Melt Viscosity Increase During Rheological Testing of Poly(phenylene sulfide)

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SYNOPSIS

Poly(phenylene sulfide) (PPS) made via the melt polymerization of p-diiodobenzene and sulfur has previously been reported to increase in melt viscosity with time during rheological testing. Analysis of the oligomer from cleavage of PPS chains at the disulfide bonds via solution in 1-chloronaphthalene demonstrated that the disulfide content of the polymer decreased with rheological testing time. DSC of the polymer before and after rheological testing in combination with the T_{cc} and T_m of the chain fragments after the dissolution/cleavage in 1-chloronaphthalene showed that many samples exhibited primarily chain extension rather than chain branching, whereas for many others, some degree of chain branching occurred. This is currently only qualitatively understood. Chain branching as the exclusive mechanism of melt viscosity increase during rheological testing appears untenable in light of the T_m, in particular, of the chain fragments and also the polymer prior to chain cleavage. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(phenylene sulfide) (PPS) has found numerous applications owing to its excellent combination of chemical resistance and thermal properties. We have recently reported a new melt-phase polymerization process for the preparation of PPS involving the reaction of p-diiodobenzene and sulfur[1-3] and some of the characteristics of the resultant polymer. In 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 allowing differentiation between chain extension and/or branching reactions as the cause of this melt viscosity increase was not, however, presented in our previous reports. We report here that the recently reported solution degradation method for this polymer that results in cleavage of the disulfide linkages in the chain by the solvent[4] combined with the recently reported DSC characteristics of a series of PPS oligomers[5] allowed correlation to DSC characteristics of PPS fragments from the solution reaction in 1-chloronaphthalene to obtain chain lengths of the resultant fragments. We now present evidence obtained via a combination of this cleavage reaction technique correlated to the oligomer data in combination with the recently reported effect of the brancher on the T_m in this system[6] that chain extension is the more likely mechanism of the observed melt viscosity increase during rheological testing for many of the polymer samples examined.

Previous workers examining commercial PPS and alternative synthetic routes have reported on a number of characteristics such as morphology and thermal stability, but little has been reported on the viscoelastic response of the polymer.[7] Investigation of model systems of PPS[8] has led to the conclusion that the process commercially practiced for some PPS production and known as "curing," heating in air above the melting point for extended time periods, produces not only some oxidation but also chain extension and chain branching, with the branching leading eventually to a cross-linked mass. Melt rheology of thermally aged PPS[9,10] showed an increase in the M_w/M_n ratio with increased heating time in the melt and also an increase in the storage modulus, G'. Both observations were, of course, consistent with branching occurring during the "curing"

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reaction. The molecular weight ratios given in previous work[10] were, incidentally, calculated from the melt rheology data and were in agreement with what was published earlier concerning the GPC analysis of PPS.[11] Subsequent work[12] clarified, however, that the previous GPC data were in error owing to an inherent bias in the detection method and found M_w/M_n ratios that were considerably larger than those reported from the rheological data.[10]

EXPERIMENTAL

Samples of PPS for this work were prepared by the previously published method[3] of melt preparation to 250°C followed by solid-state polymerization at 240°C. Percent 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 using a sample that had been previously melted at 320°C for 2 min and then quenched on a metal block cooled in dry ice. Melt and complex viscosity vs. time were determined using a Rheometrics mechanical spectrometer at 300°C oven temperature, taking measurements over a period of 35 min at a shear rate of 25 rad/s. Owing to the increase of melt viscosity with testing time, frequency sweep experiments to construct master curves of G', e.g., were not possible.

Solutions of the polymers were prepared in 1-chloronaphthalene (Kodak Laboratory Products), ca. 10 wt %, at 230°C until the solution seemed to be complete or until no apparent reduction of gel volume or solution darkening seemed to occur for samples containing gelled material. Heating was then continued for an additional 4–5 h. The total heating time varied from 6 to 7 h. Filtration was accomplished with a preheated, coarse frit Büchner funnel. The filtrate was diluted with a three- to fivefold volume of methanol and the precipitate filtered with suction, boiled in methanol, and rinsed with hot methanol after suction filtration. The products were dried in a vacuum oven at ca. 100 Torr pressure at about 100°C for 2 or 3 days.

RESULTS AND DISCUSSION

The samples for this work were chosen from among several that exhibited a very large increase in melt viscosity (Table I) during the melt viscosity testing plus one sample that actually showed degradation and two samples of very low melt viscosity that only

Table I Melt Viscosity of PPS Samples at 300°C

Sample	Initial Melt[a] Viscosity (Poise)	Final Melt[b] Viscosity (Poise)	Zero-time Melt[c] Viscosity (Poise)
1	23	41	29
2	24	68	39
3	400	27,900	3,030
4	1,200	15,700	4,100
5	980	55,500	8,270
6	3,670	67,000	17,600
7	34,700	32,700	37,200
8	33,900	148,000	38,300
9	76,000	55,000	73,200
10	45,400	133,000	74,000
11	102,000	204,000	102,000

[a] Melt viscosity immediately after full melt of sample.
[b] Melt viscosity at 35 min elapsed time from full melt.
[c] Melt viscosity at zero time extrapolated from log (melt viscosity) vs. time plot.

showed a very moderate viscosity increase. As noted in the Introduction, most of the samples of PPS by this process show an increase in melt viscosity with testing time, but the increase is generally a small one. In our experience,[13] for PPS from this melt process, the increase is usually on the order of a factor of 3 or less in the final melt viscosity vs. that which is initially observed after the sample is fully melted. Thus, most of the examples of this work represent extreme cases of the phenomenon that we wish to examine.

It is first important to consider the consequences of purely chain-extension and purely chain-branching reactions on the properties expected in the resultant polymer test sample. In both cases, the net reaction would be to reduce the disulfide content of the polymer. The chain-extension reaction would coproduce I_2, whereas the branching reaction would coproduce HI. Since analysis of the sample after rheological testing was not possible in a manner to allow detection of either I_2 or HI, we can consider only what must happen to the polymer itself. If purely chain extension occurs, the resultant polymer will have larger average distances between disulfide linkages. Since dissolution of PPS in 1-chloronaphthalene has been previously shown to cleave disulfides in the polymer chain,[4] assuming that the resultant end groups do not appreciably affect the T_g of the resultant oligomer, then the calibration[5] of T_g vs. log(dp) for oligomers can be used to determine the average fragment length. This serves as a good measure of the disulfide mole fraction of the original

polymer by simply taking the inverse of this dp and subtracting 1. The fragment T_g in the chain-extension case must therefore increase as must also the degree of perfection of the chain fragment.

This increased perfection should manifest itself in a higher T_m, an increase in the temperature of crystallization upon cooling from the melt, T_{cc}, and perhaps also a decrease in the temperature of crystallization from the glass, T_{ch}. If, however, the reaction in the mechanical spectrometer is purely chain branching, then the T_g should rise, probably more so than from fragment lengthening, but the degree of perfection of the average chain should be decreased. This would result in a decrease in the T_m and T_{cc}, and an increase of the T_{ch}. In addition, one must consider that in the case of pure chain branching that the number of branch points in the final polymer fragment can be arrived at by inspection by determining the ratio of the rheometrics fragment dp to the original fragment dp and subtracting 1. Thus, in a pure chain-branching case, if a fragment went from 10 dp, e.g., before rheological testing to 20 dp after testing, this would be the result of 1 branch point per average segment. The expected re-

sult is that for doubling of the average fragment dp by this route the melting point of the final fragment would be severely reduced if not eliminated based on our previously reported results[6] where 1 mol % of a branching agent eliminated the crystalline melting transition in high molecular weight PPS.

It should be noted here that the disulfide content determined via cleavage in 1-chloronaphthalene and comparison to the monomer calibration data agreed generally with that determined via combustion analysis data for the samples reported but that the expected error limits of the combustion analysis data make that method for disulfide level determination less desirable. It must always be borne in mind, however, that relating the T_g of these cleaved materials directly to the monomers that have different end groups may cause a bias in the fragment length obtained. Branching of a sample would also introduce error in relating the T_g to a sample dp.

DSC data (Table II) of the polymer both before and after rheological testing when dissolved in 1-chloronaphthalene showed large reductions in the polymer T_g from the original polymer as expected along with changes in the other transitions that

Table II   DSC Characteristics of PPS from Dissolution in 1-Chloronaphthalene

Sample	Sample[a]	T_g (°C)	T_{ch} (°C)	T_{cc} (°C)	T_m (°C)	Calcd dp[b]	Mol % SS[c]
1	Sstated	77	124	227	280	34.4	1.9
	Rheometrics	80	121	224	281	39.7	1.5
2	Sstated	74	123	222	275	29.9	2.3
	Rheometrics	81	122	215	279	41.6	1.4
3	Sstated	54	97	217	262	11.6	7.6
	Rheometrics	80	124	205	269	39.7	1.5
4	Sstated	58	103	201	264	14.0	6.1
	Rheometrics	70	115	226	272	24.7	3.0
5	Sstated	65	110	227	271	19.5	4.1
	Rheometrics	84	127	208	275	48.0	1.1
6	Sstated	63	108	215	271	17.7	4.6
	Rheometrics	81	130	200	276	41.6	1.4
7	Sstated	49	99	177	252	9.2	9.9
	Rheometrics	75	124	197	266	31.3	2.2
8	Sstated	68	110	224	268	22.5	3.4
	Rheometrics	86	133	213	275	52.7	0.9
9	Sstated	40	86	188	251	6.0	15.7
	Rheometrics	62	109	208	265	17.0	4.9
10	Sstated	57		214	260	13.4	6.5
	Rheometrics	80	129	218	272	39.7	1.5
11	Sstated	61	104	219	261	16.2	5.2
	Rheometrics	78	127	205	268	36.1	1.8

[a] As prepared solid-stated sample = Sstated. After rheological testing for 35 min at 300°C = rheometrics.
[b] Degree of polymerization calculated from Ref. 5.
[c] From the reciprocal of the calculated dp minus 1 mol %.

would be consistent with shorter polymer chains. The rheological test sample when cleaved via dissolution showed in each case an increase in the PPS fragment length vs. the original material prior to testing. Thus, the disulfide content of all samples did decrease during the course of the rheological measurements. All samples exhibited an increase in T_m. An increase in T_m is not consistent with pure chain branching as the mechanism of melt viscosity increase (see discussion above). Other transitions, however, gave mixed results. Some T_{cc} pairs showed a marked increase after testing (samples 4, 7, and 9), whereas some showed a marked decrease with only two and possibly three samples staying about the same (samples 1 and 10 remained essentially constant as did possibly sample 2). This would suggest that only five or six of the samples, those with no change or an increase in T_{cc}, were candidates for pure chain extension. The other samples would seem to have at least some element of chain branching consistent with the large decreases in T_{cc}.

All samples prior to rheological testing had a moderately high T_g with a reasonably high T_m (Table III). The DSC data after rheological testing was somewhat scattered. The bulk, uncleaved samples

did not show an appreciable change in T_g, but this is not definitive since the T_g was already in a region where changes in molecular weight do not show up as large changes in the T_g. The difference in T_{cc} − T_{ch} remained essentially the same for the before and after samples. The T_m remained unchanged for most samples, whereas for some it decreased. The decrease in T_m can be associated with chain branching.[6] Hence, for samples with no T_m decrease, branching would not seem to be a factor by this criterion. When the samples that did not change T_m are compared with their behavior from the dissolution test above, samples 1, 4, 9, and, possibly, 2 seem likely to be consistent with pure chain extension. Not only did the T_m remain unchanged during rheological testing, but the T_{cc} on the chain-cleaved polymer fragments increased or remained the same. By this criterion, sample 7 is close to pure chain extension with only a 3°C drop in T_m after testing, whereas the fragment T_{cc} rose 20°C. For samples showing larger changes in T_m, occurrence of some branching along with the chain-extension reaction would appear to be a reasonable explanation, with the degree of branching increasing with greater decreases in T_m.

Table III DSC and Melt Viscosity of PPS Before and After Rheological Testing

Sample	Sample[a]	T_g (°C)	T_{ch} (°C)	T_{cc} (°C)	T_m (°C)	MV (poise)[b]
1	Sstated	85	144	212	284	
	Rheometrics	84	140	222	283	29
2	Sstated	82	145	191	279	
	Rheometrics	82	141	209	278	39
3	Sstated	91	182	163	276	
	Rheometrics	89	160	184	264	3,029
4	Sstated	91	160	197	275	
	Rheometrics	94	161	198	274	4,100
5	Sstated	92	181	172	276	
	Rheometrics	92	166	185	269	8,274
6	Sstated	95	194	161	273	
	Rheometrics	95	168	188	268	17,639
7	Sstated	94	195	154	264	
	Rheometrics	94	178	162	261	37,176
8	Sstated	93	180	172	270	
	Rheometrics	93	177	175	269	38,287
9	Sstated	97	191	154	265	
	Rheometrics	96	188		264	73,235
10	Sstated	95	184	165	268	
	Rheometrics	98	208		261	73,951
11	Sstated	96	192		262	
	Rheometrics	96	185	159	262	101,950

[a] As prepared solid-stated sample = Sstated. After rheological testing for 35 min at 300°C = rheometrics.
[b] Melt viscosity in poise at 300°C and 25 rad/s shear rate.

It is thus apparent that judging the degree of branching is a complex question that is at present only qualitatively understood. The general rule is, however, to examine for change in T_m in the bulk samples and then to look at the change in T_{cc} for the dissolved/cleaved samples before and after rheological testing. Little or no change in T_m is a necessary but not sufficient condition for chain extension as the dominant mechanism. Concurrently, the greater the increase in the value of T_{cc} for the fragments after rheological testing, the less branching is occurring and the more chain extension for any given set of samples.

It is worth repeating that the amount of chain branching in any of the cases reported in this work cannot be very high or else the final polymer after testing but before dissolution and also the polymer fragments from the dissolution/cleavage reaction would not show a crystalline melting peak by analogy to the previous experience with PPS branched by addition of a trifunctional agent.[6] This previous work referred to demonstrated the effect of long-chain branches on PPS transitions as the monomer used is reasonably expected to have been incorporated early in the reaction in contrast to what one would expect for PPS made by the commercial process where a branching agent, typically 1,2,4-trichlorobenzene, was added. In this latter case, because of reactivity differences between the two chlorines on an aromatic ring vs. one chlorine and a thioether,[14] one expects that the introduction of a third chlorine to give the branching agent such as 1,2,4-trichlorobenzene will diminish reactivity of the first chlorine, even further leading to late incorporation of the brancher into the polymer chain. Since the commercial process is a nonequilibrium one, this late incorporation leads to short-chain branching. Branching effects under such conditions would likely not be seen in the DSC of the fragments as the branched material would represent a very small fraction of probably short-chain branches on the sample chain and would only affect its own short chain. Branching in the polymers of this work by contrast would be the equivalent of mostly long-chain branches since the probability of reaction of a thiyl radical (from disulfide cleavage) with a ring to form a branch point is expected to have equal probability with any monomer unit of the chain.

CONCLUSIONS

Analysis of the oligomer from cleavage of poly(phenylene sulfide) chains at the disulfide bonds via solution in 1-chloronaphthalene demonstrated that the disulfide content of the polymer decreased with rheological testing time. DSC of the polymer before and after rheological testing in combination with the T_{cc} and T_m of the chain fragments after the dissolution/cleavage in 1-chloronaphthalene showed that many samples exhibited primarily chain extension rather than chain branching, whereas for many others, some degree of chain branching occurred. This is currently only qualitatively understood. Chain branching as the exclusive mechanism of melt viscosity increase during rheological testing appears untenable in light of the T_m, in particular, of the chain fragments and also the polymer prior to chain cleavage.

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