

Poly(phenylene Sulfide): Polymerization Kinetics and Characterization

C. R. RAJAN, S. PONRATHNAM, and V. M. NADKARNI,* *Polymer Science and Engineering Group, Chemical Engineering Division, National Chemical Laboratory, Pune-411 008, India*

Synopsis

The polycondensation kinetics of aromatic nucleophilic substitution on 1,4-dichlorobenzene by sodium sulfide has been investigated at 195°C in *N*-methyl pyrrolidone. The reaction follows second-order kinetics. The rate is bimodal with an initial slow rate till 50% conversion followed by a faster rate between 50 and 97% conversion. The specific reaction rates have been evaluated as $3.97 \times 10^{-3} \text{ L m}^{-1} \text{ s}^{-1}$ and $1.02 \times 10^{-2} \text{ L m}^{-1} \text{ s}^{-1}$ for the initial and later part (50–97%) of the reaction. The development of the degree of polymerization with reaction time was followed by end-group analysis and intrinsic viscosity measurements of polymer samples collected at different conversions. The reaction differs from conventional polycondensation reactions in two aspects. Polymer formation occurs at low conversions, and a significant amount of unreacted monomer is present even at very high conversions. Unlike other precipitation polymerization reactions, the polymer chain continues to grow even after precipitation.

INTRODUCTION

Poly(phenylene sulfide) (PPS) has gained considerable importance as a speciality polymer. It has excellent chemical resistance coupled with good thermal and mechanical properties at high temperatures.¹ The formation of PPS was first reported in the reaction of benzene, sulfur, and anhydrous aluminium chloride.² A material of similar chemical composition has also been observed to occur in the synthesis of diphenyl sulfide.^{3–6} The first systematic attempt at the synthesis of PPS is the investigation by Macallum⁷ of the reaction between 1,4-dichlorobenzene, sulfur, and sodium carbonate in the melt. Lenz et al. conducted a systematic study of the formation of PPS by the self-polycondensation of cuprous thiophenoxide.⁸ The application potential of PPS were also evaluated in these investigations.^{7,8}

A commercially viable process was developed at Phillips Petroleum (USA) in 1967. The Phillips process⁹ involves polycondensation of 1,4-dichlorobenzene and sodium sulfide in polar organic solvents at 265°C and at pressures in excess of 160 psi. The process details are described exclusively in patent literature. We have been investigating the reaction at lower temperature and pressure. In this communication, we report the kinetic features of the reaction in *N*-methyl pyrrolidone at 195°C and ≈ 30 psi. Results of preliminary characterization of the polymer conducted for investigating the buildup of the degree of polymerization with reaction time are also reported.

* To whom correspondence should be addressed.

MATERIALS AND EXPERIMENTAL

1,4-Dichlorobenzene (PDCB) obtained from M/s High Purity Chemicals (Delhi, India) was 99.9% pure. It was used as received. Sodium sulfide (SS) flakes obtained from M/s Poona Chemicals (Pune, India) were purified by standard methods, analysed and used.¹⁰ *N*-methyl pyrrolidone (NMP) obtained from M/s GAF Corp. (USA) was used as received. Analytical reagents such as sodium thiosulfate, iodine, and silver nitrate were of analytical reagent grade and were used without further purification.

The polycondensation experiments were conducted in a 650 mL stainless steel reactor fitted with a mechanical stirrer, thermowell, inlet-outlet valves, pressure gauge, and cooling coil. The reactor fitted into an external heater assembly connected to a temperature controller. The temperature of the reaction was controlled within $\pm 1^\circ\text{C}$ by the use of a thermocouple.

Appropriate quantities of the reactants were charged into the reactor. The reactions were allowed to proceed for predetermined times. The reaction time was counted from the time the temperature reached 195°C . After a predetermined reaction time, the heating was discontinued, the heater assembly was dismantled, and the reactor was cooled rapidly by passing cold water through the cooling coil. The cooling time to 100°C was approximately 10 min. The reactor contents were then poured into methanol to precipitate the polymer and sodium chloride formed. The slurry was stirred vigorously and filtered. The precipitate was washed with fresh methanol, dispersed in water to dissolve sodium chloride and filtered. The methanol and water solubles were quantitatively collected and analyzed by standard procedures^{10,11} for unreacted sodium sulfide and sodium chloride formed. The polymer was obtained as insolubles in methanol and water. It was dried in oven at 140°C for 4 h. Cyclic oligomers present in the polymer were extracted out with methylene chloride by soxhlet extraction for 16 h. Methylene chloride was distilled off to get the extractable as a buff-colored powder. The extractables were found to be 3.6–3.8 wt% of the dry polymer. The number-average molecular weight (\bar{M}_n) of the polymer formed at different conversions was determined by quantitative gravimetric analysis of the chlorine end groups as silver chloride.¹²

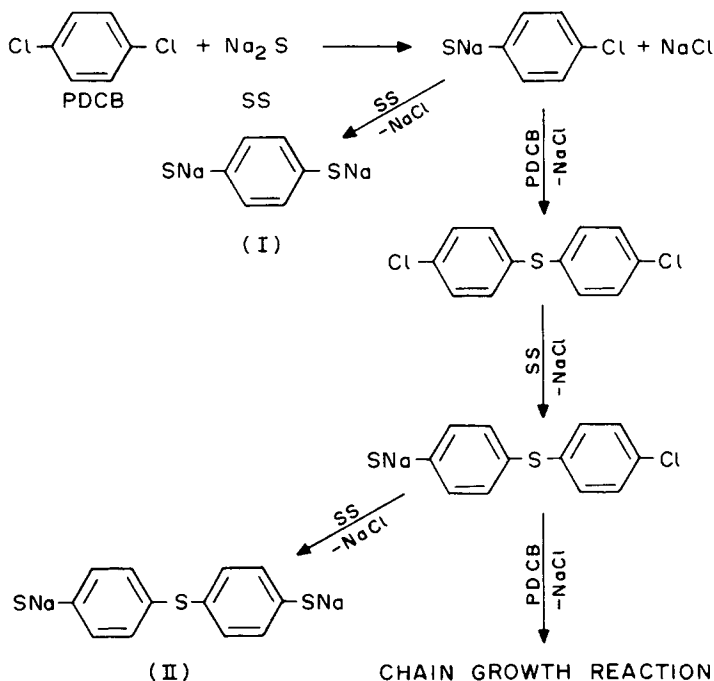
A modified Ubbelohde viscometer was used to determine the relative viscosity of 4 wt% solution of polymer in 1-chloro naphthalene at 195°C . The relative viscosity was used to monitor the change in the degree of polymerization with reaction time.

RESULTS AND DISCUSSION

The molar concentration of the two reactants PDCB and SS were kept constant in all the experiments. The molar ratio was kept nonstoichiometric with slight excess of PCDB to prepare polymers with chlorine end groups. Ideally, the rate of reaction can be determined by analyzing the rates of consumption of the reactants SS or PDCB or by the rate of formation of the side product, sodium chloride. The theoretical yield of sodium chloride that would be generated by complete conversion was assumed to correspond to twice the molar concentration of the deficient difunctional reactant, SS, in the feed. Unreacted SS was determined by volumetric titration of methanolic

and water solubles collected during the polymer isolation step. The consumption of PDCB was computed from chlorine analysis based on PDCB charged and sodium chloride formed. The consumption of SS and PDCB at different reaction times are plotted in Figure 1.

For the initial period of reaction up to 3 h the partial consumption of SS appears to be at a faster rate than that of PDCB. Referring to Figure 2, the reaction time of 3 h corresponds to 50% conversion. This implies the preferential occurrence of low molecular weight SNa terminated species such as I and II at low conversions as shown below. The course of the reaction could be described to fit the following scheme:



Beyond 50% conversion, the rates of consumption of the two reactants are comparable, indicating reaction of PDCB with SNa terminated species. It is also seen (Fig. 1) that, even at high conversions, a significant amount of unreacted SS is present in the system. This observation is different from the features of conventional polycondensation reactions. This could possibly be due to the solubility limitation of SS in NMP.

In the present polycondensation system, the first step is the formation of sodium *p*-chloro thiophenoxide, as indicated in the reaction scheme. This step is perhaps responsible for the initial slow rate in addition to the constraint posed by the limited solubility of SS in NMP.

The data on the overall rate and extent of reaction were computed from the amount of sodium chloride formed. These are reported in Table I and Figure 2 in terms of fractional conversion p defined as

$$p = \frac{\text{sodium chloride generated}}{\text{theoretical yield of sodium chloride}}$$

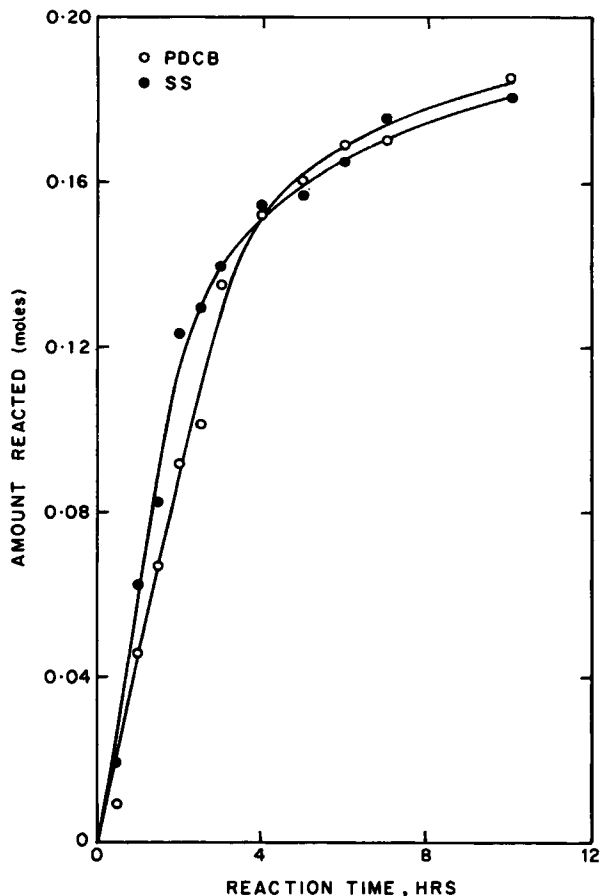


Fig. 1. Consumption of reactants as a function of reaction time: (○) PDCB; (●) SS.

The rate of formation of sodium chloride decreases gradually with reaction time and may be expressed by the initial rate. The experimental data were fitted to different rate order expressions. The data were found to fit the second order rate expression well over a wide range of conversions. This result is consistent with other reported kinetic investigations. Lenz⁸ et al. had investigated the formation of poly(phenylene sulfide) by the self-polycondensation of alkali metal salts of para halo thiophenoxide in pyridine at 250°C and found the reactions to follow the second order kinetics.

For polycondensation reactions of second order involving two different reactants, with identical initial concentration, the factor $1/(1 - p)$ should vary linearly with reaction time. Figure 3 depicts the plot of $1/(1 - p)$ vs. reaction time based on our data (Table II). The figure shows two regions of linearity. Up to a conversion of 50%, corresponding to a reaction time of 3 h, a slower rate is noted followed by a faster rate between 50 and 90% conversions. In the present investigation, the initial concentration of the two reactants were nonstoichiometric. In such cases, a second order kinetics is operational if a plot of $(1 + r)/(1 + r - 2rp)$ is linear with reaction time, where $r \leq 1$ is the mole ratio of the two reactants in the feed. The experi-

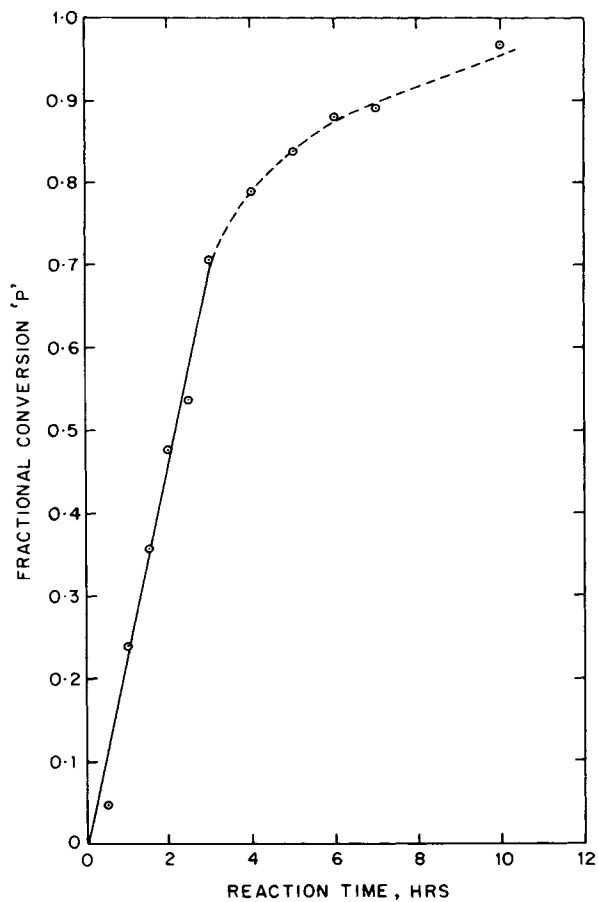


Fig. 2. Fractional polycondensation with time determined as rate of formation of sodium chloride.

TABLE I
Time Conversion Data^a

No.	Reaction time (min)	Sodium chloride formed (mol)	Fractional conversion p	Polymer yield (g)	Fractional yield ^b
1	30	0.0182	0.0474	0.59	0.0273
2	60	0.0922	0.2398	4.33	0.2001
3	90	0.1374	0.3572	6.21	0.2870
4	120	0.1836	0.4774	9.75	0.4506
5	150	0.2060	0.5357	10.72	0.4954
6	180	0.2714	0.7056	13.22	0.6109
7	240	0.3042	0.7911	16.63	0.7685
8	300	0.3220	0.8373	17.25	0.7971
9	360	0.3388	0.8809	19.05	0.8803
10	420	0.3410	0.8867	19.30	0.8919
11	600	0.3720	0.9673	20.90	0.9658

^a Temperature = 195°C, pressure = 30 psi, $[\text{NaCl}]_{\text{theor}} = 0.3846$ mol.

^b Based on theoretical yield of polymer = 21.64 g.

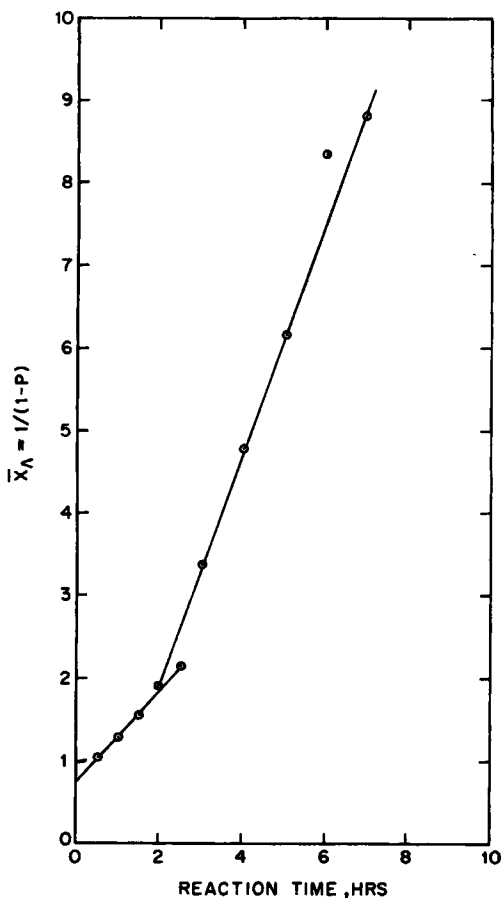


Fig. 3. Plot of the number-average degree of polymerization of poly(*p*-phenylene sulfide) as a function of reaction time.

TABLE II
Fitting Experimental Data^a

Time (min)	<i>p</i>	$1/(1 - p) = \bar{X}_n$	$\bar{X}_n = \frac{(1 + r)}{(1 + r - 2rp)}$
30	0.0474	1.0498	1.0482
60	0.2398	1.3154	1.3032
90	0.3572	1.5557	1.5304
120	0.4774	1.9135	1.8629
150	0.5357	2.1538	2.0823
180	0.7056	3.3967	3.1706
240	0.7911	4.7870	4.3021
300	0.8373	6.1463	5.3300
360	0.8809	8.3963	6.8816
420	0.8867	8.8261	7.1588

^a Temperature = 195°C, pressure = 30 psi, $p = [\text{NaCl}]/[\text{NaCl}]_{\text{theor}}$, $r = [\text{SS}]/[\text{PDCB}] = 0.9422$.

mental data reported in Table II fit a second order expression as shown in Figure 4. Again, the two regions of linearity, with a slower rate between 0 and 50% conversion followed by a faster rate, are noted. The data were subjected to regression analysis to get the rates. The two rates of polycondensation (evaluated as the rate of formation of sodium chloride) are reported below:

$$\text{rate} = 1.56 \times 10^{-4} \text{ m L}^{-1} \text{ s}^{-1}, \quad \text{up to 50\% conversion}$$

$$\text{rate} = 4.0 \times 10^{-4} \text{ m L}^{-1} \text{ s}^{-1}, \quad \text{from 50 to 90\% conversion}$$

The specific reaction rates are obtained as $3.97 \times 10^{-3} \text{ L m}^{-1} \text{ s}^{-1}$ and $1.02 \times 10^{-2} \text{ L m}^{-1} \text{ s}^{-1}$, respectively. The occurrence of varying rates at different conversions have been reported in the literature for nucleophilic polycondensation reactions. The reactions between alkali salts of aromatic diols and aromatic dihalides in dimethyl sulfoxide show two regions¹³ of second order kinetics.

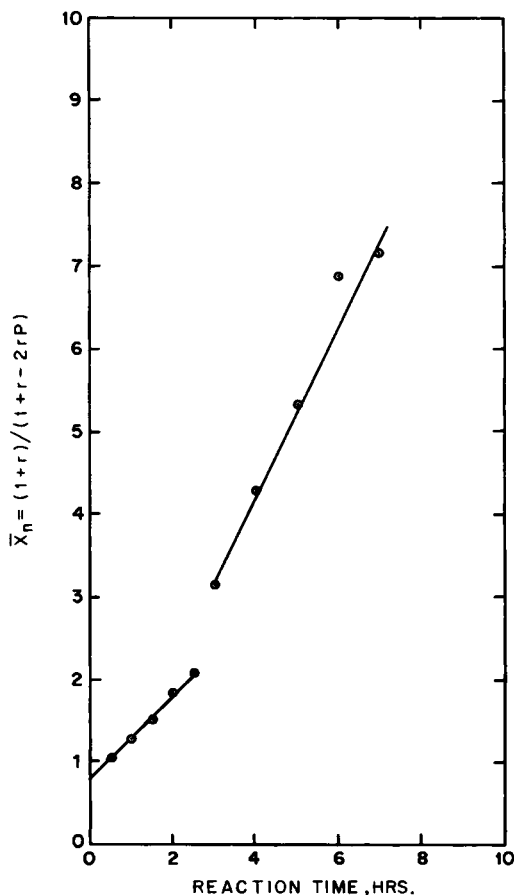


Fig. 4. Plot of \bar{DP}_n of poly(*p*-phenylene sulfide) as a function of reaction time plot, assuming stoichiometric nonequivalence between the two reactants 1,4-dichloro benzene and sodium sulfide.

MOLECULAR WEIGHT DEVELOPMENT

The yield of the polymer formed at different conversions were determined gravimetrically. Cyclic oligomers were separated by extraction with methylene chloride. The nature of cyclic products extracted compared with the reported structures.¹⁴ The reaction time-conversion data are presented in Table I. It could be seen that even for short reaction times of 30 and 60 min, corresponding to very low conversion, polymer is formed unlike conventional polycondensation reactions where the polymer is formed only at high conversions (above 90%). Also, the polymer yield is seen to increase with conversion. The percentage of chloro end groups present in the polymers were determined by elemental analysis (Table III). At complete conversion (100%), the polymer will be exclusively chlorine-terminated at both ends, as the reaction was conducted with excess PDCB. At lower fractional conversions SNa end groups will also be present. The relative ratio of chloro (X) and SNa (2-X) end groups and the empirical formula of the polymer at different experimental conversions were evaluated (Table III). The number-average degree of polymerization \overline{DP}_n and molecular weight of the polymer formed

TABLE III
Molecular Weight by End-Group Analysis

Reaction time (min)	Conversion fractional	End group		Chlorine % in polymer	\overline{DP}_n	\overline{M}_n
		-Cl	-SNa			
60	0.2398	1.0606	0.9394	3.99	8.25	919
120	0.4774	1.0751	0.9249	3.88	8.6	966
180	0.7056	1.1067	0.8933	1.91	18.5	2029
240	0.7911	1.1791	0.8209	2.14	17.3	1900
300	0.8373	1.2398	0.7602	1.76	21.3	2333
360	0.8867	1.2943	0.7057	1.47	26.7	2920
600	0.9673	1.8027	0.1973	1.26	38.2	4173

TABLE IV
Intrinsic Viscosity of PPS Formed at Different Conversions^a

Reaction time (min)	Polymer concn. (g/dL)	η_{rel}	$[\eta]^b$	$[\eta]^c$
60	4.12	1.181	0.0415	0.0416
120	4.08	1.398	0.0867	0.0871
180	4.08	1.527	0.1116	0.1115
240	3.36	1.373	0.0996	0.0998
300	4.11	1.599	0.1239	0.1234
360	4.02	1.618	0.1301	0.1295
420	4.00	1.620	0.1311	0.1306
600	3.95	1.629	0.1344	0.1338
Ryton*	4.07	1.855	0.1692	0.1669

^a $t_0 = 147.2$ s, solvent = 1-chloro naphthalene, temperature = 195°C.

^b $[\eta] = \sqrt{2/C} \cdot \sqrt{\eta_{sp} - \ln \eta_r}$.

^c $[\eta] = \frac{\eta_{sp}/C}{(1 + K\eta_{sp})}$, $K = 0.302$.

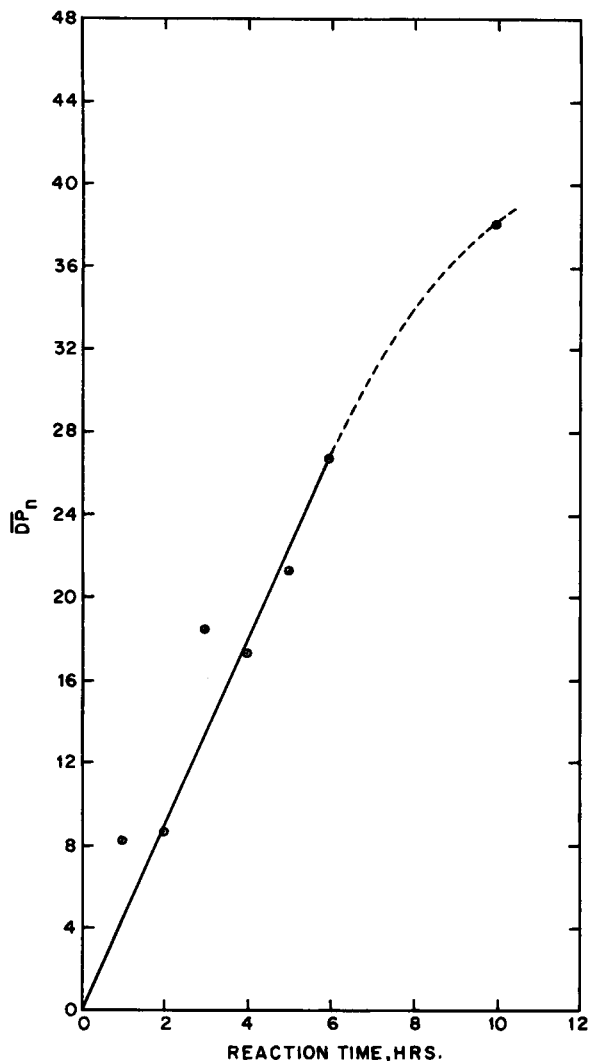


Fig. 5. \overline{DP}_n of poly(*p*-phenylene sulfide) formed as precipitate as a function of reaction time.

at different conversions were determined from the elemental analysis and the empirical formula of the polymer at the respective conversions. The \overline{DP}_n of the polymer formed (Table III) increases with reaction time and conversion (Fig. 5) but less dramatically than that observed as a general trend in polycondensation reactions. The overall number-average degree of polymerization at different conversions (p) for this system, with the molar ratio of the two reactants $r = 0.9422$, were calculated by using the expression

$$(\overline{DP}_n)_{\text{overall}} = \frac{(1 + r)}{(1 + r - 2rp)} \quad (1)$$

The \overline{DP}_n of the precipitated polymers at different conversions are much higher than the overall \overline{DP}_n (Table III and Fig. 4). In addition, unreacted

SS is present at conversions as high as 96%, indicating the occurrence of a wide molecular weight distribution in the system.

The intrinsic viscosity $[\eta]$ of the polymers formed at different conversions were calculated from single point relative viscosity measurements of 4% (by weight) solutions in 1-chloro naphthalene at 195°C using the following relationships^{15,16}:

$$[\eta] = \frac{\eta_{sp}/C}{(1 + K\eta_{sp})} \quad (2)$$

$$[\eta] = \frac{\sqrt{2}}{C} \sqrt{\eta_{sp} - \ln \eta_r} \quad (3)$$

where $K = 0.302$, η_r = relative viscosity, η_{sp} = specific viscosity ($\eta_r - 1$), and C = polymer concentration in g/dL. The relationships (2) and (3) are generally valid for very dilute (<0.5 wt%) polymer solutions. The polymers obtained in the present investigations were all oligomers with a degree of polymerization less than 40. Hence the relationships were found valid even at high polymer concentration in the present system (Table IV). The intrinsic

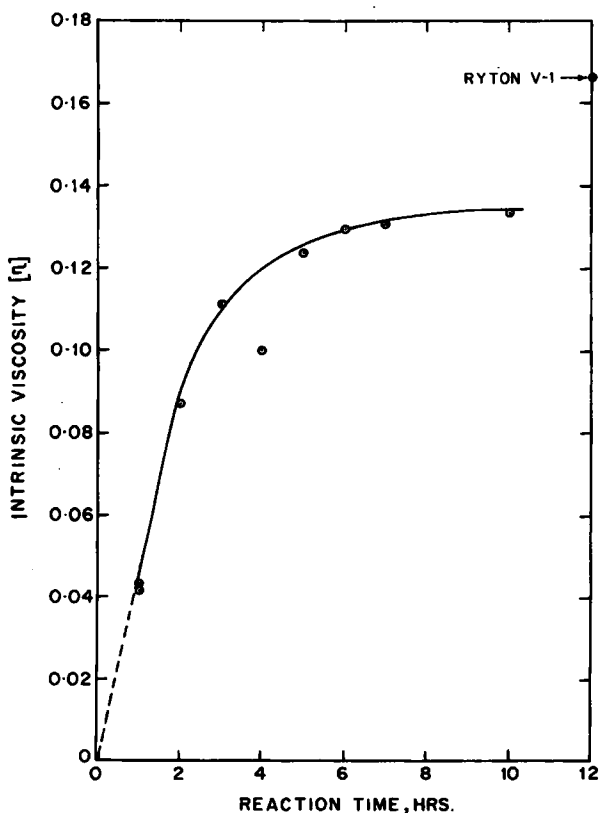


Fig. 6. Intrinsic viscosity of polymer formed at different conversions. Industrial grade PPS (Ryton) shown for comparison.

viscosity (η) of the polymer formed at different conversions increases initially and tends to level off after a reaction time of 6 h. However, the number average molecular weight as determined by the end group analysis continues to increase beyond the reaction time of 6 h (Table III). In this system the polymer precipitates out of the system once a critical molecular weight is obtained. The polymer molecular weight, thus, keeps on building up with reaction time even after precipitation. This could be either due to solvation of the growing end of the polymer or the occurrence of polymerization on the solid surface of the precipitated polymer. This behavior is dissimilar to other precipitation systems like polycarbonates where the polymer ceases to grow after precipitation.

The molecular weight of poly(phenylene sulfide) can be enhanced by controlled thermal treatment. Thus the intrinsic viscosity of the commercial sample (Ryton V-1) is much higher (Table IV). This molecular weight enhancement is also noted in our samples. Thus further polymerization can indeed take place in this system even after precipitation.

CONCLUSIONS

Poly(*p*-phenylene sulfide) was prepared by the polycondensation of 1,4-dichlorobenzene and sodium sulfide in *N*-methyl pyrrolidone at 195°C. The reaction rate is bimodal. The initial slower rate is followed by a faster rate after 50% conversion. The slow initial rate could be partially attributed to the limited solubility of sodium sulfide in *N*-methyl pyrrolidone. Therefore, the condensation reaction appears to be initiation rate controlled in the initial period, followed by propagation rate control. The overall rate follows second order.

The reaction diverges from conventional polycondensation reactions. Polymer is formed at very low conversions, and a significant amount of reactant is present even at very high conversions.

The polymer precipitates out during the reaction. The polymer chain continues to grow further even after precipitation.

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