

Synthesis and Characterization of Poly(phenylene sulfide). I. Studies on the Synthesis and the Property Differences of Poly(phenylene sulfide) with Terminal Chloro Groups and Poly(phenylene sulfide) with Terminal Thiohydroxy Groups

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SYNOPSIS

In this article, two kinds of poly(phenylene sulfide) (PPS) with terminal groups predominated by chloro and thiohydroxy groups have been synthesized using endcapping by adding monomer. Compared with PPS with terminal thiohydroxy groups, PPS with terminal chloro groups possesses a greater crystallinity, larger crystallite dimensions, a larger particle size, higher thermal stability, and a longer gelation time. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The molar ratio of *p*-dichlorobenzene and sodium sulfide will exert a great influence on the molecular weight of poly(phenylene sulfide) (PPS) produced by the process of Edmonds and Hill.¹ This can be explained by the following relationship of the degree of polymerization and the molar ratio of two reactants in a condensation reaction: $Xn = (1 + r)/(1 + r - 2pr)$, where Xn is the degree of polymerization; r , the molar ratio of the two reactants; and p , the percent conversion. The molar ratio of the two reactants must amount to about 1 : 1 in order to obtain high molecular weight polymers, or a large excess of either reactant will lead to lower molecular weight polymers. If a slight excess of sodium sulfide is used, the polymer, as formed, will be terminated with sodium thiolate groups, which can be converted into thiohydroxy groups by washing with water or acid. On the other hand, if a slight excess of *p*-dichlorobenzene is used, the polymer, as formed, will be terminated with chloro groups. The ratio of two kinds of terminal groups can be controlled by adjusting the molar ratio of the two reactants, but it is difficult

to make all the PPS prepared be of higher molecular weight. Rajan and co-workers² prepared PPS with the ratio of chloro groups and sodium thiolate groups of 1.8027/0.1973 by adjusting the molar ratio of sodium sulfide and *p*-dichlorobenzene to 0.9422, but the molecular weight was only 4173 (calculated from conversion). Sergeev and co-workers³ also prepared PPS with terminal chloro groups by adjusting the molar ratio of the reactants, but the molecular weight was quite lower (about 3000) and the contents of the terminal groups were not reported.

To offer materials for research concerning the effect of terminal groups on the properties of PPS, we prepared PPS samples according to U.S. Pat. 3,354,129 as follows: *p*-dichlorobenzene reacted with sodium sulfide in *N*-methyl-2-pyrrolidone at the molar ratio of 1 to form higher molecular weight polymers; then, *p*-dichlorobenzene was added and the reaction was continued to give PPS with terminal chloro groups, or sodium sulfide was added and the reaction was continued to give PPS with terminal sodium thiolate groups that can be converted into terminal thiohydroxy groups. This method is of a stable technology and a simple and convenient operation, and the molecular weights of all PPS can be kept in a narrow range. The virgin PPS samples are similar to common virgin PPS samples except that the contents of terminal groups

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and the research on them are significant for production, development, and application of PPS.

For polymer chains constituted of a great number of repeating structural units, the terminal groups connected with one side of the molecular chain are freer than are the middle structural units connected to both sides of the molecular chain and are the most active parts of the whole molecular chain. Although the contents of terminal groups are low, the structure, activity, and interaction of terminal groups will affect the chain motion, the state of aggregation, the thermal stability of PPS, and so on. Therefore, terminal chloro groups and thiohydroxy groups will have different effects on the properties of PPS due to their different structures and activities. After studying the thermal stability of PPS with terminal bromo groups⁴ and PPS with terminal chloro groups,⁵ Gavalyan and co-workers concluded that terminal halogen groups had some stabilizing effect on PPS at lower temperatures. But thorough research on the effect of terminal chloro groups and thiohydroxy groups on the properties of PPS prepared according to the method of Edmonds and Hill¹ has not been reported.

In this article, two kinds of PPS with terminal groups predominated by chloro and thiohydroxy groups were prepared using endcapping. The investigations on them will provide some scientific bases for developing PPS with high performance.

EXPERIMENTAL

Materials

Sodium sulfide (SS) ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) was 98% pure and the content of carbene oxide was below 0.5%. 1,4-Dichlorobenzene (PDCB) was 99% pure. *N*-Methylpyrrolidone (NMP), purified, had a boiling point 202°C and a refractive index (N_D^{25}) of 1.4610–1.4680.

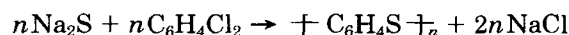
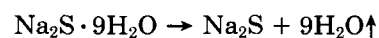
Synthesis of PPS

In a 5 L stainless-steel autoclave equipped with an inductive stirrer, a certain amount of SS was admixed with an appropriate amount of NMP and heated to remove the water of hydration from SS. To this resulting solution was then added PDCB that was equal to SS in mole quantity. This mixture was heated at 215°C for 6 h; then, an appropriate quantity of PDCB was added and the reaction was continued for 2 h for endcapping. After that, the mixture was cooled to room temperature. The prod-

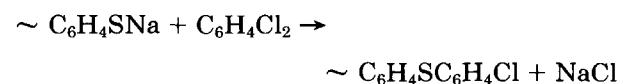
uct was centrifugalized to remove NMP and washed with dilute hydrochloric acid and hot water. In an extractor, the product was purified by extracting lower molecular weight PPS with toluene, inorganic impurity with deionized water, and residual PDCB with acetone. Then, the product was dried in vacuum and the pure virgin PPS with terminal groups predominated by chloro groups was obtained.

The preparation and purification of polymers were carried out precisely as above except that the supplied reactant for endcapping was SS; then, the pure virgin PPS with terminal groups predominated by thiohydroxy groups was obtained.

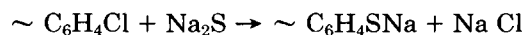
The course of the synthesis may be described in the following schemes:



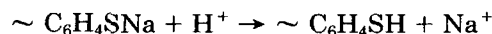
endcapped with PDCB:



endcapped with SS:



washed with dilute acid:



Terminal Groups Analysis

Pure PPS powder was dissolved in α -chloronaphthalene on heating and the solution was cooled to room temperature, admixed with ethanol, and filtered. Then, the filtrate was titrated with a standard mercuric nitrate solution to determine the chlorion content. The indicator used was diphenylcarbazone. Then, the content of free chlorion in the resin was obtained.

The total content of chlorine in the resin was determined by the oxygen flask method. The content of free chlorion was deducted from the total content of chlorine and the content of terminal chloro groups was obtained.

In alkaline α -chloronaphthalene, thiohydroxy groups of PPS reacted with 2,4-dinitrochlorobenzene to yield chlorion quantitatively. After the total content of chlorion was determined, the content of free chlorion was deducted from it and the remaining

content was converted into the content of thiohydroxy groups.

Viscosity Determination

A PPS sample of 0.1 g was dissolved in 10 mL α -chloronaphthalene and the viscosity of the solution was determined using a modified Ubbelodhe viscosimeter at $206 \pm 0.2^\circ\text{C}$. The viscosity used was a logarithmic viscosity number $[\eta]$: $[\eta] = \ln \eta_r/C$.

IR Analysis

The infrared data presented were obtained using a Shimadzu infrared spectrophotometer IR-440 (IDP-440) and tablets pressed with potassium bromide.

X-ray Data

X-ray diffraction patterns of PPS were obtained employing a Rignku D/max-rA diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation (40 kV, 50 mA, and wavelength 1.5418 \AA). Measurements were made by symmetry reflection at 2θ values from 15° to 30° . Based on the reasonable assumption that crystalline PPS makes no contributions at 2θ values of 17° and 24° and the measurements at these two values are all contributions of amorphous PPS, the boundary of the crystalline and amorphous patterns was determined according to the amorphous pattern of Brady.⁶ Dividing the area under the diffraction curve attributed to crystalline diffraction by the total areas, we obtained the ratio of areas termed the crystallinity index, C_i :

$$C_i = A_{\text{cryst}} / (A_{\text{cryst}} + A_{\text{amorp}}) \times 100\%$$

where A is the area under the diffraction curve.

After measuring the peak width at half-height of the most intensive diffraction peak, we calculated the normal grain size of the crystalline plane D_{hkl} , which we take as crystallite dimensions:

$$D_{hkl} = \kappa\lambda/\beta \cos \theta_{hkl}$$

where κ is 0.89; β , the peak width at half-height; and θ_{hkl} , the Bragg angle.

Particle-size Analysis

The particle-size data presented were obtained using a Seishin Micron Photo Sizer SKC-2000. The samples of PPS were analyzed using ethanol as the dispersion medium using gravimetric precipitation extinction.

Thermogravimetric Analysis

The thermal stability of PPS was investigated using a thermogravimetric balance WRT-2 and 5–10 mg samples. The heating rate was $10^\circ\text{C}/\text{min}$ and the air-flow rate was 40 mL/min.

Gelation Time Measurement

The gelation time of PPS was determined using a gelation time measurement instrument HG-1 and 2–3 g samples and temperature of 350°C . The gelation time used was the time from melting of PPS to curing to such an extent that resin wire could not be drawn.

RESULTS AND DISCUSSION

The viscosities and the terminal group contents of seven PPS samples prepared by endcapping by add-

Table I Appearance, Viscosities, and Contents of Terminal Groups of PPS Samples

Sample	Appearance	Viscosity	Content ^a (%)	Content ^b (%)	Molar Percentage ^a (%)	Molar Percentage ^b (%)
C-1 [#]	White	0.130	1.07	0.20	83.3	16.7
C-2 [#]	White	0.176	1.09	0.22	82.2	17.8
C-3 [#]	White	0.171	1.04	0.05	95.1	4.9
C-4 [#]	White	0.142	0.94	0.20	81.4	18.6
T-1 [#]	Light yellow	0.151	0.22	0.85	19.4	80.6
T-2 [#]	Light yellow	0.157	0.11	0.82	11.1	88.9
T-3 [#]	Light yellow	0.145	0.11	0.78	11.6	88.4
V-1 [#]	Grayish yellow	0.160	0.78	0.46	61.2	38.8

^a Terminal chloro groups.

^b Terminal thiohydroxy groups.

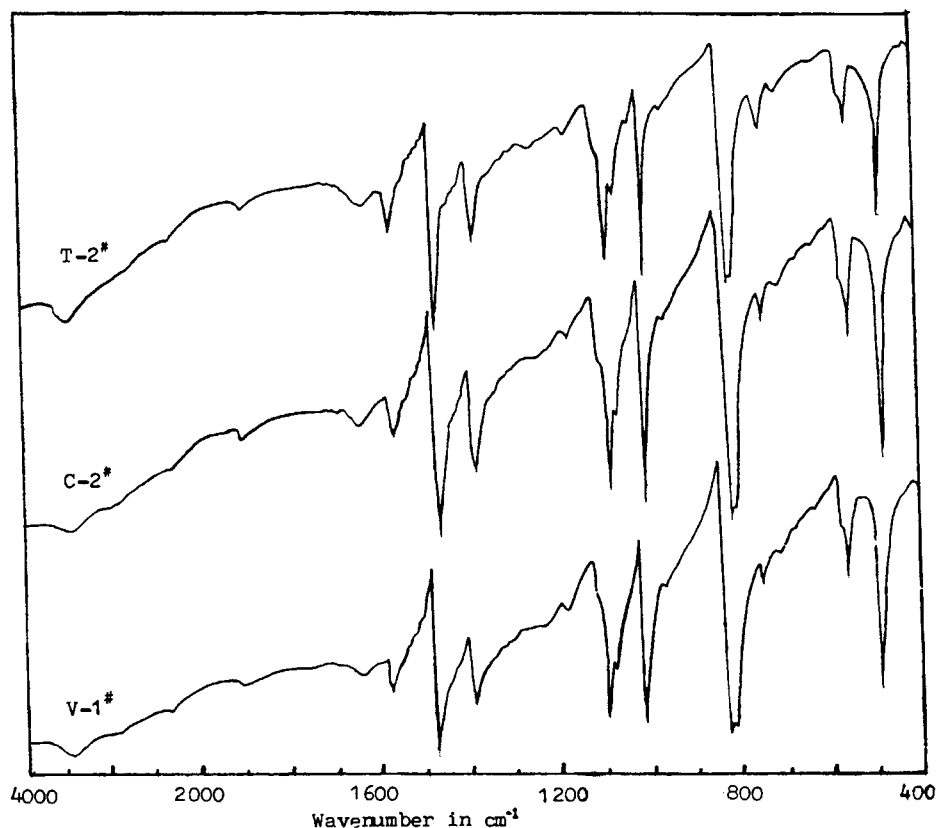


Figure 1 Infrared spectra of T-2[#], C-2[#], and V-1[#].

ing monomer and Ryton V-1[#] are listed in Table I. C-1[#], C-2[#], C-3[#], and C-4[#], whose molar percentages of terminal chloro groups are all above 80% and those of terminal thiohydroxy groups are all below 20%, are PPS with terminal groups being predominated by chloro groups. On the contrary, T-1[#], T-2[#], and T-3[#], whose molar percentages of terminal chloro groups are all below 20% and those of terminal thiohydroxy groups are all above 80%, are PPS with terminal groups predominated by thiohydroxy groups. For V-1[#], which was not endcapped, the molar percentage of terminal chloro groups being 61.2% and that of terminal thiohydroxy groups being 31.8% are all between those of two kinds of PPS, although the content of terminal chloro groups is greater than that of terminal thiohydroxy groups.

PPS samples with predominated terminal thiohydroxy groups are all light yellow, which is in agreement with PPS prepared by Hilditch⁷ by polymerization of thiophenol. On the other hand, PPS with predominated terminal chloro groups are all white. V-1[#] exposed to air for a long time is grayish yellow. Their viscosities are all in the range from 0.130 to 0.176.

The IR spectra of T-2[#], C-2[#], and V-1[#] are shown in Figure 1. Since the contents of terminal groups are rather low (below 1.5%), the absorption due to

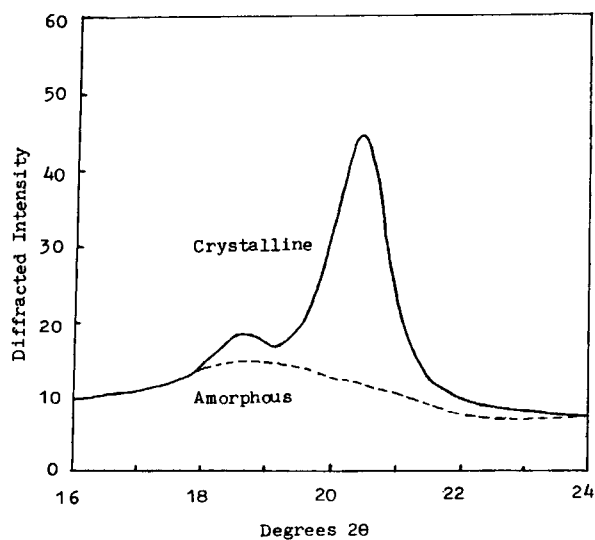


Figure 2 X-ray diffraction patterns of T-2[#].

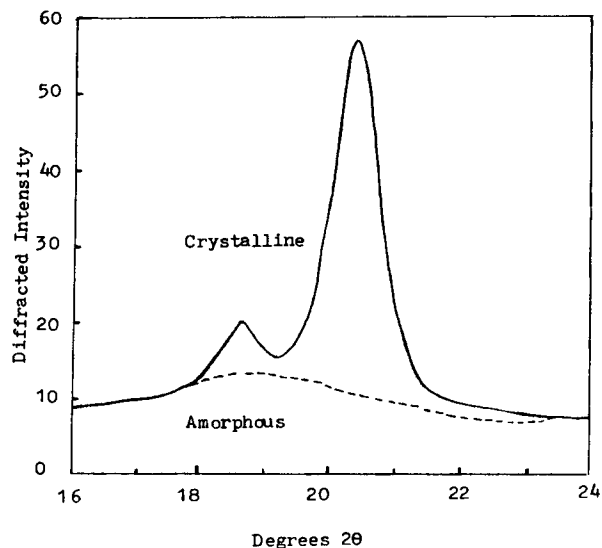


Figure 3 X-ray diffraction patterns of C-2[#].

thiohydroxy groups is quite weak, and the absorption due to C—Cl bonds is not strong either, the absorptions due to terminal groups of PPS are not shown in the IR spectra. The spectra of T-2[#] and C-2[#] are essentially identical with that of V-1[#].

The X-ray diffraction patterns of T-2[#] and C-2[#] are shown in Figures 2 and 3. The most intensive peak is at $2\theta = 20.48^\circ$ at which the reflection plane is (200);⁸ hence, the Bragg angle is 10.24° . The dotted line is the boundary of the crystalline and amorphous patterns according to the report of Brady.⁶ The crystallinity indexes and the crystallite grain sizes of T-2[#], T-3[#], C-2[#], and C-3[#] calculated from their diffraction patterns are listed in Table II. Compared with the crystallinity of 43.0% of C-2[#] and 44.3% of C-3[#], those of T-2[#] and T-3[#] are 36.8 and 37.7%, respectively. The crystallite sizes of C-2[#] and C-3[#] are 96.3 and 97.4 Å, respectively, whereas those of T-2[#] and T-3[#] are 79.9 and 75.6 Å, respectively. In contrast to PPS with terminal thiohydroxy groups, PPS with terminal chloro groups possesses a greater crystallinity and a bigger crystallite size. Crystallinities of two kinds of PPS are much lower than the maximum crystallinity of

Table II Crystallinities and Crystallite Sizes of Two Kinds of PPS

Sample	T-2 [#]	T-3 [#]	C-2 [#]	C-3 [#]
Crystallinity (%)	36.8	37.7	43.0	44.3
Crystallite size (Å)	79.9	75.6	96.3	97.4

Table III Particle-size Weight Distributions of T-3[#] and C-3[#]

Particle-size Range (μm)	Weight Percentage (%)	
	T-3 [#]	C-3 [#]
0-10	56.40	30.40
10-20	16.60	29.00
20-30	13.70	14.90
30-40	1.22	3.94
40-50	4.41	4.40
50-60	4.41	4.40
60-70	0.88	1.68
70-80	0.88	1.68
80-90	0.68	4.74
90-100	0.68	4.74

65% reported by Brady,⁶ so they are all in a semi-crystalline state.

The particle-size weight distributions and the particle-size integral distributions of T-3[#] and C-3[#] are shown in Table III and Figure 4. The peak values of the particle-size weight distributions of the two samples are all at 0-10 μm. The peak value of T-3[#] is far greater than that of C-3[#], but the distribution values at larger size ranges of C-3[#] are far greater than those of T-3[#] except the values at 40-50 and 50-60 μm. The average particle size of T-3[#] is 16.0 μm, whereas that of C-3[#] is 26.3 μm. These results

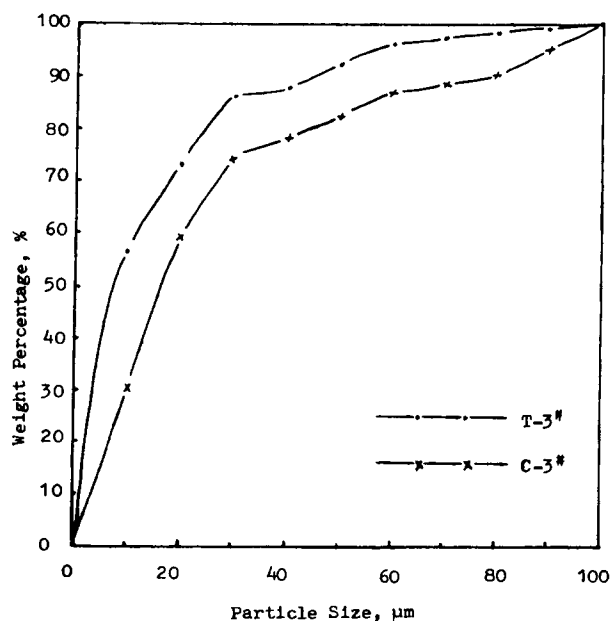


Figure 4 Particle-size integral distributions of T-3[#] and C-3[#].

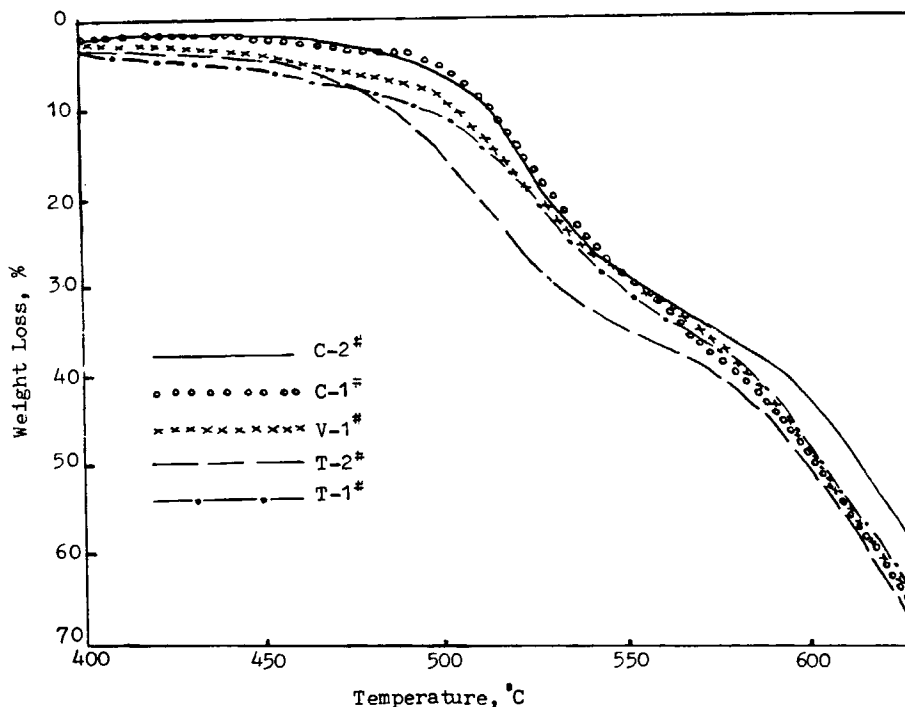


Figure 5 Thermogravimetric analysis of C-1[#], C-2[#], T-1[#], T-2[#], and V-1[#].

indicate that PPS with terminal chloro groups, compared with PPS with terminal thiohydroxy groups, possesses more larger particles, fewer smaller ones, and a greater average particle size.

The thermogravimetric analysis curves of C-1[#], C-2[#], T-1[#], T-2[#], and V-1[#] are shown in Figure 5. The temperatures of weight losses at 5, 10, 15, and 50% are listed in Table IV. At a weight loss of 5%, the temperatures of T-1[#] and T-2[#] are about 440°C, while those of C-1[#] and C-2[#] are about 490°C. The temperatures of C-1[#] and C-2[#] are about 50°C above those of T-1[#] and T-2[#]. The temperature of V-1[#] is 455°C and is between those of two kinds of PPS. The temperatures of C-1[#] and C-2[#] are about 20–30°C at a weight loss of 10% and about 10–20°C at a weight loss of 15% above those of T-1[#] and T-2[#]. Accordingly, the temperatures of V-1[#] are all between those of T-1[#] and T-2[#] and those of C-1[#] and C-2[#]. It can be concluded that the thermal stability of PPS with predominated terminal chloro groups is higher than that of PPS with predominated terminal thiohydroxy groups at a lower weight loss. The thermal stability difference of two kinds of PPS decreases as the weight loss increases and that of V-1[#], which was not endcapped, is between those of two kinds of PPS. It is shown that the terminal groups of PPS exert an important effect on the thermal stability of PPS at a lower weight loss and the

effect of terminal groups on the thermal stability decreases as the weight loss increases.

When the weight loss increases to 50%, the temperatures of T-1[#], T-2[#], V-1[#], and C-1[#] are about 600°C, but that of C-2[#] is 616°C and is obviously higher than those of the others. This can be explained as follows: C-2[#] possesses a greater viscosity and a higher molecular weight and the molecular weight exerts a main effect on the thermal stability of PPS at the higher weight loss.

The gelation times and apparent changes of two kinds of PPS and V-1[#] are listed in Table V. It can be seen that the gelation times of C-1[#], C-2[#], C-3[#], and C-4[#] are between 16 and 20 min and those of T-1[#], T-2[#], and T-3[#] are between 7 and 9 min. On the whole, the gelation time of PPS with terminal chloro groups is twice as long as that of PPS with

Table IV Temperatures (°C) of PPS at Different Weight Losses

Sample	C-1 [#]	C-2 [#]	T-1 [#]	T-2 [#]	V-1 [#]
5%	495	492	434	446	455
10%	514	513	490	485	503
15%	523	523	512	500	515
50%	598	616	603	597	605

Table V Gelation Times and Appearance Changes of Two Kinds of PPS and Ryton V-1[#]

Sample	Gelation Time	Virgin Appearance	Appearance Changed
C-1 [#]	16 min 34 s	White	Grayish brown
C-2 [#]	16 min 18 s	White	Grayish brown
C-3 [#]	18 min 4 s	White	Grayish brown
C-4 [#]	19 min 30 s	White	Grayish brown
T-1 [#]	7 min 20 s	Light yellow	Dark brown
T-2 [#]	8 min 44 s	Light yellow	Dark brown
T-3 [#]	7 min 34 s	Light yellow	Dark brown
V-1 [#]	10 min 2 s	Grayish yellow	Dark brown

terminal thiohydroxy groups. Hence, we may conclude that the curing of PPS with terminal thiohydroxy groups proceeds much faster than that of PPS with terminal chloro groups. For V-1[#], which was not endcapped, the gelation time is 10 min 2 s and is between those of two kinds of PPS. C-1[#], C-2[#], C-3[#], and C-4[#] changed from white to grayish brown, whereas T-1[#], T-2[#], T-3[#], and V-1[#] changed from light yellow or grayish yellow to dark brown. It may be that compared with terminal chloro groups terminal thiohydroxy groups are more active and are oxidized more easily and make PPS with terminal thiohydroxy groups change more quickly in appearance.

CONCLUSIONS

These investigations have shown that the method of preparing PPS with terminal chloro groups predominating and PPS with terminal thiohydroxy groups predominating using endcapping is feasible. Except for terminal group contents and appearance, the polymers prepared are similar to V-1[#] in structure, viscosity, and so on. Compared with PPS with terminal thiohydroxy groups predominating, PPS with chloro groups predominating possesses greater crystallinity, larger crystallite dimensions, a larger mean particle size, and a longer gelation time. Two

kinds of PPS are in the semicrystalline state. Terminal groups exert a main effect on the thermal stability of PPS at lower weight losses. On the other hand, the molecular weight of PPS may exert a main effect on the thermal stability of PPS at higher weight losses.

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