of dry benzene were added and removed similarly. The residue was heated at 100° under vacuum for 0.5 hour, then in cold nitrobenzene (40 ml.) added dropwise to a stirred suspension of aluminum chloride (7 g.) in nitrobenzene (40 ml.) at 0°. With stirring the reaction mixture warmed to room temperature during 3 hours, stood 18 hours, then was poured into cold dilute hydrochloric acid and the mixture extracted with chloroform. The organic solution was washed with dilute hydrochloric acid and water, then steam distilled. The resulting residue was dissolved in chloroform and washed with sodium carbonate solution. Solvent removal left an oil (3.5 g., 68%) which crystallized within 24 hours, m.p. 90–110°; $\lambda_{max}$ 288, 380 m$\mu$ (log $\epsilon$ 4.1, 3.4); infrared $\lambda_{max}$ 5.7, 5.8 $\mu$. Recrystallization from ethanol–water, from isoöctane, then twice from ethanol–water gave the analytical sample, m.p. 118–128°.

*Anal.* Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.35. Found: C, 79.62; H, 6.24.

The 2,4-dinitrophenylhydrazone derivative melted at 285–290° after recrystallization from acetic acid–water and chloroform–isoöctane.

*Anal.* Calcd. for $C_{21}H_{18}O_5N_4$: N, 13.79. Found: N, 13.62.

**1,2-Benz-5-keto-3a,6-methano-3,3a,4,5,6,7,8,8a-octahydroazulene (XII).**—A mixture of XI (1 g.), ethylene glycol (8 ml.), $p$-toluenesulfonic acid (50 mg.) and benzene (50 ml.) was refluxed 8 hours with an azeotroper. A few drops of absolute ethanolic sodium ethoxide was added then the reaction mixture was diluted with chloroform and washed with dilute potassium carbonate solution. Removal of the solvent gave an oil (infrared $\lambda_{max}$ 5.7 (weak), 5.8 (strong) $\mu$) which was mixed with 85% hydrazine hydrate (5 ml.) and dimethylene glycol (20 ml.) and heated at 120° for 15 minutes. Potassium hydroxide (0.7 g.) was added and the mixture held at 170° for 17 hours then cooled, diluted with water and extracted with chloroform. The residue from the washed chloroform solution showed no carbonyl absorbtion in the infrared. Hydrolysis was accomplished with 75% acetic acid (13 ml.) at 100° for 1 hour. The acid mixture was neutralized with aqueous potassium carbonate, extracted with chloroform and the solvent removed. The residue, in benzene, was chromatographed on neutral alumina (30 g.). Benzene (75 ml.) eluted 0.3 g. (35%) of oil which could not be crystallized; infrared $\lambda_{max}$ 5.7 $\mu$.

The 2,4-dinitrophenylhydrazone derivative melted at 209–211° after recrystallization from ethanol–ethyl acetate.

*Anal.* Calcd. for $C_{21}H_{20}O_4N_4$: C, 64.27; H, 5.14; N, 14.28. Found: C, 64.13; H, 5.17; N, 14.33.

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[CONTRIBUTION NO. 169 FROM THE CENTRAL RESEARCH LABORATORIES OF MINNESOTA MINING AND MANUFACTURING CO.,[1] ST. PAUL 9, MINN.]

# The Chemistry of Xylylenes. VI. The Polymerization of $p$-Xylylene[2]

BY L. A. ERREDE, R. S. GREGORIAN AND JOHN M. HOYT

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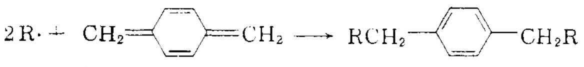
Polymerization of $p$-xylylene is initiated at −78° when a solution of the monomer is disturbed by momentary contact with a warm surface. This presumably creates diradical $n$-mers that continue to grow by successive addition of monomer units and/or by coupling. Apparently termination does not occur by chain transfer with solvent nor by interaction with atmospheric oxygen. Consequently propagation continues at −78° until all monomer is consumed or the free radical end groups are entrapped in the chain mesh affording a linear polymer whose molecular weight is greater than $2 \times 10^5$. The polymerization is first order with respect to monomer and second order with respect to free radical end groups. Low molecular weight cyclic products such as cyclo-tri-$p$-xylylene or cyclo-di-$p$-xylylene can be formed selectively by proper control of the reaction conditions.

## Introduction

$p$-Xylylene is a diamagnetic compound and yet it is so reactive that it behaves chemically as if it were a diradical.[3] Thus it reacts readily at low temperature with monoradicals such as nitric oxide and diphenylpicrylhydrazyl to afford linear telomeric products and with diradicals such as oxygen to afford polymers.[4] In all instances, reaction occurs at the two terminal methylene groups.



Solutions of this unusual monomer were prepared by fast flow pyrolysis of $p$-xylene at low pressure[5] and subsequent condensation of the pyrolyzate into a well-stirred solvent, such as hexane or toluene kept at −78°.[6] The solvent serves to protect the accumulated monomer from the activating effect of incoming hot molecules. The resulting solutions obviously are not pure and, indeed, it was shown that the condensable portion of the pyrolyzate is a mixture of $p$-xylene, $p$-xylylene, toluene, $p$-ethyltoluene, styrene, 1,2-di-$p$-tolylethane, diphenylmethanes and anthracenes.[7] The proportion of each component is dependent upon the pyrolysis conditions. The concentration of $p$-xylylene in the mixture is determined iodometrically by the difference of its titer at −78° and that observed after it is warmed to room temperature.[6] Thus these solutions afforded a convenient medium in which to study the polymerization of $p$-xylylene.

**Products of Polymerization.**—$p$-Xylene is so reactive that polymerization occurs slowly even at temperatures as low as −78° and the reaction is not arrested even by large concentrations of the usual inhibitors. The polymerization is extremely rapid when solutions of the monomer are warmed to room temperature. When the degree of polymerization exceeds about 20, polymer molecules precipitate throughout the solution. The polymer is obtained in a highly swollen state whose bulk appears to fill the flask, and it can be removed easily by filtration. Once the polymer is dried, however, it cannot be made to swell again, let alone dissolve, in the usual solvents at room temperature. It does dissolve at

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(1) Most of this work was carried out in the laboratories of The M. W. Kellogg Co. The data were acquired by Minnesota Mining and Manufacturing Company with the purchase of the Chemical Manufacturing Division of The M. W. Kellogg Co. in March, 1957.

(2) Presented before the Gordon Conference on Polymers, A.A.A.S., New London, N. H., July, 1959.

(3) L. A. Errede and J. M. Hoyt, THIS JOURNAL, **82**, 436 (1960).

(4) L. A. Errede and S. L. Hopwood, Jr., *ibid.*, **79**, 6507 (1957).

(5) M. Szwarc, *J. Polymer Sci.*, **6**, 319 (1951).

(6) L. A. Errede and B. F. Landrum, THIS JOURNAL, **79**, 4952 (1957).

(7) L. A. Errede and J. P. Cassidy, *ibid.*, **82**, 3653 (1960).

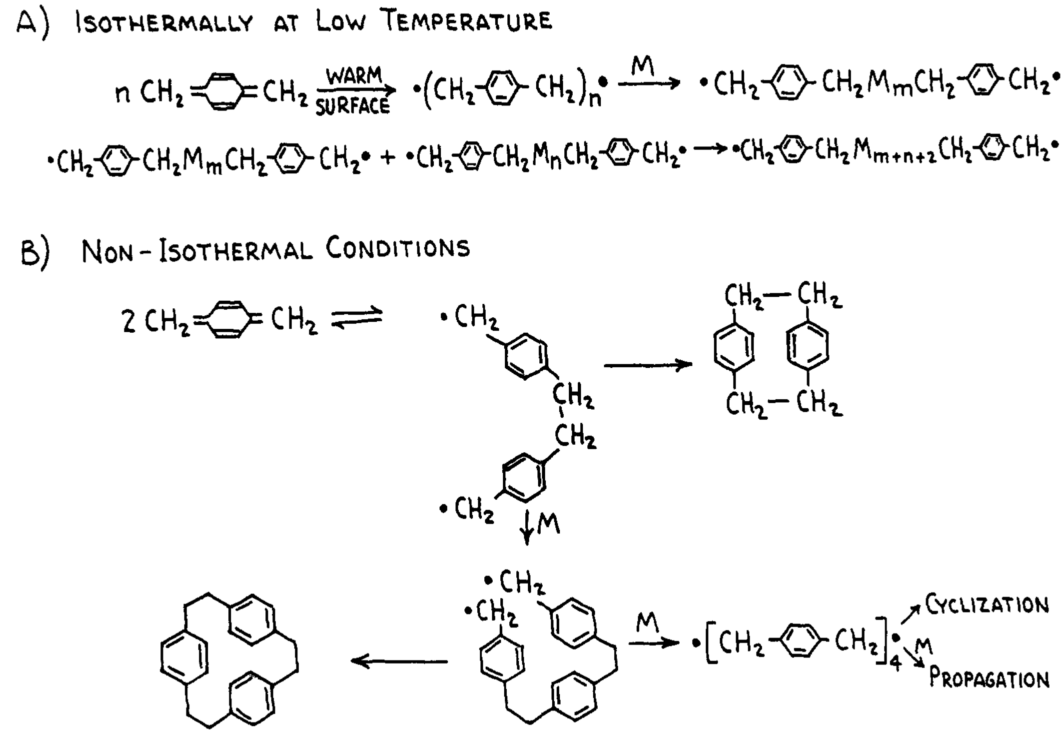

Fig. 1.—Mechanism of *p*-xylylene polymerization.

about 300° in solvents such as the Aroclors,[8] benzyl benzoate[9] and certain fused ring aromatic compounds,[10,11] but this is concomitant with considerable chain rupture as evidenced by steadily decreasing inherent viscosity[8-12] of the solutions. Moreover it was shown in our laboratory that interaction with the solvent is appreciable. Thus the polymer, reprecipitated from Aroclor 1254 (pentachlorobiphenyl), contained 4.1% chlorine and this amount was not decreased appreciably by reprecipitation from benzyl benzoate. This insolubility at low temperature and instability at high temperature discouraged attempts to determine the true molecular weight or the molecular weight distribution by the usual methods. In one experiment, however, a molecular weight of $2.4 \pm 0.3 \times 10^6$ was calculated from the number of radioactive iodine end-groups incorporated into the polymer when the reaction was quenched with labeled iodine after polymerization had proceeded to 95% completion.[13] This can only be considered approximate, however, because of uncertainty in removing last traces of adsorbed radioactive iodine.

When *p*-xylylene is caused to polymerize in solution at low temperature, some soluble low molecular weight products are formed in addition to insoluble high molecular weight polymer. The former are separated easily from the latter by filtration. Cyclo-tri-*p*-xylylene, cyclo-tetra-*p*-xylylene, 1,4-bis-(2-*p*-tolylethyl)-benzene and low molecular weight poly-*p*-xylylene were some of the products isolated from the residues obtained when the mother liquors were evaporated to dryness. The average degree of polymerization of the low molecular weight polymer was about 16.[14] Its infrared spectrum was virtually identical with that of the high molecular weight polymer although its X-ray diffraction pattern indicated that it was amorphous. The low molecular weight material melted over a wide temperature range (180–220°) which is considerably lower than that of the high molecular weight polymer (400–420°).

The reactions outlined in Fig. 1 were postulated in order to account for the polymerization products isolated from the reaction mixture. The product distribution obtained as a function of the polymerization conditions is consistent with the postulated mechanism. Thus high molecular weight insoluble polymer is obtained almost exclusively when polymerization is carried out at −78° (column A of Table I). Under these conditions monomeric *p*-xylylene is consumed by addition to benzyl radical end groups already produced during the preparation of the solution as shown in part A of Fig. 1. The proportion of high molecular weight polymer is decreased considerably however when the solution is warmed rapidly from −78° to room temperature (column B of Table I). The rate of propagation of the relatively few growing chains increases with temperature but under these conditions the residual *p*-xylylene molecules are also activated by the rapid

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[8] L. A. Auspos, C. W. Barnam, L. A. R. Gall, J. K. Hubbard, W. Kirk, Jr., J. R. Schaefgen and S. B. Speck, *J. Polymer Sci.*, **15**, 19 (1955).

[9] M. A. Kaufman, H. F. Mark and R. B. Mesrobian, *ibid.*, **13**, 3 (1954).

[10] R. N. Roper, private communication.

[11] A. A. Vansheidt, E. P. Melnikova, L. V. Kukhareva and M. G. Krakovyak, *Zhur. Priklad. Khim.*, **12**, 1898 (1958).

[12] J. R. Schaefgen, *J. Polymer Sci.*, **41**, 133 (1959).

[13] The authors are indebted to Dr. J. P. Ryan and T. N. Lahr of the Minnesota Mining and Manufacturing Co. for assistance in this experiment.

[14] This implies that a growing polymer chain precipitates from −78° when its degree of polymerization is about 20.

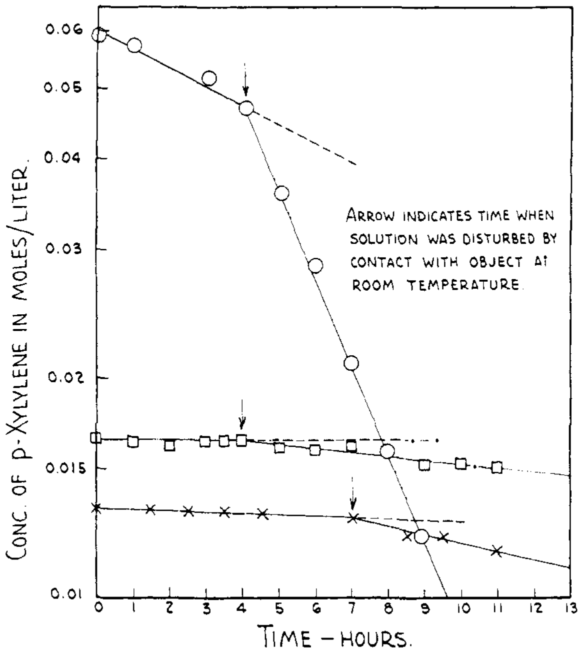

Fig. 2.—Polymerization of *p*-xylylene at −78°.

increase in temperature. Hence, coupling of the monomer units to afford diradical dimers, trimers and tetramers occurs very rapidly as shown in part B of Fig. 1. Since these low molecular weight diradical *n*-mers are formed in dilute solution, coupling of the end-groups occurs intramolecularly rather than intermolecularly. Cyclization is particularly facile at the trimer stage but becomes increasingly less probable with each new addition of monomer. These low molecular weight compounds (mostly cyclic-trimer) are the major products of polymerization if the "living polymer" chains, created during the preparation of the solution, are first removed by filtration and the mother liquor then diluted considerably with cold solvent before it is warmed to room temperature (column C of Table I). It is noted that the proportion of cyclo-di-*p*-xylylene in the products of polymerization in experiments A, B and C remains low despite the wide variation in polymerization conditions.

Table I

Polymerization of *p*-Xylylene

A, 7.7 moles of *p*-xylylene (0.03 molar solutions in heptane or toluene) polymerized at −78°; B, 38.4 moles of *p*-xylylene (0.1 molar solutions in hexane or toluene) polymerized by warming from −78° to room temperature; C, 0.08 mole of *p*-xylylene in 1 liter of hexane, diluted to 0.008 molar with hexane and then warmed from −78° to room temperature; D, 0.12 mole of *p*-xylylene in one liter of hexane at −78° added dropwise to toluene kept at about 100°.

| | A | B | C | D |
|---|---|---|---|---|
| Cyclo-di-*p*-xylylene | 2% | 1% | 1% | 41% |
| Cyclo-tri-*p*-xylylene | 3 | 15 | 93[a] | 58[a] |
| Cyclo-tetra-*p*-xylylene | . . | 0.05 | [a] | [a] |
| Soluble poly-*p*-xylylene av. mol. wt. about 1600 | 3 | 20 | [a] | [a] |
| Insoluble poly-*p*-xylylene av. mol. wt. about $2 \times 10^5$ | 92 | 64 | 6 | 0.5 |

[a] A mixture of soluble low molecular weight products of polymerization was obtained and its infrared spectrum indicated that cyclo-tri-*p*-xylylene was its major component.

This indicates that cyclic dimer is not formed in solution at low temperature but rather in the gas stream prior to condensation since a considerable activation energy must be supplied to the diradical dimer intermediate in order to force ring closure into the highly strained configuration of cyclo-di-*p*-xylylene.[15] The diradical dimer either regenerates two monomer units[16] or adds a third monomer unit to form the diradical trimer which ring closes immediately yielding cyclo-tri-*p*-xylylene.

Although cyclo-di-*p*-xylylene is not formed at low temperature, it is obtained in good yield when a cold solution of *p*-xylylene (−78°) is added dropwise to an inert solvent such as toluene kept at about 100°. Under these conditions the diradical dimer is formed in infinite dilution at elevated temperature enabling ring closure to compete favorably with propagation.

**Initiation of Polymerization.**—A small amount of polymerization occurs during the preparation of *p*-xylylene solutions. Undoubtedly, condensation of *p*-methylbenzyl radicals accounts for one mode of initiation, since it was shown in another experiment[17] that benzyl radicals in minute amounts are still present in the gas stream of pyrolyzed toluene a considerable distance away from the furnace. *p*-Methylbenzyl radicals, however, serve a dual role, since termination by coupling of two monoradicals occurs to afford low molecular weight linear products such as 1,4-bis-(2-*p*-tolylethyl)-benzene, which was one of the compounds isolated in small amount from the mixture of soluble nonvolatile reaction products.

Polymerization sites are also created when the stirred solvent comes into contact with the warmer surface above the level of the cold liquid. Indeed it was shown that the rate of polymerization, which is first order with respect to monomer, is markedly increased when an aliquot is drawn up into a warm pipet and then allowed to flow back into the solution (Fig. 2). Moreover, the magnitude of change increases markedly with concentration as noted in Fig. 2. Thus the relative magnitude of increase per disturbance at 0.0129,[18] 0.0165 and 0.0470 mole per liter was about 1, 2 and 30, respectively. It appears as though molecules of *p*-xylylene might be adsorbed on the solid surface in a fortuitious end to end alignment of several monomer units being subjected simultaneously to a momentary exposure of heat energy that enables the polymerization to proceed beyond the critical stage for cyclization, and thereby affords a finite amount of diradical *n*-mers (where $n$ is > about 6) that continue to grow in solution by successive addition of monomer. In the absence of the solid surface, the thermal activation favors cyclization to low molecular weight products ($n < 6$) as described previously.

The number of polymerization sites produced in one way or another during the preparation of the monomer solution accumulates with time duration of pyrolysis. As a result, the rate of polymerization

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[15] D. J. Cram and H. Steinberg, This Journal, **73**, 5691 (1951).

[16] M. Szwarc, *J. Polymer Sci.*, **13**, 317 (1954).

[17] L. A. Errede and J. P. Cassidy, *J. Org. Chem.*, **24**, 1890 (1959).

[18] The total increase noted at 0.0129 mole per liter is the result of four successive disturbances and therefore this was divided by four to obtain the average increase per disturbance for purposes of comparison.

increases and eventually it exceeds the rate of monomer formation which is determined by the conditions of pyrolysis. At this stage the concentration of accumulated monomer decreases despite continued pyrolysis.[6]

Apparently the number of polymerization sites does not increase after termination of pyrolysis unless the solution is disturbed as described previously. Since the polymer molecules precipitate from solution when the degree of polymerization exceeds about 20, the polymerization sites created during the preparation of the solution are removed easily by filtration. Unfortunately, this does not arrest polymerization completely but only serves to decrease its rate, since new sites are created as the liquid cascades down the walls of the filtration flask.

Oxygen is not an initiator for polymerization. Thus no increase (or decrease) in the rate of polymerization was observed when a slow stream of nitrogen containing 1% oxygen was bubbled through a solution of *p*-xylylene at −62°. Addition of an occasional oxygen molecule to a free radical end-group most certainly occurs,[4] but this affords a peroxy radical which in turn adds to a monomer unit thereby regenerating the usual benzyl radical end-group that continues to propagate.

$$M_n \xrightarrow{O_2} M_nOO\cdot \xrightarrow{M} M_nOOM\cdot \xrightarrow{M} M_nOOM_m\cdot$$

The net effect is to produce poly-*p*-xylylene interspaced randomly with peroxide units.

**Propagation.**—The rate of monomer consumption is given by

$$dM/dt = -kPM \qquad (1)$$

where $k$ is the specific rate constant for addition of monomer to a benzyl radical end group, $M$ is the concentration of monomeric *p*-xylylene and $P$ is a number of free radical end-groups. As pointed out above, the growing polymeric chains precipitate out of solution when the degree of polymerization is still low and the polymer remains in a highly swollen state easily permeated by solvent and monomeric *p*-xylylene. Under these conditions the polymerization continues unimpaired, although the interaction of one insoluble free radical end-group with another is markedly reduced. Consequently, the number of end-groups remains sensibly constant over a 10-hour interval and the kinetics of polymerization is first order. Although the apparent rate constant, *i.e.*, the product of $k$ and $P$, is readily calculated from the slope of the line obtained when log $M$ is plotted as a function of time, one still cannot determine the specific rate constant unless the concentration of the polymerization sites is also established. In one experiment,[13] however, the reaction mixture was quenched at −78° with radioactive iodine after the apparent rate constant was found to be 1.22 $\times 10^{-5}$ sec.$^{-1}$. Subsequent radioactive countings on polymer samples indicated a total of $1.3 \times 10^{-4}$ mole of free radical end-groups was present in the insoluble polymer contained in the 4.5 liters of solution. This value is considered high, however, owing to the uncertainty of removing the last traces of adsorbed radioactive iodine.

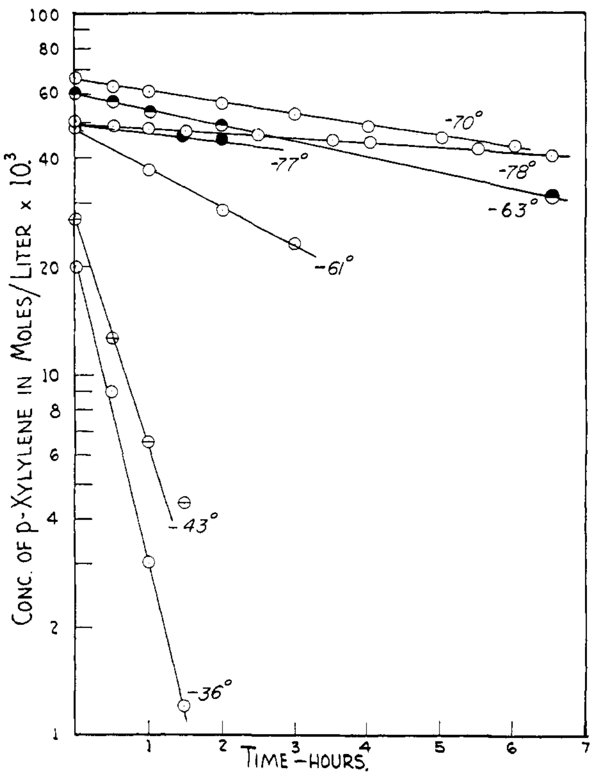

Fig. 3.—Polymerization of *p*-xylylene solutions having an apparent rate constant ($kP$) at −78° equal to $9 \pm 1 \times 10^{-6}$ as a function of temperature.

It was observed that solutions with apparent rate constants of $9 \pm 1 \times 10^{-6}$ sec.$^{-1}$ could be reproduced fairly consistently if the polymer accumulated during the pyrolytic preparation of the solution was first removed by rapid filtration through a bed of crystalline *p*-xylene using apparatus that was prechilled to −78°. The clear solutions were then used to study the effect of temperature on the rate of polymerization. Each solution was divided in two portions. The first was kept at −78° to ensure reproducibility of the apparent rate constant within the limits specified, whereas the second was used to determine the corresponding value at a higher temperature. The results are summarized in Fig. 3 and it is seen that these solutions have a half-life of 22 hr. at −78°, whereas it is only 22 min. at −36°. The observed log $kP$ values were plotted as a function of reciprocal of absolute temperature and a straight line was obtained. Hence the activation energy was calculated to be 8.7 kcal.

**Termination.**—Although the decrease in number of polymerization sites is insignificant over a 10-hour period, the magnitude of this reaction becomes appreciable when the polymerization is continued for a long time. The apparent rate constant ($kP$) decreases slowly but steadily and deviation from first-order kinetics is observed as shown in Fig. 4. A straight line is obtained, however, when the reciprocal of the apparent rate constant is plotted as a function of time as shown in Fig. 5 indicating that the disappearance of free radical end groups is second order despite the

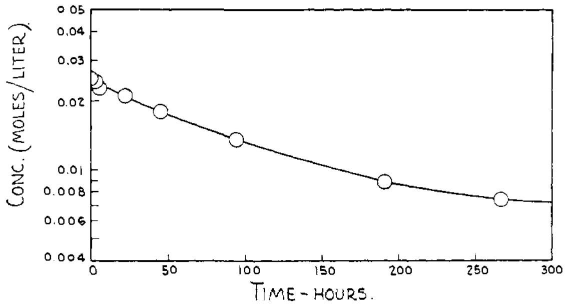

Fig. 4.—Polymerization of *p*-xylylene at −78°.

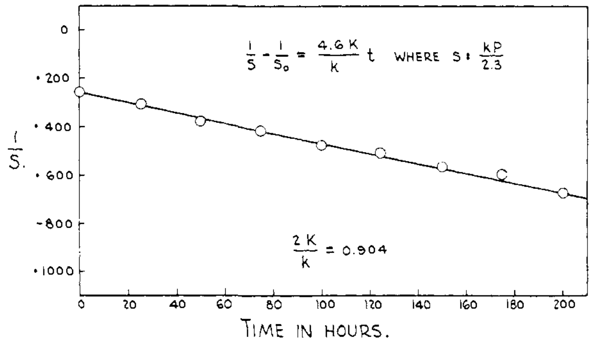

Fig. 5.—Reciprocal of the apparent rate constant ($kP$) of *p*-xylylene polymerization at −78° as a function of time.

heterogeneous character of the system. Hence the relation is given by

$$\frac{1}{S} - \frac{1}{S_0} = 4.6\,\frac{K}{k}\,t \qquad (2)$$

where $S$ is the apparent rate constant ($kP$) divided by 2.3, and $K$ is the specific rate constant for coupling of one insoluble free radical end-group with another. It follows that the number of free radical end-groups $P$ at any given time $t$ is given by

$$P = P_0/(1 + 2KP_0t) \qquad (3)$$

where $P_0$ is the initial number of polymerization sites. Hence eq. 1 can now be integrated to give

$$[M_0/M]^{2K/k} = 1 + 2KP_0t \qquad (4)$$

where $2K/k$ is 0.90 as calculated from the slope of the line shown in Fig. 5. Accordingly a straight line was obtained when $(M_0/M)^{0.90}$ was plotted as a function of $t$ as shown in Fig. 6. Thus the kinetics of polymerization are consistent with the over-all polymerization mechanism outlined in Fig. 1.

Termination by chain transfer does not occur significantly at these low temperatures of polymerization.[3] Thus unmodified polymer, without even a trace of positive evidence for solvent end-groups, was obtained when polymerization was carried out at −78° in solvents such as $CCl_4$, $CHCl_3$ and in the presence of amines, aldehydes, ethers, ketones, nitro compounds, quinones, hydroquinones, phenols, diphenylmethanes and triphenylmethanes. Chain transfer does occur however, with mercaptans and compounds of comparable reactivity.[3] Moreover homopolymerization of *p*-xylylene occurs at −78° in the presence of olefins even when the latter are used as solvents.[3] Post polymerization of the olefin is undoubtedly initiated when the reaction mixture is warmed to room temperature, but the small amount of available free radical end-groups (about $10^{-4}$ mole) is rapidly destroyed by the usual termination reactions before much block polymerization occurs.

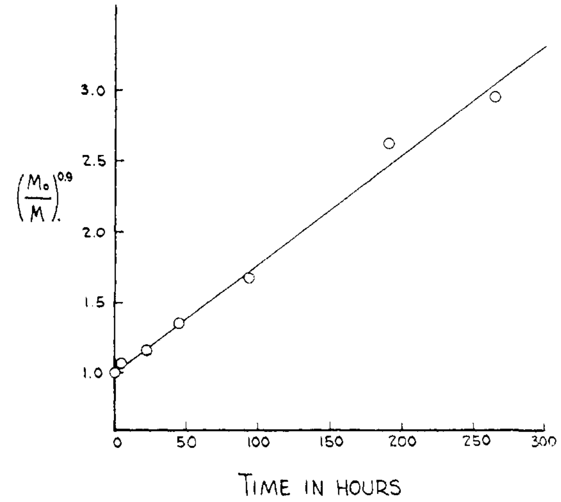

Fig. 6.—Polymerization of *p*-xylylene at −78°; $(M_0/M)^{0.9} = 1 + 2P_0Kt$.

## Experimental

**Non-isothermal Polymerization of *p*-Xylylene at Low Temperature.**—Solutions of *p*-xylylene in hexane or toluene (0.08 to 0.12 molar) were prepared *via* fast flow pyrolysis of *p*-xylene at 1065 ± 5°, 4.0 ± 0.1 mm. pressure and 0.0041 ± 0.003 sec. residence time and the pyrolyzate produced thereby was condensed into 4 liters of hexane or toluene kept at −78° as described previously.[3,6,7] These solutions were then warmed from −78° to room temperature and a copious precipitate of poly-*p*-xylylene formed throughout the liquid. The insoluble polymer was removed by filtration and the soluble non-volatile components in the mother liquor were recovered by evaporation to dryness. In this way 2.5 kg. of insoluble poly-*p*-xylylene and 2.3 kg. of a mixture of soluble non-volatile products were accumulated.

The mixture of soluble non-volatile products was separated laboriously as described in detail in a previous publication.[7] The products isolated were 701 g. of soluble poly-*p*-xylylene (m.p. 180–220°), 565 g. of cyclo-tri-*p*-xylylene (m.p. 166–167°), 20 g. of cyclo-di-*p*-xylylene (m.p. 281–283°), 1 g. of cyclo-tetra-*p*-xylylene (m.p. 179–182°), 28 g. of 1,4-bis-(2-*p*-tolylethyl)-benzene (m.p. 141–142°), 242 g. of 1,2-di-*p*-tolylethane (m.p. 81–82°), 250 g. of diphenylmethanes (b.p. 82–83° (0.06 mm.)), 115 g. of anthracenes (2,6-dimethylanthracene, m.p. 239–241°; 2-methylanthracene, m.p. 206–207°; anthracene, m.p. 214–215°) and 370 g. remained unaccounted for.

From these data it was calculated that the distribution of polymerization products obtained when a 0.1 molar solution of *p*-xylylene is warmed from −78° to room temperature is as summarized in column B of Table I. The amount of 1,2-di-*p*-tolylethane, diphenylmethanes and anthracenes isolated in this experiment were ignored in the data given in Table I, since it was shown[7] that these compounds are products of pyrolysis rather than of post polymerization of *p*-xylylene.

In another experiment a 0.080 molar solution of *p*-xylylene in hexane was prepared as described above. Crystalline *p*-xylene and poly-*p*-xylylene were removed by filtration. One liter of the clear filtrate, still 0.080 molar with respect to *p*-xylylene, was diluted at −78° with 9 liters of oxygen-free hexane. The resulting 10-liter solution was warmed to room temperature in the absence of oxygen to afford only 0.5 g. of insoluble polymer. An additional 8 g. of soluble products of polymerization was recovered from the mixture remaining after the excess solvent was removed by distillation. The major component was identified by infrared analysis as cyclo-tri-*p*-xylylene; only a trace amount (0.1 g.) of cyclo-di-*p*-xylylene was isolated as described previously.[7] A second one-liter aliquot of the original solution was polymerized by warming to room temperature without prior dilution as a control experiment to afford 4.6 g. of insoluble polymer and 4 g. of soluble low molecular weight products of polymerization and pyrolysis, only 0.1 g. of which was cyclo-di-*p*-xylylene.

**Isothermal Polymerization of *p*-Xylylene. A. Kinetic Studies.**—Solutions of *p*-xylylene in 4 liters of toluene (0.08 to 0.12 molar) were prepared as described previously.[6] Insoluble *p*-xylene and a small amount of poly-*p*-xylylene were removed by rapid filtration in the absence of oxygen through a bed of crystalline *p*-xylene using equipment that was prechilled to −78°. This afforded a filtrate whose apparent rate constant was $9 \pm 1 \times 10^{-6}$ sec.$^{-1}$. The filtrate was divided into two portions. One was placed in a constant temperature bath at −78° and the other in a bath set at the desired higher temperature for polymerization. The polymerizations were carried out in the absence of light, although it was observed later that light from the room did not modify the polymerization. When thermal equilibrium was established, the rate of decrease of titratable monomer was followed by the periodic iodometric titration of an aliquot sample. The aliquot was taken by means of a rapid flow 25-cc. pipet that was pre-chilled to −78° as described previously.[6] When the experiment was completed, the solutions were warmed to room temperature and a final titration was made in order to establish the blank. The polymerization study at −78° was used as a control experiment to ensure that the reproducible concentration of polymerization sites was present in each freshly prepared solution. The results are shown in Fig. 3.

To determine whether or not new polymerization sites are created when the temperature of *p*-xylylene solution is raised from −78° to −50°, the following kinetic study was carried out. A solution of *p*-xylylene was prepared in the usual fashion. The apparent rate constant at −78° was determined to be $1.06 \times 10^{-5}$ sec.$^{-1}$ by following the disappearance of monomer over a 6-hour period during which time the concentration fell from 0.0355 to 0.0285 molar. The temperature of this solution was raised to −50°, and then rechilled to −78° during which time the concentration fell to 0.0025 molar. The second kinetic study at −78° established that the apparent rate constant was $1.22 \times 10^{-5}$ sec.$^{-1}$, indicating only a minute increase in the number of polymerization sites, and may only represent uncertainty in the analytical method at extremely low concentration.

In order to demonstrate that new polymerization sites are created by momentary contact with a warm surface, solutions of *p*-xylylene were prepared at −78° in the usual fashion, and the apparent rate constants of the unfiltered solutions were established by kinetic study as described above. Each solution was then disturbed by drawing a 25-cc. sample of the liquid into a warm (room temperature) pipet and then allowing the aliquot to flow back into the monomer solution. The kinetic study was resumed without further disturbance. The reaction was again first order, but the apparent rate constant was increased as shown in Fig. 2. The magnitude of increase was greater than first order with respect to monomer concentration at the time of disturbance. Thus, one disturbance increased the apparent rate constant of a 0.047 molar solution from $1.6 \times 10^{-5}$ to $7.6 \times 10^{-5}$, and that of a 0.0165 molar solution from virtually zero to $3.6 \times 10^{-6}$, whereas 4 successive disturbances at −78° were required to increase the apparent rate constant of 0.013 molar solution from $1.2 \times 10^{-6}$ to $7.4 \times 10^{-6}$.

**B. Product Distribution.**—Three hundredths molar solutions of *p*-xylylene in heptane or toluene were prepared at −78° in the usual fashion. These were stored in a Dry Ice chest until virtually all the available monomer had undergone polymerization before the reaction was terminated by warming the solution to room temperature. The insoluble polymer was removed by filtration and the soluble non-volatile products of pyrolysis and polymerization were recovered from the mother liquor by evaporation to dryness. In this way 348 g. of polymer and 448 g. of low molecular weight soluble product were accumulated. The latter was separated laboriously as described previously[7] and the following components were isolated: 250 g. of 1,2-di-*p*-tolylethane (m.p. 78–80°); 104 g. of diphenylmethanes (b.p. 150–160° (1 mm.)); 21 g. of anthracenes; 10 g. of cyclo-tri-*p*-xylylene (m.p. 166–167°); 10 g. of 4,4-dimethylstilbene; 7 g. of cyclo-di-*p*-xylylene; 11 g. of soluble poly-*p*-xylylene whose average molecular weight was 1600 (determined by the procedure of Neumeyer[19]); 12 g. of 1,4-bis-(2-*p*-tolylethyl)-benzene (m.p. 141–142°).

**Cyclo-di-*p*-xylylene.**—A solution of *p*-xylylene in hexane was prepared as described above and separated by filtration. One liter of cold (−78°) filtrate containing 13 g. of *p*-xylylene was added dropwise over a period of 1 hour to a liter of toluene kept at 90°. A small amount of monomer (1.5 g.) polymerized in the cold solution during the addition and this was removed by filtration. The hot toluene solution was evaporated to dryness. The residue (15 g.) was leached with acetone leaving 4.7 g. of insoluble cyclo-di-*p*-xylylene which after one recrystallization from toluene was obtained as white crystals (m.p. 283–285°). The major component of the acetone-soluble products of polymerization was identified as cyclo-tri-*p*-xylylene. A second one-liter aliquot of the original *p*-xylylene solution was polymerized by warming to room temperature as a control experiment to afford 5 g. of insoluble polymer, 12 g. of soluble products, only trace amount of which was cyclo-di-*p*-xylylene.

**The Use of Radioactive Iodine to Determine Molecular Weight and Number of Free Radical End-groups.**[13]—Four and a half liters of a *p*-xylylene solution in toluene, which was 0.036 molar with respect to monomer, was polymerized at −78° until the *p*-xylylene concentration decreased to 0.002 molar. The apparent rate constant at this point was established to be $1.22 \times 10^{-5}$ sec.$^{-1}$. The reaction was then terminated immediately by quenching the mixture with a known excess of iodine containing 500 millicuries of radioactive iodine. The resulting solution was warmed to room temperature and the insoluble polymer was removed by filtration. The polymer was slurried in one liter of 0.25 $N$ $I_2$ in $CCl_4$ and then recollected by filtration. The polymer was washed with benzene until the washings contained no further trace of $I_2$ color. The polymer was retreated with one liter of 0.25$N$ $I_2$ in $CCl_4$ and the wash cycle was repeated to ensure removal of all traces of adsorbed radioactive iodine. The polymer was then mixed with 15 g. of *p*-xylylene di-iodide. The mixture was then extracted continuously with ethanol for 3 days in a Soxhlet extractor and then for an additional 6 days with benzene. At the end of this time all traces of *p*-xylylene di-iodide appeared to be removed and the benzene extract was free of radioactivity.

Small samples of the polymer were withdrawn each day of the extraction for radioactive counting. A stabilized value of 1.07 ± 0.09 mg. of $I_2$ per gram of polymer was obtained and no significant trend in iodine concentration deviating from the natural rate of iodine decay was noticed with continued time duration of extraction during the last 4 days. The calculated molecular weight of the poly-*p*-xylylene was 237,000 ± 25,000. This is not considered a maximum value, since polymerization was only 95% complete and higher molecular weight polymer would have formed *via* coupling and propagation if the reaction mixture had not been quenched with iodine. A total of 15.3 g. of polymer was obtained from the 4.5 liters of solution, so that the total number of free radical end-groups was $1.26 \times 10^{-4}$.

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(19) J. J. Neumeyer, *Anal. Chim. Acta*, **20**, 519 (1959).