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Polymerization Kinetics and Characterization of a Poly(phenylquinoxaline)

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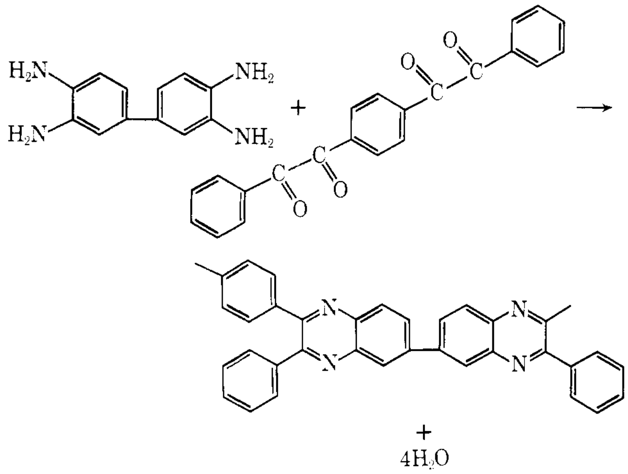
ABSTRACT: The polymerization of a poly(phenylquinoxaline) was studied in *m*-cresol solution at 25° and the polymerization products were characterized using dilute solution techniques. The polymerization is a second order condensation reaction catalyzed by *m*-cresol. Unusually high molecular weight polymers with broad molecular weight distributions are produced. The data are interpreted in terms of a polymer chain branching model—a polydisperse polymer with random, trifunctional branching and a large primary chain length. It is proposed that branch formation occurs during the early stages of polymerization and becomes increasingly more probable as reactant concentrations are raised. The principle cause of branching is thought to be partial failure of quinoxaline ring closure. For different molecular weight samples prepared from 5 wt % monomers, the calculated branching frequency is relatively constant with 1 branch unit/180 ± 10 chain units. Unperturbed chain dimensions are calculated and indicate an apparent flexibility which may be more a consequence of structural isomerism than rotational mobility.

In recent years the syntheses of a number of poly(phenylquinoxalines) have been reported.[1-7] These polymers have been prepared both in the melt and in solution by cyclocondensation of aromatic tetraamines with aromatic tetracarbonyls. The quinoxaline-forming reaction gives nearly quantitative yields of high molecular weight polymers. These polymers have inherently high glass transition temperatures[8] and high thermal and oxidative stabilities.[9] Unlike nonphenylated polyquinoxalines, poly(phenylquinoxalines) have good solubility in a number of halogenated and phenolic solvents and should therefore lend themselves to investigation by conventional solution techniques.

Poly[2,2′-(1,4-phenylene)-6,6′-bis(3-phenylquinoxaline)] (PPQ) is representative of this class of polymers and is prepared by reacting 3,3′-diaminobenzidine with 1,4-bis(phenylglyoxaloyl)benzene. This step-growth reaction is essentially irreversible as suggested by the resistance of PPQ to hydrolysis. When high monomer concentrations (>15 wt %) or elevated temperatures (>200°) are used during polymerization, the product is oftentimes insoluble. PPQ is a tough, amorphous, yellow polymer which is thermally stable (to 570° in air)[9] and has a glass transition at 372°.[8]



In this paper the polymerization kinetics of PPQ in *m*-cresol solution are investigated. In order to gain a better understanding of the polymer's structure and of the effect of polymerization conditions on polymer structure, PPQ was synthesized under a variety of conditions and characterized in *m*-cresol using dilute solution techniques. To produce soluble polymers, monomer concentrations ranging from 0.1 to 7 wt % were used in preparing the polymers and initial reaction temperatures were maintained at 25°.

Experimental Section

Polymer Preparation. The monomers for this study were furnished by Dr. J. M. Augl of the Naval Ordnance Laboratory, White Oak, Silver Spring, Md. The monomers were subjected to melting point analysis, differential scanning calorimetry, elemental analysis, and infrared and uv-visible spectroscopy for determination of monomer purity. No monomer impurities could be detected using these techniques. The uncorrected melting point ranges were 174–176° (lit.[10] mp 179–180°) for 3,3′-diaminobenzidine (DAB) and 120–122° (lit.[11] mp 125–126°) for 1,4-bis(phenylglyoxaloyl)benzene (PGB). The elemental analyses of DAB (C, 66.96; H, 6.68; N, 26.33) and of PGB (C, 76.78; H, 4.16) were in

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(1) P. M. Hergenrother and H. H. Levine, *J. Polym. Sci., Part A-1*, **5**, 1453 (1967).

(2) P. M. Hergenrother, *J. Polym. Sci., Part A-1*, **6**, 3170 (1968).

(3) W. Wrasidlo and J. M. Augl, *J. Polym. Sci., Part B*, **7**, 281 (1969).

(4) P. M. Hergenrother and D. E. Kiyohara, *Macromolecules*, **3**, 387 (1970).

(5) W. Wrasidlo and J. M. Augl, *J. Polym. Sci., Part A-1*, **7**, 3393 (1969).

(6) W. Wrasidlo and J. M. Augl, *J. Polym. Sci., Part B*, **8**, 69 (1970).

(7) W. Wrasidlo and J. M. Augl, *Macromolecules*, **3**, 544 (1970).

(8) W. Wrasidlo, *J. Polym. Sci., Part A-2*, **9**, 1603 (1971).

(9) W. Wrasidlo, *J. Polym. Sci., Part A-1*, **8**, 1107 (1970).

(10) H. Vogel and C. S. Marvel, *J. Polym. Sci.*, **50**, 511 (1961).

(11) J. Schmitt, P. Comoy, J. Boitard, and M. Suguet, *Bull. Soc. Chim.*, 636 (1956).

Table I
Poly(phenylquinoxalines)

Sample	Concn (Monomer mol/l.)	Polymerizn Condns	Terminal (25°) Soln Viscosity (cSt) η	Terminal (25°) Inherent Viscosity η_{inh}(dl/g)
S1	0.005	2 weeks at 25°	13.6	0.3
S2	0.20	1.3 hr at 25°	201	0.57
S3	0.20	6 hr at 25°	374	0.69
S4	0.20	1 day at 25°	1030	0.90
S5	0.20	6 hr at 25° 1 hr at 90°	1440	0.97
S6	0.30	6 hr at 25° 1 hr at 90°	>8160	>0.86
S7	0.20	3 days at 25°	1900	1.03
S8	0.20	6 hr at 25° 1 hr at 90°	4300	1.20
S9	0.04	3 days at 25°	32.2	0.93

good agreement with the theoretical values (C, 67.26; H, 6.59; N, 26.17) and (C, 77.19; H, 4.09), respectively. On the basis of this information, the maximum concentration of monomer impurity would be about 1:100. The solvent *m*-cresol (Fisher Spectroanalyzed) was purified by reduced pressure distillation (bp 97–99° (13 mm)).

A series of polymers were prepared by mixing equal volumes (10 ml) of *m*-cresol solutions of the monomers in a 1:1 stoichiometric ratio. Monomer concentrations ranged from 0.1 to 7 wt % and are reported as molarity in Table I. Reaction times and temperatures were also varied. The polymerizations were conducted in a thermostated, 100-ml round-bottom flask with continuous stirring and under an argon atmosphere. To measure extents of reaction in the viscometric rate studies, the procedure was altered. After vigorously stirring the reactants for 1 min the reaction solution was swiftly transferred to an Ubbelohde viscometer where effluxing provided adequate mixing and an argon atmosphere was maintained over the solution. Inherent viscosities η_{inh} calculated from terminal solution viscosities are given in Table I.

At the concentrations and temperatures employed in this study, the monomers and polymer were soluble throughout the polymerization. Reactions were terminated by dilution with chloroform followed by precipitation with methanol. The precipitated polymers were filtered, then washed with several portions of hot methanol and dried overnight in a vacuum oven at 60°. However, according to thermal gravimetric analysis, residual *m*-cresol (*ca.* 10 wt %) was retained in the samples and could be eliminated only after heating above 200°. But drying the polymer at elevated temperatures alters the structure of PPQ as is indicated by an increased intrinsic viscosity. To correct polymer solution concentrations for dilute solution studies, a portion of each sample was subjected to thermal gravimetric analysis to ascertain *m*-cresol (and water) content.

Initially attempts were made to prepare and characterize PPQ in chloroform solution. However the monomers and polymer were poorly soluble. Polymer was lost on filters, viscosity determinations gave anomalously large Huggins constants, and extremely large molecular weights were obtained by osmometry. This suggested that PPQ forms a gel phase in chloroform even at low concentrations (<0.1 g/dl). No gel phase was detectable for the polymer in *m*-cresol at the concentrations used in this work.

Kinetics Study. A Beckman Model DK 1A spectrophotometer with matched 1-cm cells was used to study the rate of polymerization of 0.005 *M* solutions at 25°. The quinoxaline ring has a characteristic absorption in the visible spectrum (*ca.* 390–406 mμ). At timed intervals 0.1-cm^3 aliquots were removed from the reaction solution and diluted to 10 ml with *m*-cresol. Dilution reduced the polymerization rate to such an extent that the reaction was essentially quenched. The spectra were then scanned and absorption maxima *A* were recorded as a function of reaction time τ. Identical techniques were used to determine the rate of formation of the model compound 2,3-diphenylquinoxaline prepared from stoichiometric amounts of *o*-diaminobenzene and benzil in *m*-cresol at 25°.

For more concentrated reaction solutions (>1 wt %), the rate of polymerization was too rapid for reliable spectrophotometric analysis. In these cases the polymerization was monitored by measuring the change in viscosity of the reaction solution with time. Ubbelohde viscometers with 8-ml bulbs and capillary constants of 0.0993 cSt/sec for 0.04 *M* solutions and 4.562 cSt/sec for 0.20 *M* solutions were used. The viscometers were suspended in a thermostated bath at 25 ± 0.02° and a Hewlett-Packard autoviscometer continuously effluxed and recorded solution flow times. Viscosities are plotted as a function of reaction time in Figure 1. The viscometric technique was limited to solutions with <7 wt % monomers since adequate mixing could not be provided for more concentrated solutions.

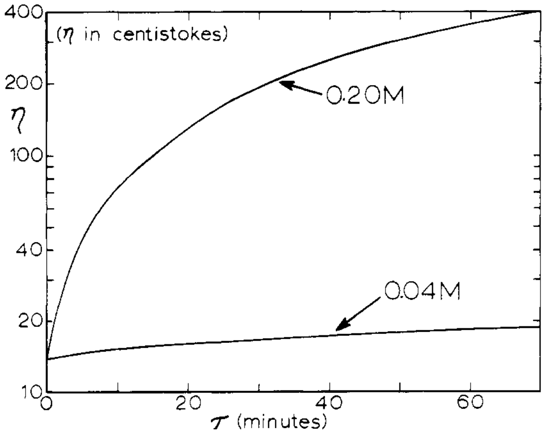

Figure 1. Polymerization of PPQ in *m*-cresol at 25°.

Characterization Techniques. A Hewlett-Packard autoviscometer operated with Cannon-Ubbelohde dilution viscometers was employed in intrinsic viscosity determinations. The temperature was controlled at 40 ± 0.02° and solvent efflux times were sufficiently long to justify neglecting kinetic energy corrections. Intrinsic viscosities were calculated by a least-squares computer program from the Huggins[12] and Kraemer[13] relations

$$\eta_{sp}/C = [\eta] + k'[\eta]^2C \tag{1}$$

$$\frac{\ln \eta_r}{C} = [\eta] - k''[\eta]^2C \tag{2}$$

where η_{sp} and η_r are the specific and relative viscosities, respectively. Huggins constants were in the range $0.38 < k' < 0.45$ expected for well-behaved polymer solutions.

A Hewlett-Packard Model 501 high-speed membrane (gel cellophane 600) osmometer was used to measure osmotic pressures at 37°. Osmometry data were evaluated using

$$(\pi/C)^{1/2} = (\pi/C)_0^{1/2}[1 + (A_2M_nC/2)] \tag{3}$$

where the number-average molecular weight $M_n = RT/(\pi/C)_0$, π is the osmotic pressure, T is the absolute temperature, R is the corrected gas constant, and A_2 is the second virial coefficient.

A Model 701 Sofica instrument, operated at 40° with unpolarized light of wavelength 5461 Å, was used to measure scattered light intensities at angles from 30 to 150°. The instrument was calibrated with benzene ($R_B = 16.3 \times 10^{-6}$), and a glass working standard was checked prior to each measurement to maintain the calibration. The average value of the refractive index increment as determined using a Brice-Phoenix differential refractometer was $(\partial n/\partial C) = 0.30$ ml/g. No fluorescence correction was necessary; however a small correction for absorption was required since the molar absorptivity for PPQ at 5461 Å is ϵ 0.032 l. cm^{-1} g^{-1}. The intensity of scattered light was corrected for absorption by

$$I_{cor} = I_{obsd}e^{\epsilon bC} \tag{4}$$

where b is the light-scattering cell diameter and C is the polymer solution concentration. Zimm plots were constructed to evaluate the weight-average molecular weight M_w, second virial coefficient B_2, and *z*-average radius of gyration $\langle S^2\rangle_z^{1/2}$. The second virial coefficients in Table II have units of (ml mol)/g^2.

Results and Discussion

Polymer Characterization. Osmometry and light-scattering data in Table II suggest that PPQ is not a simple,

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[12] M. L. Huggins, *J. Amer. Chem. Soc.*, 64, 2716 (1942).

[13] E. O. Kraemer, *Ind. Eng. Chem.*, 30, 1200 (1938).

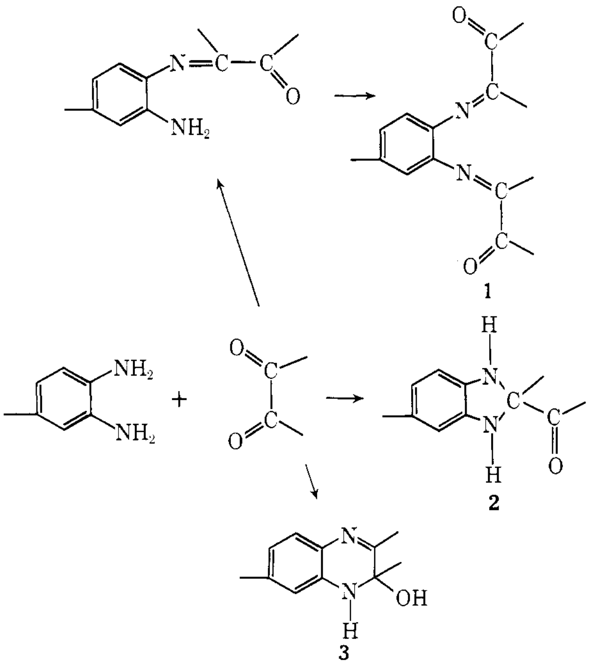
Table II
Dilute Solution Parameters

Sample	$[\eta]$ (dl/g)	M_n (10^{-4})	A_2 (10^4)	M_w (10^{-4})	B_2 (10^4)	$\langle S^2\rangle_z^{1/2}$ (Å)
S1	0.29	0.61		1.1	20	
S2	0.72	1.4	25	4.4	22	310
S3	1.01	2.1	13	7.2	16	390
S4	1.43	2.7	18	14	12	400
S5	1.83	3.0	20	17	15	410
S6	1.91	3.0	16	18	7.0	430
S7	1.90	3.2	22	26	4.1	460
S8	2.62	3.5	13	35	1.6	520

linear polymer molecule. For linear, condensation polymers the molecular weight ratio M_w/M_n should be no greater than 2. For flexible, linear polymers $\langle S^2\rangle_z^{1/2}$ should be at least proportional to the square root of the molecular weight. However, as indicated in Figure 2, $\langle S^2\rangle_z^{1/2} = 33M_w^{0.21}$. And since polydispersity increases with molecular weight, the low molecular weight exponent cannot be attributed to the molecular weight distribution.

Polymer chain branching would explain the experimental results. Although quinoxaline ring formation should be favored due to resonance stabilization, trifunctional and to a lesser extent tetrafunctional branching might occur during polymerization. A number of intermediates to branch formation may be proposed (see Scheme I). Under the rather mild reaction conditions, benzimidazoline formation 2 does not seem plausible. Branch formation *via* intermediate 3 involves reaction of the protonated nitrogen with an available carbonyl. However the short lifetime of 3 probably precludes branching. Analogous to the poly(phenyl-*as*-triazines),[14] a gradual decrease in the inherent viscosity of PPQ in concentrated sulfuric acid is observed over a period of several days. This behavior suggests that 1 is the most likely intermediate to branch formation since -C=N- is susceptible to acid hydrolysis.

Scheme I



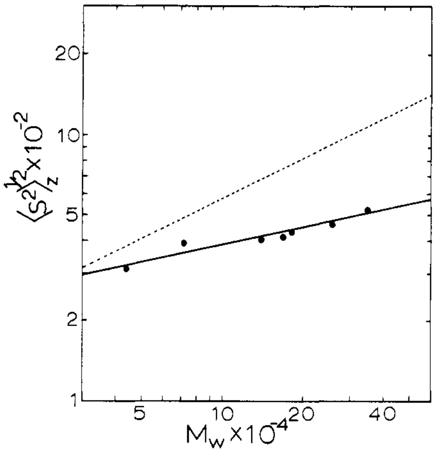
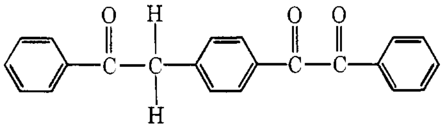


Figure 2. Logarithmic plot of $\langle S^2\rangle_z^{1/2}$ *vs.* M_w: (●) experimental data, (- - -) calculated values for linear PPQ.

The presence of monomer impurities may also cause branching. For instance, the preparation of PGB[15] includes an oxidation step which, if incomplete, could give rise to impurities such as



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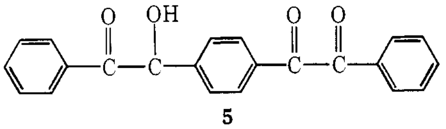
or



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Incomplete nitration of benzidine or reduction of dinitrobenzidine could also cause impurities to be present in DAB. However the monomers were extensively purified and, as mentioned previously, the level of monomer impurities is relatively low and probably does not exceed 1:100.

Since branch units could not be detected by ordinary analytical technques, there are probably relatively few branches in PPQ. If either tetrafunctional or trifunctional branching were prevalent, gelation would have been observed during polymerization. But high extents of reaction were achieved with no insoluble material produced. In addition, if the polymers were highly branched, an appreciable reduction in chain dimensions might be expected. As a consequence the exponent *a* in the Mark-Houwink relation could have a value less than 0.5, especially when determined using $[\eta] - M_w$ data. However $a = 0.63$ and $\langle S^2\rangle_z^{1/2}$ was measurable for PPQs with relatively low degrees of polymerization which further suggests that the branching density is probably not very large.

$$[\eta] = KM_v^{\,a} \qquad (5)$$

Chain Structure. To evaluate the extent of branching from dilute solution data, it is advisable to have well-characterized fractions of the branched polymer to compare with fractions of the corresponding linear polymer. Unfortunately, PPQ was not fractionated and a linear polymer is not available for comparison. However Shultz[16] provides a branching model which most likely represents the type of branching present in PPQ and which can be utilized to estimate the extent of branching in terms of the branching parameter γ. A polydisperse polymer with random, trifunctional branching and a large primary chain length is selected as the branching model.

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(14) P. M. Hergenrother, *Poly. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 13, 930 (1972).

(15) W. Wrasidlo and J. M. Augl, *J. Polym. Sci., Part B*, 7, 281 (1969).

(16) A. R. Shultz, *J. Polym. Sci., Part A*, 3, 4211 (1965).

Table III
Poly(phenylquinoxaline) Branching Parameters

Sample	$\bar{x}_w$	$\bar{x}_w/\bar{x}_n$	γ	$\bar{y}_n$	B_n	B_w	N/X (10^3)
S1	45	1.8					
S2	180	3.1	0.45	50	0.35	1.6	5.9
S3	300	3.5	0.53	71	0.44	2.3	5.1
S4	580	5.2	0.71	84	0.63	4.9	5.7
S5	700	5.7	0.74	91	0.66	5.7	5.3
S6	750	6.0	0.75	93	0.67	6.0	5.3
S7	1070	8.1	0.82	96	0.75	9.1	5.7
S8	1450	10	0.86	99	0.81	12	5.6

In Shultz's formulation a random or "most probable" distribution of linear chains is assumed. That is, the assumed distribution is that which would be obtained by replacing every two trifunctional branch producing monomers by three nonbranching monomers. The ratio of weight- to number-average number of units per chain in the primary distribution is then $\bar{y}_w/\bar{y}_n = 2$, where

$$\bar{y}_n = \bar{x}_n[1 - (\gamma/3)] \tag{6}$$

$$\bar{y}_w = \bar{x}_w(1 - \gamma) \tag{7}$$

The weight- and number-average degrees of polymerization are $\bar{x}_w = M_w/M_0$ and $\bar{x}_n = M_n/M_0$, respectively, with the chain unit molecular weight $M_0 = 242$ g/mol.

In principle γ may be determined for the branched polymer from its molecular weight ratio M_w/M_n

$$\gamma = (M_w/M_n - 2)/(M_w/M_n - {}^2/_3) \tag{8}$$

In applying eq 8 it is assumed that γ depends only on M_w/M_n and that there is no deviation from Shultz's distribution function. It follows from Shultz[16] that the number- and weight-average number of branched monomer units per polymer molecule are

$$B_n = \frac{2\gamma}{3[1 - \gamma/3]} \tag{9}$$

$$B_w = 2\gamma/(1 - \gamma) \tag{10}$$

the branching frequency or number of branch units N per total number of units X in the polymer is then

$$N/X = B_n\sqrt{\bar{x}_n} = (4/3)[\gamma/(1-\gamma)](1/\bar{x}_w) \tag{11}$$

Calculated values in Table III indicate that the branching frequency is relatively low and the primary chain length $\bar{y}_n$ is large. A large primary chain length was assumed in the chain model, but the low branching frequency is consistent with empirical observations. It is significant that γ increases uniformly with $\bar{x}_w$ and that the branching frequency remains relatively constant, $N/X = (5.5 \pm 0.4)10^{-3}$.

The light-scattering second virial coefficient B_2 and weight-average number of branches per molecule are compared in Figure 4. The branching parameter shows the following dependence on molecular weight

$$B_w = 2.9 \times 10^{-5}M_w \tag{12}$$

whereas B_2 declines precipitously as M_w increases above 1×10^5. Polymer solubility is apparently a function of the number of long chain branches rather than branching frequency, since N/X is relatively constant.

Still relying on the chain branching model, radii of gyration $\langle S^2\rangle_{z,L}^{1/2}$ and intrinsic viscosities $[\eta]_L$ of linear PPQ may be estimated from the respective experimental values of the branched polymers. Additionally, it is assumed that the linear polymers have the same total molecular weight as the branched polymers. According to Zimm and Stockmayer[17]

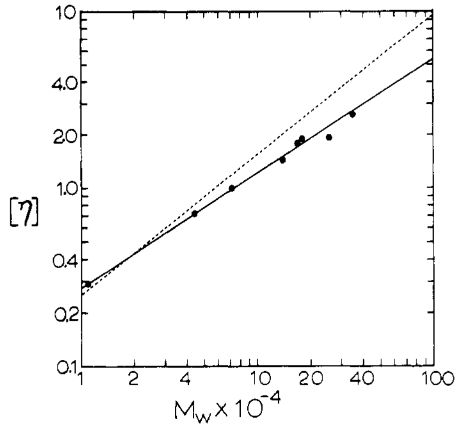

Figure 3. Mark-Houwink plot: (●) experimental data, (- - -) calculated values for linear PPQ.

$$\langle S^2\rangle_{z,L} = \langle S^2\rangle_z/\langle g\rangle_z \tag{13}$$

where $\langle g\rangle_z = (1 + B_w/3)^{-1}$. The mean-square radius of gyration for linear PPQ (Figure 2) is directly proportional to the molecular weight, $\langle S^2\rangle_{z,L} = 2.0M_w$, as expected for flexible, linear polymers. However this result is tentative in discussing polymer chain configuration since information is lacking regarding z-average molecular weights and polymer-solvent interactions of linear PPQ.

The intrinsic viscosity of the linear polymer may be calculated using the Zimm-Kilb expression[18]

$$[\eta]_L = [\eta]/g_w^{1/2} \tag{14}$$

where

$$g_w = \frac{6}{B_w}\left[\frac{1}{2}\left(\frac{2+B_w}{B_w}\right)^{1/2} \ln\left(\frac{(2+B_w)^{1/2} + B_w^{1/2}}{(2+B_w)^{1/2} - B_w^{1/2}}\right) - 1\right]$$

Calculated values are plotted in Figure 3 and the following relation is obtained for linear PPQ

$$[\eta]_L = 2.3 \times 10^{-4}M_w^{0.76} \tag{15}$$

as compared to the relation for the branched polymer

$$[\eta] = 8.6 \times 10^{-4}M_w^{0.63} \tag{16}$$

The large molecular weight exponent for linear PPQ is indicative of a somewhat expanded chain structure in m-cresol.

The unperturbed dimensions of linear PPQ may be estimated from eq 15 using the Stockmayer-Fixman expression[19]

$$[\eta]/M^{1/2} = K_\theta + 0.51\Phi_\theta BM^{1/2} \tag{17}$$

where $K_\theta = [\eta]_\theta/M^{1/2}$, $[\eta]_\theta$ is the intrinsic viscosity and $\Phi_\theta \approx 2.6 \times 10^{-3}$ dl mol^{-1} Å^{-3} is the viscosity constant of the polymer in a Θ solvent,[20] and B is constant for a given polymer-solvent system. The values $K_\theta = 2.13 \times 10^{-3}$ and $B = 6.3 \times 10^{-3}$ are determined by plotting $[\eta]_L/M_w^{1/2}$ *vs.* $M_w^{1/2}$. The characteristic ratio for PPQ is then

$$\langle R^2\rangle_0/M = (K_\theta/\Phi_\theta)^{2/3} = 0.88 \tag{18}$$

where $\langle R^2\rangle_0$ is the unperturbed mean-square end-to-end distance and the unperturbed effective bond length is

(17) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).

(18) B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, **37**, 19 (1959).

(19) W. H. Stockmayer and M. Fixman, *Ann. N. Y. Acad. Sci.*, **57**, 334 (1953).

(20) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience-Wiley, New York, N. Y., 1969.

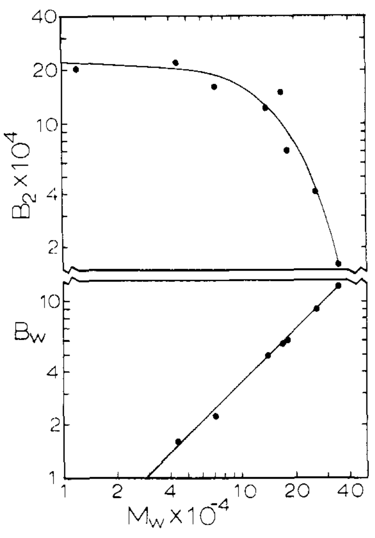

Figure 4. Dependence of the second virial coefficient B_2 and the weight-average number of branched units B_w on M_w.

$$b_0 = (\langle R^2\rangle_0/n)^{1/2} = 15 \text{ Å} \tag{19}$$

with $n = 3M/2M_0$ as the number of backbone virtual bonds. Due to sample polydispersity, $\langle R^2\rangle_0/M$ and b_0 may be slightly underestimated.

The unperturbed chain dimensions of linear PPQ may also be predicted by assuming a hypothetical chain model. The chain has n virtual bonds of length $l = 9.3$ Å joined at fixed bond angle $\theta = 60°$ (Figure 5). Assuming free rotation statistics, the unperturbed mean-square end-to-end distance is[20]

$$\langle R^2\rangle_0 = nl^2\left(\frac{1 + \cos\theta}{1 - \cos\theta}\right) = 259\ n\text{Å}^2 \tag{20}$$

which gives $b_0 = 16$ Å and $\langle R^2\rangle_0/M = 1.1$. These values are slightly larger than the experimentally based values. This result may partly be a consequence of the presence of structural isomers (Figure 5). If equally probable, the structural isomers may create chain configurations similar to those generated by free rotation.

It is also possible to predict the polymer expansion factor α and second virial coefficient A_2' of linear PPQ from eq 15. The expansion factor is related to molecular weight through the ratio of intrinsic viscosities in m-cresol and in a Θ solvent at the same temperature[21]

$$\alpha^{2.43} = [\eta]_L/[\eta]_\theta = 0.11M_w^{0.26} \tag{21}$$

The calculated α value may then be used to estimate A_2' using[22]

$$A_2' = ([\eta]_L/M_w)188 \ln[1 + 0.886(\alpha^2 - 1)] \tag{22}$$

The average value $A_2' = 1.6\ (\pm 0.2) \times 10^{-3}$ is in close agreement with osmometry and light-scattering second virial coefficients of polymers having fewer than five branch units.

Polymerization Kinetics. The polymerization kinetics in dilute (0.005 M) m-cresol solutions were studied using the spectrophotometric technique. The extent of reaction ρ is equal to the ratio of absorbances A/A_∞, where A_∞ is the absorbance at infinite reaction time ($\rho = 1$). The number-average degree of polymerization is

$$\bar{x}_n = 1/(1 - \rho) \tag{23}$$

The polymerization is second order and the rate constant

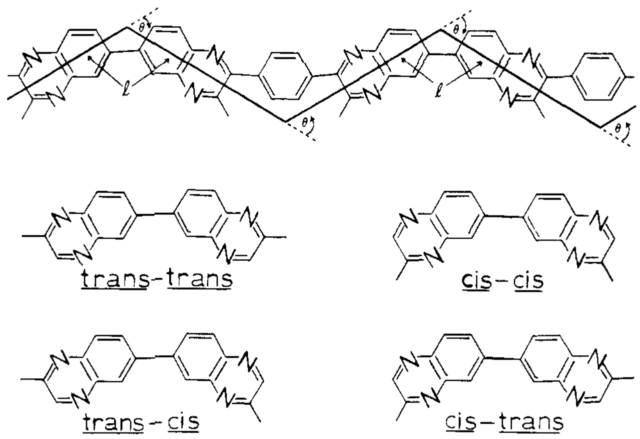

Figure 5. Hypothetical chain model for linear PPQ and structural isomers.

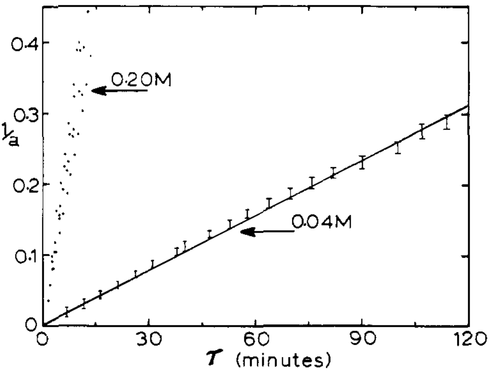

Figure 6. The relationship between $[\eta]^{1/a}$ and reaction time τ for second-order polymerization kinetics.

$$k_2 = \frac{1}{C_0}\frac{\mathrm{d}(\bar{x}_n)}{\mathrm{d}\tau} = 13.3M^{-1}\text{ min}^{-1} \tag{24}$$

has an unusually large value for a condensation polymerization. To ascertain whether polymer chain structure (*e.g.*, chain stiffness and branching) is an important rate contributing factor, the kinetics for the formation of 2,3-diphenylquinoxaline was investigated. The formation of this model compound was also second order and the constant $k_2 = 11.1\ M^{-1}$ min^{-1} was only slightly smaller than the PPQ value. Consequently, the large rate constant does not result from the structure of the polymer chain, but rather is inherent in the formation of the quinoxaline ring in m-cresol. Since acidic solvents are known to catalyze benzaldehyde phenylhydrazone formation,[23] the solvent m-cresol could be catalyzing the polymerization. The catalytic influence of m-cresol is also indicated when the polymerization reaction is examined in less acidic solvents. For example, the rate constant is much smaller, $k_2 \approx 0.15$ M^{-1} min^{-1}, when calculated from data obtained with chloroform as the solvent.[5]

The viscometric method was used to follow the polymerization reaction of more concentrated solutions (>0.04 M). Solution efflux times t were recorded as a function of reaction time τ and converted to intrinsic viscosities using the Kraemer relation[13]

$$[\eta] = \frac{1 - \sqrt{1 - 4k'' \ln(t/t_0)}}{2k''C_0} \tag{25}$$

where t_0 is the solvent efflux time, $k'' = 0.14$ is the average value of the Kraemer constant (eq 2), and C_0 is the initial monomer concentration in g/dl. For a second-order

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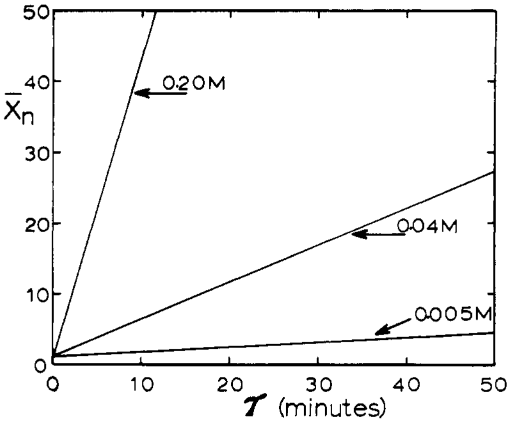

Figure 7. The number-average degree of polymerization x_n *vs.* reaction time τ.

reaction the molecular weight is proportional to $[\eta]^{1/a}$ with a as the exponent from eq 5 (Figure 6). If it is assumed that no significant branching occurs in the initial stage of reaction and $M_w \approx M_v$, then $a = 0.76$ and $K = 2.3 \times 10^{-4}$. To evaluate rate constants a most probable distribution $M_w/M_n \approx 1 + \rho$ is assumed within the primary region of data interpretation; *i.e.*, $0 < [\eta] < 0.5$ dl/g. Branching should not raise the ratio M_w/M_n much above 2 since $M_w < 24{,}000$ in this region. Consequently, the number-average degree of polymerization may be written as

$$\bar{x}_n = ([\eta]^{1/a} / 2k^{1/a}M_0) + \tfrac{1}{2} \tag{26}$$

Equation 24 can then be used to calculate k_2 from the dependence of $\bar{x}_n$ on reaction time τ (Figure 7). The result $k_2 = 13.2 \pm 10\ M^{-1}\ \text{min}^{-1}$ for the 0.04 M solution is in agreement with the spectrophotometric value. However the 0.20 M solution has a significantly larger value, $k_2 = 21 \pm 2\ M^{-1}\ \text{min}^{-1}$. If branching were present from the onset of polymerization, k_2 would be overestimated. From characterization studies both the Mark–Houwink equation for the branched polymer and the branching frequency provide means to correct k_2 for branching. Using the K and a parameters from eq 16, the predicted value of the rate constant is $k_2 = 15 \pm 2\ M^{-1}\ \text{min}^{-1}$ for the 0.20 M solution. The other correction leaves the linear chain parameters a and K unchanged but involves dividing $\bar{x}_n$ by the average number of chains created by removing the branch units; *i.e.*, $1 + \bar{x}_n/180$. This correction gives $k_2 = 14 \pm 2\ M^{-1}\ \text{min}^{-1}$. Both corrections yield second order rate constants which agree within experimental error with values obtained for 0.005 and 0.04 M solutions. If anything the 0.20 M rate constant is slightly underestimated since η was not corrected for the kinetic energy effect. A kinetic energy correction was not required for the 0.04 M solution.

At high monomer concentrations (>15 wt %) other effects may influence the polymerization kinetics. Under such conditions poor mixing and insolubility may give rise to interfacial polymerization as proposed by Wrasidlo[24] and Hergenrother.[25] Also the reaction is exothermic to the extent that, if not adequately thermostated, the temperature of a 0.20 M solution rises about 5° during the initial stage of polymerization. And this temperature increase produces a higher molecular weight polymer. Another possible effect is that high concentrations of the tetraamine might lower the initial rate of polymerization by reducing solvent acidity.

Conclusion

The high molecular weight of PPQ when prepared from 0.20 M solutions is primarily a consequence of polymer chain branching during the initial stage of polymerization. Assuming Shultz's model the branching frequency of 0.20 M preparations is relatively constant with 1 branch unit per 180 ± 10 chain units. Polymers prepared from lower monomer concentrations (0.005 M) do not attain high degrees of polymerization and apparently have little or no branch formation. It is also observed that the second virial coefficient decreases markedly as the number of chain branches increase. These results along with the observed insolubility of PPQ prepared from higher monomer concentrations (>15 wt %) suggest that branch formation increases with increasing monomer concentrations.

Two factors may be contributing to branch formation—the presence of monomer impurities and incompleted ring closure in forming the quinoxaline ring (see intermediate 1). Branching due to monomer impurities would be independent of solvent, temperature, and monomer concentration and would be manifested as an inflated rate constant. However this would not necessarily be the case for branches produced by partial failure of ring closure. The polymerization mechanism can be viewed as an initial rate-determining reaction between an amine and a ketone group, followed by a much faster ring closure reaction. If the rate of the initial reaction is increased, branch formation becomes more probable. Since *m*-cresol catalyzes the reaction, more branching and consequently a higher molecular weight polymer would be produced with *m*-cresol rather than chloroform as the solvent. Also branch formation should become increasingly more probable as the initial monomer concentration is increased since the polymerization reaction is second order. This mechanism of incomplete ring closure is consistent with experimental results. If incomplete ring closure is the major contributor to branch formation in the 0.20 M preparations, then the rate of ring closure must be at least 180 times greater than the initial rate of polymerization or about 10^2 M/min.

Unperturbed chain dimensions calculated from the intrinsic viscosity-molecular weight relation for linear PPQ are slightly smaller than dimensions predicted by assuming free rotation statistics. Since motion in the PPQ chain is probably highly restricted due to steric and resonance effects, the apparent flexibility may be more a consequence of structural isomerism than rotational mobility. This analysis is in accord with the observed high glass transition temperature and the lack of crystallinity of PPQ.[8]

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