Interfacial Syntheses of Polyphosphonate and Polyphosphate Esters. III. Influences of Solvents, Diffusion Rates, Temperature, and Other Factors on Yield and Molecular Weight in the Alkaline Interfacial Polycondensation of Hydroquinone and Phenylphosphonic Dichloride[1]

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ABSTRACT: Increases in polymer yield are produced in the pH-controlled, alkaline interfacial polycondensation of hydroquinone with phenylphosphonic dichloride by the use of water-immiscible organic solvents of low viscosity, by increase in the reaction temperature, and by increase in the rate of high-speed stirring. Viscometric data show that the molecular weights of the polymer product remain substantially constant in the cases of the first two operational factors, but increase with increased stirring rate.

This study continues the examination[3–5] of various parameters in interfacial polymerization which affect polymer yield and molecular weight. The polycondensation of hydroquinone (HQ) with phenylphosphonic dichloride (PPD) in pH-controlled, strongly basic media has been chosen as a challenging system because of the marked sensitivity of the reagents, intermediates, and product toward degradative attack under basic reaction conditions. Experiences with this system should serve as a reference for the extension of this polycondensation reaction to include the use of other phosphorylhalo acid anhydrides.

The previous publications reported the effects of alkaline media,[3,4] solvent volume ratio, and comer concentrations.[5] This paper describes the influences of the temperature of reaction, the rate of high-speed stirring, and the nature of the organic phase, and it briefly reviews how the physical phenomena involved can act to influence the polymer yield and molecular weight.

TABLE I
THE RESULTS OF VARIOUS RATES OF STIRRING FOR THE INTERFACIAL POLYCONDENSATION OF HYDROQUINONE (0.021 MOL) AND PHENYLPHOSPHONIC DICHLORIDE (0.021 MOL), EMPLOYING CARBON TETRACHLORIDE (50 ML) AND pH-CONTROLLED AQUEOUS ALKALINE SOLUTIONS AT 24 ± 1°

Aqueous vol, ml	Amount of base, mol	Rotor speed, rev/min	Total yield, %	LVN[a] of total product, ml/g
100	0.050 Na_2PO_4	12,600	51	8
100	0.050 Na_3PO_4	15,000	56	10
100	0.050 Na_3PO_4	20,500	75	13
50	0.030 $Ba(OH)_2$	12,600	56	13
50	0.030 $Ba(OH)_2$	15,000	67	23
50	0.030 $Ba(OH)_2$	20,000	93	26

[a] Limiting viscosity number. Viscometry was performed in dimethyl sulfoxide at 25°.

TABLE II
THE RESULTS OF VARIOUS REACTION TEMPERATURES FOR THE INTERFACIAL POLYCONDENSATION OF HYDROQUINONE (0.021 MOL) AND PHENYLPHOSPHONIC DICHLORIDE (0.021 MOL), EMPLOYING CARBON TETRACHLORIDE (100 ML), WATER (100 ML), TRISODIUM PHOSPHATE (0.028 MOL), AND DISODIUM HYDROGEN PHOSPHATE (0.056 MOL)

Temperature, °C, av	Total yield, %	LVN of total product,[a] ml/g
20	46	13
25	49	14
41	54	13
50	58	12
60	64	13

[a] Limiting viscosity number. Viscometry was performed in dimethyl sulfoxide at 25°.

Results

Most of the procedural details are described in a previous paper.[4] All polymerizaitons were conducted in a Waring Blendor, Model 1001 (rotor speed rating 15,000 rpm), except that the same jar and Waring blendor, Model 1003 (rotor 12,600 and 20,500 rpm) were used for the investigation of the effect of stirring rate. For the polymerizations in which the temperatures were changed the reactant solutions and container were separately heated or cooled to the desired temperature before combination. The addition procedure was carried out in the fastest possible manner, and reactions were usually complete in less than 1 min of stirring, at which time the temperature was again measured. The average temperatures listed in Table II differ by less than 1.5° from the initial and final temperature determinations.

Table I shows the effects of change in the rate of high-speed stirring on the polymer yield and molecular weight in the pH-controlled, alkaline condensation of equimolar amounts of HQ and PPD. The initial and final values of pH of the hydroquinone-containing

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[1] Taken in part from the doctoral thesis of C. E. C., University of Missouri-Kansas City, Kansas City, Mo., 1968.

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[3] F. Millich and C. E. Carraher, U. S. Patent 3,491,061 (Jan 20, 1970).

[4] F. Millich and C. E. Carraher, *J. Polym. Sci., Part A-1*, 7, 2669 (1969).

[5] F. Millich and C. E. Carraher, *ibid., Part A-1*, in press.

TABLE III
THE RESULTS OF EMPLOYING VARIOUS WATER-IMMISCIBLE ORGANIC SOLVENTS (50 ML) FOR THE INTERFACIAL POLYCONDENSATION OF HYDROQUINONE (0.021 MOL) AND PHENYLPHOSPHONIC DICHLORIDE (0.021 MOL), IN THE PRESENCE OF WATER (50 ML) AND BARIUM HYDROXIDE (0.040 MOL) AT 25°

Organic solvent	LVN[a] of total product, ml/g	Total yield, %	Solvent viscosity[b] Temp, °C	η, cP	$[10^5 D]_{I_2}$,[c] cm²/sec	γ,[d] dyn/cm	γ_i,[e] dyn/cm
1,2-Dibromoethane	36	23	21.1	1.70	0.83	37.6	37
Bromobenzene	36	61	18.2	1.17	1.20	35.1	40
Carbon tetrachloride	37	67	20.2	0.97	1.36	26.2	45
Chlorobenzene		70	20.1	0.80		32.1	37
Toluene	36	78	20.0	0.59	1.95	27.3	36
n-Heptane	36	97	21.7	0.40	2.67	19.3	

[a] Limiting viscosity number. Viscometry was performed in dimethyl sulfoxide at 25°. [b] International Critical Tables, E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1926, Vol. V, pp 10–12, and Vol. VII, pp 211–224. [c] Diffusion coefficients of iodine at 20° from International Critical Tables,Vol. V, E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p 75. [d] Surface tension of solvents at 30° from J. A. Riddick and E. E. Toops, Jr. in "Technique of Organic Chemistry," Vol. 7, 2nd ed, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1955. [e] Water-solvent interfacial tension at 20° (toluene at 25°) from International Critical Tables, Vol. IV, E. W. Washburn, E. D., McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 436.

TABLE IV
THE RESULTS OF EMPLOYING VARIOUS WATER-IMMISCIBLE ORGANIC SOLVENTS (50 ML) FOR THE INTERFACIAL POLYCONDENSATION OF HYDROQUINONE (0.021 MOL) AND PHENYLPHOSPHONIC DICHLORIDE (0.021 MOL), IN THE PRESENCE OF AQUEOUS 5 *N* SODIUM HYDROXIDE (25 ML) AT 25°

Organic solvent	LVN[a] of total product, ml/g	Total yield, %	Solvent viscosity[b] Temp, °C	η, cP	γ,[c] dyn/cm	γ_i,[d] dyn/cm
Bromobenzene		88	18.2	1.17	35.1	40
Carbon tetrachloride	22	85	20.0	0.97	26.2	45
Toluene	11	12	20.0	0.59	27.3	36
Cyclohexane	4	5	20.0	0.96	23.8	
Benzene	2	2	20.2	0.65	27.5	35

[a] See Table III, footnote *a*. [b] See Table III, footnote *b*. [c] See Table III, footnote *d*. [d] See Table III, footnote *e*.

aqueous phase were measured with a pH meter at 20° and found to be between 11.5 and 11.9 for the trisodium phosphate system, and at 12 for the barium hydroxide system. The data show increases in both product yield and molecular weight with increase in rate of stirring.

Table II shows the effects of change in reaction temperature on the polymer yield and molecular weight. The latter property is seen to remain substantially constant; however, the polymer yield increases with increase in temperature over the range investigated. The aqueous buffer solutions gave an initial pH value of 10.0 at 25° and were never less than 9.7 at 25° after polymerization. The increase in yield would be reasonable if the rise in temperature to 60° produced a shift in pH of the medium to a value of 10.2 (*cf.* ref 4, Figure 1), but the change in the second (and undoubtedly the third) ionization constant of phosphoric acid is small and in the wrong direction over this temperature range. Appropriate data on the variation of the ionization constants of HQ are not available for this entire temperature range, but if the variation for HQ in the buffered medium is equal to or less than that for the buffer substance (as is probable), then the effects shown in Table II may be attributed to other factors.

Table III shows the effects of varying the nature of the water-immiscible organic solvent in the interfacial polycondensation. The molecular weight of the polymeric product remains constant; however, the polymer yield varies inversely with values of solvent viscosity in substantially a linear relation. The yield varies smoothly with values of the diffusion constant of iodine in these solvents. It can be seen that the values of the surface tension and the interfacial tension of the solvents are not useful for correlation with the other data.

Table IV presents data of a comparative study in which sufficient sodium hydroxide solution is employed to consume the liberated hydrochloric acid and other acidic functions generated during the course of reaction (*e.g.*, phosphoric acid groups). The pH during the entire course of reaction is maintained alkaline so that a low yield cannot be attributed to a drop to low pH. It may be seen that the results are distinctly different from those obtained in the pH-controlled alkaline polymerization of Millich and Carraher.[3–5] As in the previous studies, here too the molecular weights obtained in the sodium hydroxide system are inferior.

Characterization of the HQ–PPD condensation polymer is the subject of the next paper in this series. However, some relation of molecular weight to the limiting viscosity number, LVN, obtained in dimethyl sulfoxide at 25° with Ubbelohde viscometers, briefly should be given here: for LVN (ml/g) 4, 5, 6, 10, 13, 14, 20, and 48, $\bar{M}_w$ 10^{-3} values are 5.0, 7.4, 8.3, 18.2, 34,2, 36.0, 76.7, and 199, respectively. The weight average molecular weights were obtained, on fractionated samples in dimethyl sulfoxide at 20–25°, by light

TABLE V
RESULTS OF ALKALINE INTERFACIAL POLYMERIZATION OF HQ WITH PPD AT CONSTANT pH

Variable	Mol wt	Yield
(1) pH increase	Increase	Increase
(2) Vary mole ratio of reactants from unity	Increase	Increase
(3) Stirring rate increase	Increase	Increase
(4) Organic solvent viscosity decrease	Constant	Increase
(5) Temperature increase	Constant	Increase
(6) Decrease concentration of reactants	Increase	Constant
(7) Vary solvent phase volumes	*a*	*a*

[a] As the organic volume is varied, molecular weight remains essentially constant and yield goes through a maximum. As the aqueous volume is varied, both yield and molecular weight go through a maximum.

scattering, using Zimm plots and assuming a rodlike polymer conformation for the dissymmetry correction. The above data produce the following equation for the Mark–Houwink relationship: $\mathrm{LVN} = 2.40 \times 10^{-2}(\bar{M}_w)^{0.61}$.

Discussion

There are numerous factors involved in the alkaline polycondensation of HQ with PPD by means of interfacial polymerization. The most important chemical consideration is that the basic reaction promotors also rapidly attack the reagent PPD, the chlorophosphoryl end groups of oligomeric intermediates, and the phosphonic ester linkages in the polymer product. Some of the physical factors which influence the yield and molecular weight of the polymer product are the insolubility of the polymer product in the system, the rate of stirring, the temperature of reaction, comer ratio and concentration, organic–aqueous solvent ratio and volumes, and the nature of the solvent. Success in achieving polymer of high yield and molecular weight requires that the reaction conditions favor the polycondensation reaction relative to the degradative and terminating competing reactions. When a physical factor is varied the change must be more favorable to the polycondensation than to the competing reactions in order to produce a beneficial effect. The results of the present and previous investigations of the pH-controlled polymerization of HQ with PPD are summarized in Table V, from which it can be seen that changes can be made which beneficially affect polymer yield and, in some cases, molecular weight.

The individual factors can be rationalized separately without difficulty; however, the quantitative effects of varying solvent ratio and volumes make it difficult to draw a self-consistent set of conclusions. The first two factors of Table V are attributable to mass law effects. Over the pH range of the ionization of HQ the increase in yield is quantitatively correlated to the pK_{a_1} of HQ, reaching a plateau just beyond that range.[4] Further, as the mole ratio of comers is varied in either direction from unity, the yield (based on the comer which is present in limited amount) and the molecular weight also increase.[5]

Increase in the rate of stirring can produce several changes.

(1) Increased number of dispersed droplets increase the solvent interface surface area, providing an increased number of collisions among reactants and a shorter period of conversion time for *all* reactions. No attempt has been made in this study to determine the number or distribution of size of the droplets. It has been found, though, that the addition of Fuller's Earth to the polycondensation, when conducted in the presence of barium hydroxide solutions, improves polymer yield and average molecular weight.[1]

(2) Increased yield is favored by the mechanical agitation of high-speed stirring, which can serve to dislodge insoluble polymer as it forms at the interface that would otherwise have retarded most of the generative reactions, but would not have significantly changed the degradative attack of base on the phosphonic ester bonds of the high polymer. The mechanical removal of insoluble polymer from the reaction zone at the solvents interface, however, would act to interrupt the rapid growth of each polymer chain or to make its further growth dependent upon reactants—primarily HQ anions—which are dissolved in the aqueous phase. (Examination of the CCl_4 phase after reaction revealed that solubility of the condensation products in the organic phase at room temperature is limited to oligomers of $\overline{DP} < 4$.[1]) The results in Table I show increases in *both* yield and molecular weight as stirring rate is increased.

(3) High-speed stirring may produce microsized droplets, with droplet sizes and reaction efficiencies which are related in different solvents to the interfacial tension. The polycondensation under study has a low activation energy, and in such systems a very rapid rate of reaction may act to deplete the concentration of the phosphonylating agent to very low levels in the zone of the interface. Thus, the reaction could also become diffusion controlled. In such reactions, only that part of the phosphonylating solution located at the fringe of the depleted zone will be effective in establishing a concentration gradient of PPD across this depleted zone. With very large droplets, the major amount of PPD solution, at the gross value of the initial concentration, is remote from the reaction zone and for a large part of the reaction period will not influence the rate of conversion of PPD. In contrast, very small droplets, if in sufficient number, can provide a greater total involvement[6] of reagent in establishment of concentration gradients, in addition to providing a larger reaction interface. Of course, the turbulence induced by high-speed stirring can act against the limitations of diffusion control of reaction rates, and can act against the occlusion of reactants by the mass of precipitated polymer.

Table III shows an inverse correlation between polymer yield and the viscosities of organic solvents. This relationship has now been shown also to hold for the interfacial polycondensation of bisphenol-A with di-

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(6) In the extreme case of large "droplets" (*i.e.*, unstirred interfacial polymerization) the concentration of reagent at the fringe of the depleted zone is effective in maintaining a density gradient in only one direction, whereas, situated at the center of appropriate sized microdroplets the same reagent concentration is effective in three dimensions.

chlorodiphenylsilane.[7a] The intrinsic viscosities of poly(terephthalamides), prepared by interfacial polymerization in the presence of base (*i.e.*, diamines), have been shown to vary with the nature of the solvent.[7b] The variations were attributed to the interfacial tension, which varied as a function of the concentrations of the aliphatic or aromatic diamines in the aqueous solutions, as well as the nature of the organic solvent. In the latter case, especially, the data do not support a quantitative correlation, although a general trend can be discerned. In contrast to this study of poly(terephthalamide) formation, the present study does not show a variation of molecular weight, but one of yield, as organic solvent is varied. Another distinction of the present study is that evidence indicates the polymerization is probably taking place on the aqueous side of the interface,[5] whereas, in the interfacial polymerization of nylon-6,6 the reaction zone is reported to be on the organic side, as has been most nearly always claimed for interfacial polycondensations.[8]

The variation of yield with solvent viscosities leads to the conclusion that yield is significantly enhanced with greater diffusivity of PPD through the organic phase to the solvent interface. This fact does not certify that the polycondensation is solely diffusion controlled, but that the energy of activation, E_a, for polymer formation is so small such that differences in the rates of reagent diffusion have a noticeable effect.

Morgan reports that rate constants for rapid interfacial polycondensations fall in the range of 10^2–10^6 l./mol sec[9a] (ref 8, p 66). North[9b] states, "as a general rule, bimolecular processes with rate constants close to 10^{11} l./mole sec, or (less reliably) with activation energies of less than 3.0 kcal/mol, will usually be diffusion controlled. In the case of two polymeric reactants, the rate constant may be as low as 10^8 l./mol sec." The figure given by North is in a reasonable range for the E_a of the basic polycondensation of HQ with PPD. The overall "E_a," evaluated in this study from the change in yield due to change in temperature, is 1.5 kcal/mol; it is a differential value, and represents a minimum value for the condensation reaction. The change in *yield* might be taken as highly representative of the *rate* of polymerization, *relative to the rates* of the competing reactions. (Any minor amount of degradation taking place by random cleavages of the polymer chain can decrease the molecular weight without diminishing the yield of total product.) It is acknowledged that temperature change will also affect the physical factors discussed above, including decrease in the viscosities of the solvents, increase in solubility of the oligomers (and thus in the limiting degree of polymerization at which polymer precipitation occurs.)

There are very little E_a data reported in the chemical literature which is relevant to the present study. However, values of E_a, ranging from 6.3 to 8.5 kcal/mol at −20–0°, have been reported for the (nonalkaline) hydrolysis of $C_2H_5OP(O)ClCH_3$ in aqueous acetone solutions, and values of 8.7–11.0 kcal/mol are found in the more aqueous solutions;[10] the same authors note that the presence of a phenyl group in place of a methyl group directly bonded to phosphorus results in a significant decrease in E_a (7.7 *vs.* 8.7 kcal/mol). In another study, values of E_a, for the hydrolyses of $RP(O)Cl_2$ in the presence of KOH, of 6.2, 5.2, and 4.3 kcal/mol are reported, where R = methyl, vinyl, and phenoxy radicals, respectively.[11] Thus, the value of E_a for the attack by HQ anion upon PPD probably lies between 1.5 and 5 kcal/mol, and is comparable to, if not less than, the E_a maximum of diffusion controlled reactions suggested by North.

It is obvious that much more data are needed in order to describe quantitatively the interfacial polymerization process in definitive terms. Synthetic control of the buffered HQ–PPD polycondensation has been achieved to the point that data of polymer yield and molecular weight can be obtained in reliable and reproducible manner so as to reveal significant correlations. This system is recommended for further studies.

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[7] (a) C. E. Carraher and G. H. Klimiuk, *Makromol. Chem.*, in press; (b) L. V. Turetskii and L. B. Sokolov, *Vysokomol. Soedin.*, **3**, 1449 (1961).

[8] P. W. Morgan, "Condensation Polymers by Interfacial and Solution Methods," John Wiley & Sons, Inc., New York, N. Y., 1965, p 91.

[9] (a) See ref 8, p 66; (b) A. M. North, *Quart. Rev.* (London), **20**, 421 (1966).

[10] R. F. Hudson and L. Keay, *J. Chem. Soc.*, 1859 (1960).

[11] D. Israilova and L. A. Rodivilova, *Vysokomol. Soedin.*, **7**, 2089 (1965).