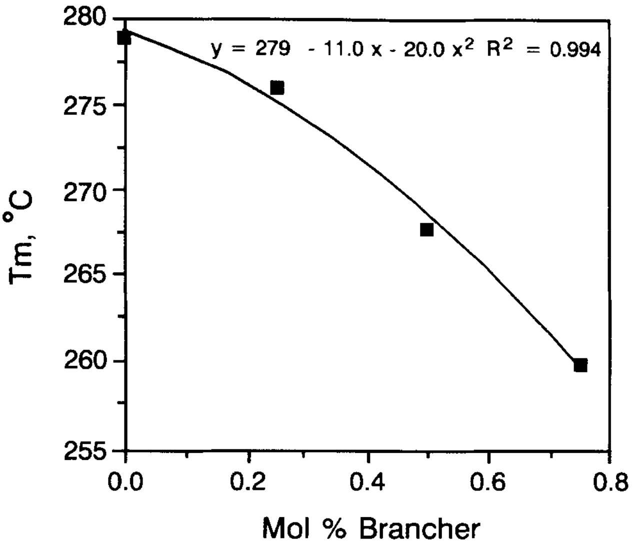

FIG. 1. Effect of branching on T_m.

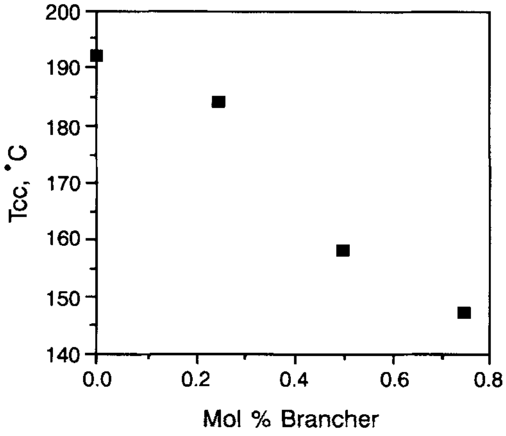

FIG. 2. Effect of branching on crystallization from the melt (T_{cc}).

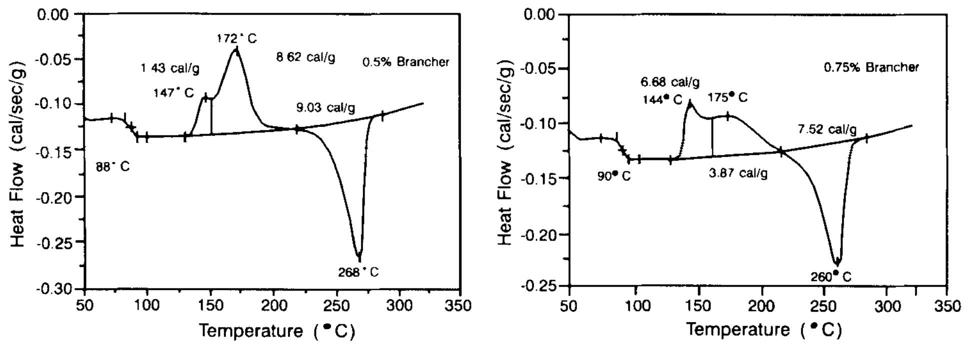

FIG. 3. Second cycle DSC scans—heating from the glass.

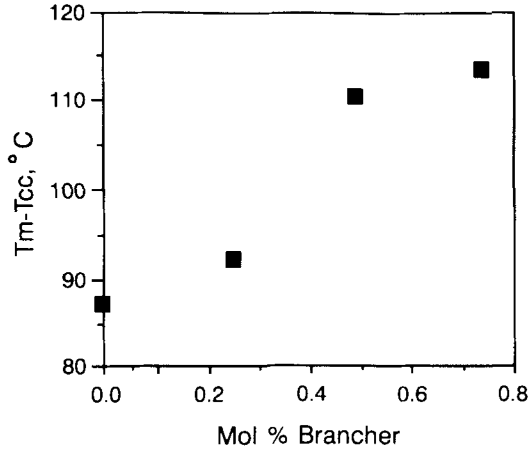

FIG. 4. Effect of branching on the quantity crystalline melting point minus the crystallization on cooling from the melt ($T_m - T_{cc}$).

increase in the brancher level. This also provides a rough correlation of the magnitude of the effect versus brancher level. In addition to these observations, one should note that the heat released or absorbed by these transitions diminished with increasing brancher level, although the effect was not as pronounced as seen with the value of T_m, for example. The combination of these DSC data can serve to give a good semiquantitative idea of the level of brancher in a particular system.

Assuming complete reaction of the brancher, the data using tris(*p*-bromophenyl)amine (TBPA) as the branching agent for PPS would imply that the actual functionality of the 1,2,4-triiodobenzene (TIB) preparations was only slightly above 2, since at the 2 mol% TIB level there was still an observable T_m. The melting point seen with the 2 mol% TIB runs with terminator had about the same melting point as 0.75 mol% of TBPA while the TIB samples had a higher crystallization rate,

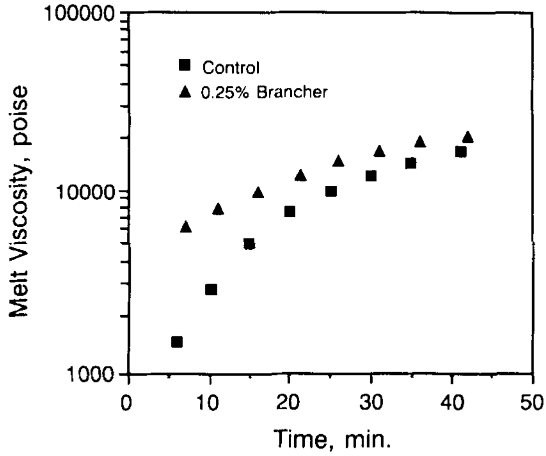

FIG. 5. Melt viscosity at 300°C vs time.

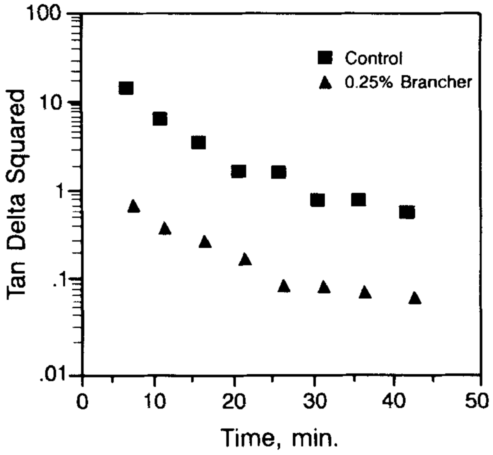

FIG. 6. (Tan δ)^2 at 300°C vs time.

which may be due in part to the lower chain length as evidenced by the T_g. Thus, the functionality of the TIB must have been much less than the theoretical 3.0.

Melt rheology on the branched series showed similar melt viscosities for the control and the 0.25 mol% brancher sample (Fig. 5) but a marked decrease in the value of (tan δ)^2 for the branched sample (Fig. 6), indicating the branched sample to be far more elastic than the control. Samples with 0.5 mol% brancher and above were reported not to melt at 350°C, making rheological testing impossible. From the DSC behavior it is evident that the samples would certainly be melted by that temperature. However, the "no melt" observation can also arise with a melt so elastic as to preclude closing the gap on the instrument prior to testing. This latter case obviously holds for the more branched samples. It is thus apparent that brancher levels of as low as 0.5% were sufficient to cause a nonflowable melt even at the moderate melt viscosity of these systems.

CONCLUSIONS

Tris(*p*-bromophenyl)amine was effective in producing a reference series of branched PPS samples where 1,2,4-triiodobenzene did not. A combination of T_m, T_{cc}, $T_m - T_{cc}$, and the heats involved in these transitions in the DSC can serve to ascertain a semiquantitative level of brancher in PPS preparations. Effects of increased branching on the thermal characteristics were seen to be quite large for even a 0.25 mol% brancher. Melt rheology also confirmed the large effects on melt elasticity in this system even at the moderate melt viscosities of the polymers of this work.

REFERENCES

[1] See, for example, M. Rule, D. R. Fagerburg, J. J. Watkins, and J. S. Fauver, U.S. Patent 4,786,713 (November 22, 1988); *Chem. Abstr.*, *110*, 174004j, and subsequent patents.

[2] M. Rule, D. R. Fagerburg, J. J. Watkins, and P. B. Lawrence, *Makromol. Chem., Rapid Commun.*, *12*, 221-226 (1991).

[3] M. Rule, D. R. Fagerburg, J. J. Watkins, P. B. Lawrence, R. L. Zimmerman, and J. D. Cloyd, *Makromol. Chem., Symp. Ser.*, *54/55*, 233-246 (1992).

[4] See M. Rule, U.S. Patent 4,746,758; *Chem. Abstr.*, *110*, 38720n, and subsequent patents.

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