$$R_p = (2k_d[S_2O_8^{2-}])^{1/2}k_p[M]/(2k_t)^{1/2}$$

where $k_d = 0.478 \times 10^{-5}$ s^{-1},[8] $(2k_t)^{1/2}/k_p = 40$ M$^{1/2}$ s$^{1/2}$,[21] and [M] = 4.31 M. This value of R_p is 3.6 times as high as the largest value of excess R_p achieved for 0.037 M $K_2S_2O_8$ under the experimental conditions reported in Table II (column 5). Inasmuch as $R_p \propto R_i^{1/2}$ only $1/3.6^2$ fraction, i.e., about $^1/_{13}$, of the total $SO_4^{-}\cdot$ generated is transported to the organic phase for the most favorable case, i.e., at the highest [Bu_4NBr] used, viz., 0.025 M. From these considerations it follows that for [Bu_4NBr] at 0.025 M, k_w is 12 times as high as $k_{p,t}[Q^+]_w$. Similarly, it can be shown that for the lowest [Bu_4NBr] used in the series of experiments reported in Table II, viz., 0.0075 M, k_w is 33 times as high as $k_{p,t}[Q^+]_w$. These considerations allow us to approximate eq 21 as

$$R_i \simeq 2k_dk_{p,t}[Q^+]_w[S_2O_8^{2-}]_wV_w/(k_wV_o) \qquad (22)$$

and thus R_p should be proportional to the square root of the quaternary ammonium salt concentration also.

Conclusion

This study suggests that in phase-transfer polymerization using $K_2S_2O_8$ and QX a significant part of initiation could be effected also by phase-transferred $SO_4^{-}\cdot$ generated in the aqueous phase. With Bu_4NBr as the phase-transfer agent, initiation is predominantly effected by this process. It further shows that the extent of phase transfer of $S_2O_8^{2-}$, a divalent anion, is greater than that of the monovalent Br^-. However, the amount transferred is a very small percentage of the total [$S_2O_8^{2-}$] when Bu_4NBr is used as the phase-transfer agent.

Acknowledgment. Thanks are due to Dr. Nira Misra for helpful discussion.

Registry No. $K_2S_2O_8$, 7727-21-1; Bu_4NBr, 1643-19-2; styrene, 100-42-5.

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(30) $R_{p,t}$ is based on the aqueous phase volume, while R_i is based on the organic phase volume. One referee points out that the dependence of R_p on V_w may be a surface area effect. This view is also compatible with the mechanism of initiation by $SO_4^{-}\cdot$ transported from the aqueous phase since the latter process is rate-controlling.

Preparation of 3,6-Bis(hydroxymethyl)pyridazine and Poly(3,6-pyridazinediylbis(methylene) terephthalate)

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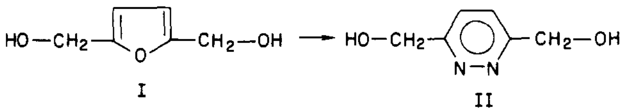
ABSTRACT: 3,6-Bis(hydroxymethyl)pyridazine (II) was prepared from 2,5-bis(acetoxymethyl)furan (VII) by way of 1,6-diacetoxy-3-hexene-2,5-dione (VIII) without the use of electrolytic methoxylation of 2,5-bis(hydroxymethyl)furan (I). This new synthetic method avoids the tedious electrolytic methoxylation step and is suitable for scaled-up operations. A new polymer, poly(3,6-pyridazinediylbis(methylene) terephthalate) (X), was synthesized from II and terephthaloyl chloride. A comparison of the thermal properties of X with those of analogous poly(*p*-xylylene terephthalate) (XI) shows that X is subject to thermal decomposition at about 310 °C, attributed to the resonance stabilization of the benzylic-like 3,6-pyridazinedimethyl radicals.

The objective of this study was the development of a process for the conversion of 2,5-bis(hydroxymethyl)furan (I) to 3,6-bis(hydroxymethyl)pyridazine (II) (eq 1) and the use of the latter as a difunctional monomer. The work was motivated by the expectation that the strong intermolecular forces exhibited by pyridazine would affect favorably the mechanical and thermal properties of polymers con-



I

II

(1)

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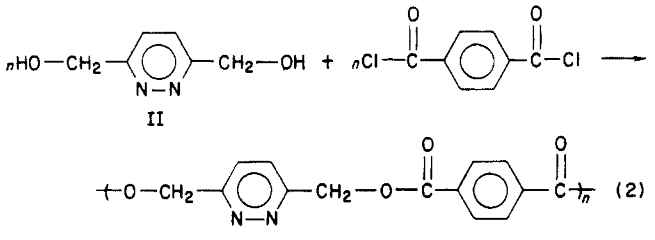
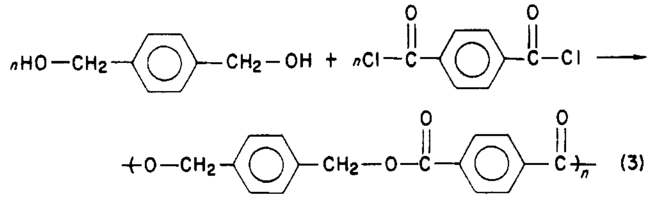
taining this moiety. Thus, the polyesters of terephthaloyl chloride with both II and the analogous benzene compound were prepared for comparison by an interfacial polycondensation reaction[1,4] at low temperature (eq 2 and 3).



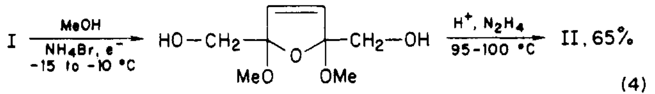
X



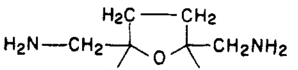
XI

The preparation of the polymer X by the high-temperature polycondensation reaction[2,5] of II with dimethyl terephthalate was also attempted in the presence of various catalysts, such as dibutylstannous oxide (Bu_2SnO),[6] zinc acetate [$Zn(OAc)_2$],[7] lead oxide–antimony trioxide (PbO/Sb_2O_3),[5] and calcium acetate dihydrate–antimony trioxide [$Ca(OAc)_2\cdot 2H_2O/Sb_2O_3$].[3] However, II began to decompose before the desired temperature of 220 °C was reached.

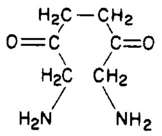
The preparation of II on a small scale with a 56.7% overall yield was reported recently,[8] and it involved an electrolytic methoxylation of I. We duplicated this synthetic method on a somewhat larger scale by using the electrolytic cell shown in Figure 1, but the overall yield of II from I was only 33% (eq 4). The instability of the intermediate III requires the use of low temperatures, and this, in turn, limits the rate at which the electrolytic methoxylation can be carried out.



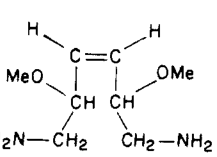
The reaction of III with hydrazine gave, in addition to a 65% yield of II, three byproducts that were not reported previously. They were separated by means of preparative TLC, and on the basis of NMR spectra they were assigned structures IV, V, and VI. Variations of experimental conditions designed to avoid the formation of byproducts IV–VI were unsuccesful.



IV, 15%



V, 10%



VI, 10%

Direct conversion of I to II was also attempted under a variety of experimental conditions, but II could not be detected and only small amounts of 3-methyl-6-(hydroxymethyl)pyridazine were isolated. Variations in the nature of catalyst, reaction time, stoichiometric ratios of reactants, and the mode of addition of reactants did not yield II. Similarly, the conversion of I to II by way of the diacetate VII[9] (eq 5) failed to give the desired pyridazine, and almost all of VII was recovered.

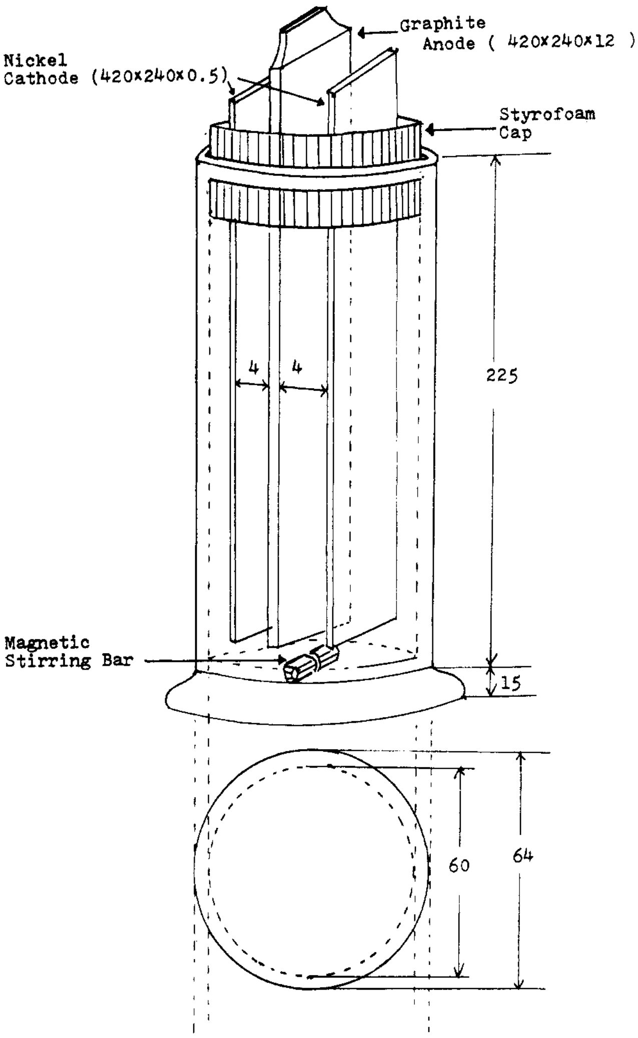
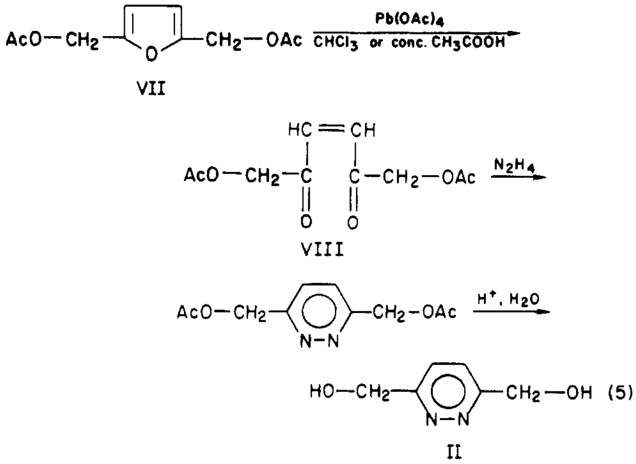
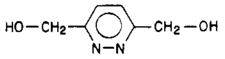
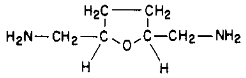
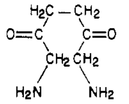
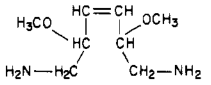


Figure 1. Electrolytic cell (all dimensions shown in mm).



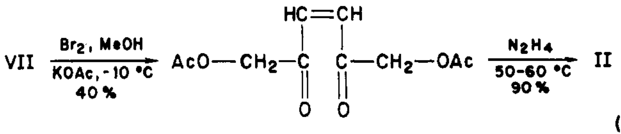
A convenient preparation of II that avoids the tedious electrolytic methoxylation and the formation of undesired byproducts IV, V, and VI and that is also suitable for scaleup involves the formation of a new compound, 1,6-

Table I
TLC Results and Assignments of NMR Data of II and of Byproducts

R_f value	yield, %	^{1}H NMR data CDCl$_3$/Me$_4$Si (ppm)	assigned structure
0.40	65	*a*	 II
0.55	15	1.80 (NH_2, s, r) 1.87 (CH_2-cyclic, t, 4, J = 10 Hz) 2.80 (CH_2NH_2, d, 4, J = 4 Hz) 3.33 (CH-O, q, 2, J = 4 Hz)	 IV
0.65	10	1.80 (NH_2, s, r) 1.87 ($CH_2C{=}O$, t, 4, J = 10 Hz) 3.27 (CH_2NH_2, s, 4)	 V
0.75	10	1.40 (NH_2, s, 4) 2.40 (CH_2NH_2, d, 4, J = 2.0 Hz) 3.37 (-OCH_3, s, 6) 5.90 (=CH, d, 2, J = 2.0 Hz)	 VI

[a] Fully characterized; see Experimental Section for details.

diacetoxy-3-hexene-2,5-dione (VIII) as an intermediate, as shown in eq 6.



$$\mathrm{VII} \xrightarrow[\substack{\mathrm{KOAc,\,-10\,^\circ C}\\ 40\%}]{\mathrm{Br_2,\,MeOH}} \mathrm{AcO{-}CH_2{-}C(=O){-}CH{=}CH{-}C(=O){-}CH_2{-}OAc} \xrightarrow[\substack{50\text{-}60\,^\circ\mathrm{C}\\ 90\%}]{\mathrm{N_2H_4}} \mathrm{II} \qquad (6)$$

VIII

Experimental Section[10]

Purification of 2,5-Bis(hydroxymethyl)furan (I). In order to obtain reproducible results, it was necessary to purify the technical grade I purchased from Quaker Oats Co. A satisfactory procedure for the purification of I follows.

Crude I (50 g) was dissolved in 400 mL of warm ethyl acetate (60 °C) or in a benzene/methanol (9:1, v/v) mixture (60 °C), and the solution was then cooled to room temperature. The supernatant solution of I was separated from the brownish, oily mixture of decomposition products by decantation. On occasion this procedure had to be repeated. The solution was poured into 400 mL of cold hexane and allowed to evaporate slowly in the hood. Crystallization was initiated by scratching the wall and bottom of the beaker with a stirring rod. After the crystallization started, the solution was kept overnight at -5 °C and 40 g (80%) of pure I was obtained by filtration. Pure I, colorless crystals with mp 75–76 °C similar to that (74.5–75 °C) reported previously,[11] gave the expected NMR spectra and showed a single spot in TLC. The R_f value of I is 0.56 with ethyl acetate/2-propanol (1:1) as eluent and siilica gel adsorbent: ^{1}H NMR (CDCl)$_3$/Me$_2$SO-d_6/Me$_4$Si) (ppm) 4.37 (CH_2, s, 4), 5.07 (OH, s, 2), 6.10 (furan ring-H, s, 2).

Preparation of 2,5-Dimethoxy-2,5-bis(hydroxymethyl)-furan (III) from I. Electrolytic methoxylation of I was carried out with ammonium bromide as an electrolyte, nickel cathode, graphite anode, and a current strength of 5–8 A at 12 V. A solution of 32.0 g (0.25 mol) of I and 12.25 g (0.125 mol) of ammonium bromide in 450 mL of methanol was cooled to -15 °C and electrolyzed slowly for 5 h in order to prevent a rise in the temperature maintained between -15 and -10 °C. The reaction mixture was then dried over anhydrous potassium carbonate and poured into a sodium methoxide solution prepared from 2.5 g of sodium metal and 100 mL of methanol. The solvent was removed from the reaction mixture under reduced pressure with a rotatory evaporator. A mixture of 600 mL of ethyl ether and 100 mL of acetone was then added to the reaction mixture, and the inorganic precipitate was removed by filtration. Removal of solvents under reduced pressure gave 59.0 g of a yellowish-orange oil that was partially crystallized by cooling. To maximize crystallization the mixture was kept overnight at -5 °C. Crystals of III were separated by filtration and the contaminants were washed out with cold acetone. After recrystallization from diethyl ether, 24.1 g (50.8%) of III was obtained: colorless crystals, mp 101.0–102.0 °C (lit.[8] mp 101–101.5 °C). The structure of III was confirmed by ^{1}H NMR spectroscopy and by elemental analysis. III gave a single spot in TLC with a R_f value of 0.77 with methylene chloride/2-propanol (4:1) as eluant: ^{1}H NMR, (CDCl$_3$/Me$_2$SO-d_6/Me$_4$Si) (ppm) 3.27 (OCH_3, s, 6), 3.44 (OCH_2, d, 4, J = 2.4 Hz), 4.77 (OH, t, 2, J = 3.8 Hz), 5.90 (furan ring-H, s, 2).

Anal. Calcd for $C_8H_{14}O_5$: C, 50.52; H, 7.42. Found: C, 50.55; H, 7.68.

Preparation of 3,6-Bis(hydroxymethyl)pyridazine (II) from III. III (4.75 g, 0.025 mol) was heated with 50 mL of 0.2 N hydrochloric acid for 10 min in a boiling water bath until the mixture became dark red. The mixture was quickly cooled to -5 °C and 3.54 g (3.50 mL) of anhydrous hydrazine was added with stirring. The reaction mixture was heated for 30 min at 100 °C, cooled, and extracted continuously for 24 h with 600 mL of ethyl acetate. The solvents were removed under reduced pressure to give 9.0 g of yellow oil. TLC showed four spots with R_f values of 0.75, 0.65, 0.55, and 0.40, respectively. The products (9.0 g) were dissolved in methylene chloride by heating the solution to the boiling point. The solution was cooled to start crystallization and kept overnight at -5 °C, and then the solvent was removed by decantation. After crystallization from ethyl acetate, 2.30 g (65.6% yield) of II was obtained as slightly yellow crystals. Colorless crystals of II were obtained after a second crystallization from ethyl acetate: mp 105.5–106 °C (lit.[8] mp 105–105.5 °C). The R_f value of II is 0.40 on silica gel with acetone as an eluent. ^{1}H NMR, (CDCl$_3$/Me$_2$SO-d_6/Me$_4$Si) (ppm) 4.65 (OCH_2, d, 4, J = 6.0 Hz), 5.47 (OH, t, 2, J = 5.0 Hz), 7.57 (aromatic-H, s, 2).

Anal. Calcd for $C_6H_8N_2O_2$: C, 51.42; H, 5.75; N, 20.00. Found: C, 51.25; H, 5.93; N, 19.76.

The byproducts were successfully separated by preparative TLC and acetone. They were assigned structures IV, V, and VI, respectively, on the basis of their NMR spectra (Table I).

Preparation of 1,6-Diacetoxy-3-hexene-2,5-dione (VIII) from 2,5-Bis(acetoxymethyl)furan (VII). Potassium acetate (39.3 g, 0.4 mol) and 21.2 g (0.1 mol) of VII[9] were dissolved in a stirred solution of 7.2 mL (0.4 mol) of water and 400 mL of methanol, and the solution was cooled to -10 °C in a 1-L, three-necked flask equipped with a magnetic stirrer. If the potassium acetate solidified before reaching the temperature of -10 °C, more methanol was added and the solution was stirred more vigorously. A solution of 10 mL (0.2 mol) of bromine in 100 mL of methanol was cooled to -10 °C and added slowly to the reaction mixture with stirring during 15 min. The reaction mixture was allowed to stand for an additional 15 min at -10 °C in a dry ice–acetone bath and then poured into 100 mL of cold water saturated with sodium bicarbonate. The reaction mixture was concentrated by evaporation overnight at room temperature in a hood and then extracted with ethyl acetate. The ethyl acetate extract was dried over anhydrous potassium carbonate and concentrated by means of a rotatory evaporator under reduced pressure to give a yellowish residue. The residue was dissolved in 300 mL of ethyl acetate/benzene (3:1) and the solution was filtered to remove the inorganic precipitate. The filtrate was concentrated again by means of a rotatory evaporator under reduced pressure, the semisolid residue was dissolved in 100 mL of a warm mixture (60 °C) of toluene/ethyl acetate (3:1 by volume), and the solution was then slowly poured into 600 mL of cold petroleum ether. VIII was crystallized by slow evaporation of the solvent in a hood and by cooling the residual solution in an ice–water bath and at -5 °C. Upon filtration, 9.13 g (40% yield) of crude VIII was obtained as slightly yellow crystals. After two crystallizations, first from ethyl ether and then from a mixture of ethyl ether and petroleum ether (1:1 by volume), the colorless crystal had a melting point of 91.5–92.0 °C. The R_f value of VIII is 0.27 [toluene/ethyl acetate (3:1 by volume), silica gel]. VIII gave the expected NMR spectrum: ^{1}H NMR, ($CDCl_3/Me_4Si$) (ppm) 2.16 (CH_3, s, 6), 4.83 (OCH_2, s, 4), 6.97 (=CH, s, 2).

Anal. Calcd for $C_{10}H_{12}O_6$: C, 52.63; H, 5.30. Found: C, 52.74; H, 5.22.

Preparation of 3,6-Bis(hydroxymethyl)pyridazine (II) from VIII. A solution of 2.12 g (0.01 mol) of VIII in 5 mL of water and 1.28 mL (0.04 mol) of 95% hydrazine was prepared at -5 to -10 °C, warmed at 60 °C for 20 min, and then poured over 3 g of potassium carbonate. The product was extracted with 500 mL of hot ethyl acetate and the extract was dried over anhydrous potassium carbonate. The extract was concentrated by means of a rotatory evaporator under reduced pressure and showed a single TLC spot that corresponds to the desired II. After crystallization from methylene cloride, 1.26 g (90% yield) of crude II was obtained as a slightly yellow crystal. After two crystallizations from ethyl acetate, the colorless crystals gave a melting point of 105.5–106 °C and showed the correct NMR spectrum.

Anal. Calcd for $C_6H_8N_2O_2$: C, 51.42; H, 5.75; N, 20.00. Found: C, 51.62; H, 5.85; N, 20.13.

Attempted Preparation of Poly(3,6-pyridazinediylbis(methylene) terephthalate) (X) by High-Temperature Polycondensation Reaction[2,5] from II and Dimethyl Terephthalate. Because of the loss of dimethyl terephthalate due to sublimation, an extra amount of dimethyl terephthalate was used. In a polymer tube bearing a side arm and a vacuum connection were placed 2.80 g (0.02 mol) II, 4.85 g (0.025 mol) of dimethyl terephthalate, 0.002 g of lead oxide, and 0.005 g of antimony trioxide.[5] The tube was partially immersed in a silicone oil bath (150–180 °C) equipped with a sensor connected to an automatic temperature control device, and a capillary tube was introduced that reached the bottom of the tube. The side arm of the tube was heated to prevent clogging from the distillation of some dimethyl terephthalate. A slow stream of nitrogen was passed through the melt, and the melt was heated for 1 h at 150–180 °C, 1 h at 200–205 °C, and 2 h at 220–225 °C. Transesterification was supposed to be completed at this point, and the melt was to be heated for 2–3 h at 280 °C under vacuum (~0.5 mmHg) in order to increase the molecular weight. However, II began to decompose at 200 °C, before reaching the desired temperature. Attempts to prepare the polymer (X) in the presence of various other catalysts, such as dibutyl stannous oxide,[6] zinc acetate,[7] and calcium acetate dihydrate–antimony trioxide,[3] were also unsuccessful because of the decomposition of II.

Preparation of Poly(3,6-pyridazinediylbis(methylene) terephthalate) (X) by Interfacial Polycondensation. Interfacial polycondensation[1,4] was successful for the preparation of X. Alcohol-free chloroform was dried by washing with concentrated sulfuric acid and kept over reagent grade molecular sieves (pellets Type 3 A, $^1/_{16}$ in. MX 1583-80, MCB Manufacturing Chemicals Inc.). A solution of 1.75 g (0.0125 mol) of II and 1.0 g (0.025 mol) of sodium hydroxide in 85 mL of water was prepared in a household blender at low speed. A standardized, carbonate-free volumetric solution of sodium hydroxide (Acculate NaOH) was used. A second solution of 2.54 g (0.0125 mol) of reagent grade terephthaloyl chloride in 37.5 mL of alcohol-free chloroform was prepared in a 100-mL beaker. A 10% aqueous solution of sodium lauryl sulfate (7.5 mL) was added to the blender operated at maximum speed, and the chloroform solution of terephthaloyl chloride was then quickly added. The rapidly stirred solution had a tendency to foam. The emulsion was stirred for 8 min and the reaction mixture was poured into 1 L of acetone to coagulate the polymer. The product was filtered and washed once with acetone. The granular polymer was transferred to the blender and washed there with 500 mL of water to remove salt and the dispersing agent. The polymer was filtered again and washed twice with water and once more with acetone. The air-dried polymer was dissolved in 50 mL of hot (90–100 °C) dimethyl sulfoxide (Me_2SO) with stirring and the solution was poured into 800 mL of acetone and cooled. The polymer was filtered and washed with acetone, and the purification with Me_2SO was repeated. Finally the polymer was dried for 24 h at 110 °C in a vacuum oven (10 mmHg) to give 2.9 g of X.

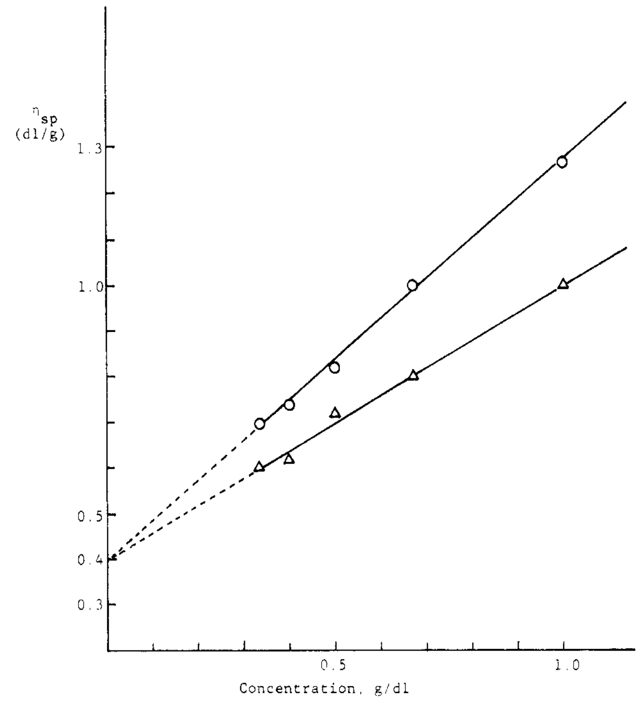


Figure 2. Reduced viscosity–concentration curves for a poly(3,6-pyridazinediylbis(methylene)terephthalate) (X) and a poly(*p*-xylylene terephthalate) (XI) in 1,1,2,2-tetrachloroethane–phenol (40/60 by weight) at 30 °C: (○) polymer X; (△) polymer XI.

Table II
Solution Viscosities of Poly(3,6-pyridazinediylbis(methylene) terephthalate) (X) and Poly(*p*-xylylene terephthalate) (XI)

polym	concn, g/dL	t,[a] s	$\eta_{sp} = (t - t_0)/t_0$	$\eta_{red} = \eta_{sp}/C$	$[\eta]$[b]
X	1.00	537	1.2563	1.26	0.4
	0.67	397	0.6681	1.00	
	0.50	336	0.4118	0.82	
	0.40	308	0.2941	0.74	
	0.33	293	0.2311	0.70	
XI	1.00	476	1.0000	1.00	0.4
	0.67	365	0.5336	0.80	
	0.50	324	0.3613	0.72	
	0.40	297	0.2479	0.62	
	0.33	285	0.1975	0.60	

[a] Solution viscosities were measured from the efflux time t required for a specified volume of polymer solution by comparison with the corresponding efflux time for the solvent at 30 °C (t_0 = 328 s). [b] The intrinsic viscosity $[\eta]$ was obtained by extrapolation of reduced viscosity (η_{red}) to $C = 0$:$[\eta] = (\eta_{sp}/C)_{C=0}$.

The polymer solution viscosity was measured in an Ubbelohde viscometer. The polymer had an intrinsic viscosity of 0.4 dL/g (Table II and Figure 2) in 1,1,2,2-tetrachloroethane/phenol (40/60 by weight) at 30 °C. The crystalline melting point (T_m) of the polymer at 215 °C was determined by differential scanning calorimetry (DSC) (Figure 3). T_m of tin (505 K) was used to standardize the apparatus, and it agreed with the theoretical T_m (505.06 K). The degradation of X was measured both in argon and in air by thermal gravimetric analysis (TGA). In both cases X started to decompose at 310 °C, but it decomposed more rapidly in air than in argon during the initial stage of decomposition. X

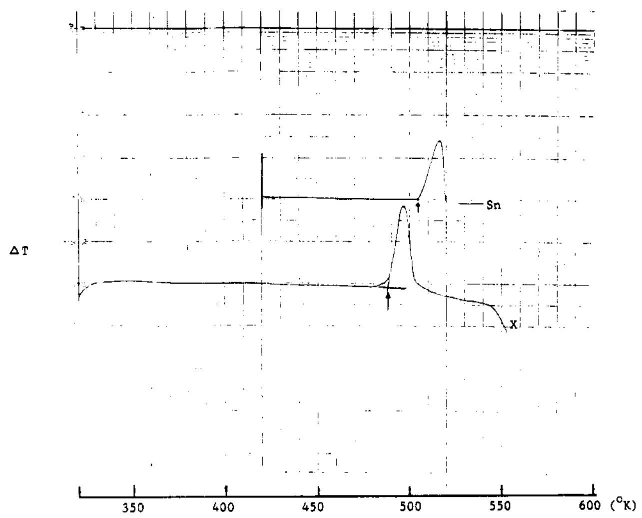


Figure 3. DSC data of X.

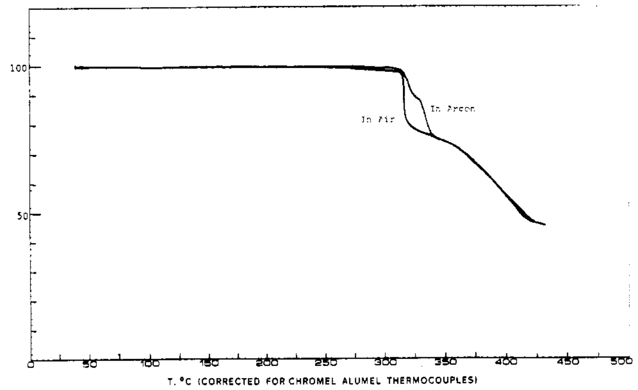
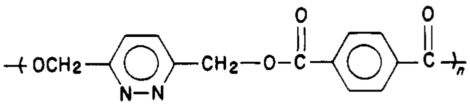


Figure 4. TGA data of X.

showed 10 and 50% weight losses at 325 and at 390 °C, respectively, in argon, while it showed 21 and 50% weight losses at 325 and 390 °C, respectively, in air (Figure 4). X is soluble in 1,1,2,2-tetrachloroethane, dimethyl sulfoxide, and dimethylformamide. Films of X were cast from solutions in 1,1,2,2-tetrachloroethane (5% by weight) and found to be brittle.

Anal. Calcd for $C_{14}H_{10}N_2O_4$ assuming the structure of X to be as shown below: C, 62.22% H, 3.73; N, 10.37. Found: C, 61.95; H, 3.93; N, 9.98.



Preparation of Poly(*p*-xylylene terephthalate) (XI) by Interfacial Polycondensation. XI was prepared by an interfacial polycondensation reaction in order to duplicate the conditions used for the synthesis of X. A solution of 1.75 g (0.0125 mol) of reagent grade 1,4-bis(hydroxymethyl)benzene and 1.0 g (0.025 mol) of sodium hydroxide in 85 mL of water was prepared in a household blender at low speed. The rest of the procedure was the same as that described for the preparation of X, and 2.8 g of XI was obtained. XI gave an intrinsic viscosity of 0.4 dL/g in 1,1,2,2-tetrachloroethane/phenol (40/60 by weight) at 30 °C (Table II and Figure 2). T_m of XI at 291 °C was determined by DSC (Figure 5) with tin as the reference substance. The degradation of XI was measured both in argon and in air by TGA. In both cases XI started to decompose at 320 °C, but it decomposed more rapidly in air than in argon as the decomposition progressed. XI showed 10 and 50% weight loss at 370 and at 405 °C, respectively, in argon, while it showed 10 and 50% weight loss at 370 and at 394 °C, respectively, in air (Figure 6). XI is soluble in 1,1,2,2-tetrachloroethane, dimethyl sulfoxide, and dimethylformamide. Films of XI were cast from solutions in 1,1,2,2-tetrachloroethane (5% by wt) and found to be brittle.

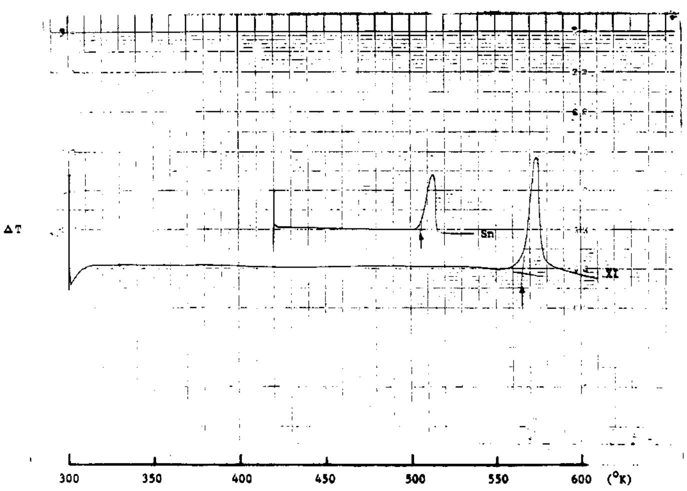


Figure 5. DSC data of XI.

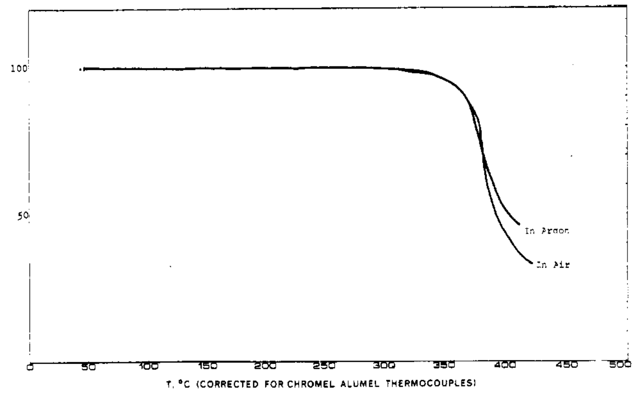


Figure 6. TGA data of XI.

Anal. Calcd for $C_{16}H_{12}O_4$ assuming the structure of XI to be $(OCH_2C_6H_4CH_2OOCC_6H_4CO)_n$: C, 71.64; H, 4.51. Found: C, 70.98; H, 4.76.

Preparation of 3,6-Pyridazinediylbis(methylene) Dibenzoate (XII). Standardized sodium hydroxide (4 mL, 0.32 g, 0.008 mol) (0.1 N Acculate NaOH) were added in several portions with vigorous stirring to a solution of 0.5 g (0.0035 mol) of II, 2 mL of water, and 0.9 mL (1.089 g, 0.0077 mol) of benzoyl chloride. The mixture was stirred for 5 min and then tested with litmus paper to make sure that it was still alkaline. The product was extracted with ethyl ether and dried by evaporation of the solvent. After crystallization from methanol–hexane (1:1), 1.04 g (85.3% yield) of XII was obtained as a white crystalline solid: mp 114–115 °C; single TLC spot (R_f = 0.90, silica gel, acetone). XII gave the expected NMR spectrum, XII turned brown at 160 °C on heating in a capillary tube, darkened upon further heating, liberated a gas at 300 °C, and turned to a black tar at 310 °C. ^{1}H NMR ($CDCl_3/Me_4Si$) (ppm) 5.70 (OCH_2, s, 2), 7.50 (benzene ring-H, m, 5), 8.01 (pyridazine ring-H, d, 1, J = 3.0 Hz).

Anal. Calcd for $C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.62; N, 8.04. Found: C, 68.83; H, 4.57; N, 7.97.

Polymerization of Styrene. Samples of freshly distilled styrene were polymerized with or without initiator in polymerization bottles sealed under an argon atmosphere as summarized in Table III. The polymerization mixture was dissolved in 80 mL of toluene, and the solution was poured with vigorous stirring into 800 mL of methanol. The precipitate was redissolved and reprecipitated to give a fluffy, white solid that was dried and weighed. The molecular weights of the polystyrene samples were determined from viscosity measurements of solutions in toluene at 25 °C as summarized in Tables III and IV and in Figures 7 and 8.

Visualization Methods of TLC Spots. The most commonly used visualization reagent was 1% (w/v) ceric sulfate [$Ce(SO_4)_4$] solution in a dilute sulfuric acid. TLC plates were sprayed by this reagent and heated for 3–5 min at 150–160 °C. All TLC spots, in our studies, were visualized by this method unless mentioned otherwise. The procedure for the preparation of this reagent is

Table III
Polymerization of Styrene

expt no.	reacn temp, °C	reacn time	initiator, 1% (w/w)	amt of styrene used, g	amt of polystyrene obtained, g	$[\eta]$,[a] dL/g	mol wt of polystyrene
1	85–90	3 days	benzoyl peroxide	10.0	9.0	0.24	4.67×10^4
2	85–90	3 days	XII	10.0	3.6	2.70	1.35×10^6
3	85–90	3 days	none	10.0	3.5	2.58	1.27×10^6
4	125–135	10 min	XII	3.0	0.2	0.94	3.11×10^5
5	125–135	10 min	none	3.0	0.05	1.50	5.96×10^5

[a] Intrinsic viscosity was obtained by extrapolation of reduced viscosity (η_{red}) to $C = 0$:$[\eta] = (\eta_{sp}/C)_{C=0}$ (see Table IV for details).

Table IV
Solution Viscosities and Molecular Weight of Polystyrenes

expt no.[a]	concn, g/dL	t,[b] s	$\eta_{sp} = (t - t_0)/t_0$	$\eta_{red} = \eta_{sp}/C$	$[\eta]$[c]	mol wt of polystyrene[d]
1	1.00	66.0	0.4667	0.47	0.24	4.67×10^4
	0.67	56.8	0.2622	0.39		
	0.50	53.0	0.1778	0.36		
	0.40	51.0	0.1333	0.33		
	0.33	49.8	0.1067	0.32		
2	1.00	323	6.1778	6.18	2.70	1.35×10^6
	0.67	192	3.2667	4.87		
	0.50	144	2.2000	4.40		
	0.40	118	1.6222	4.05		
3	1.00	307	5.8222	5.82	2.58	1.27×10^6
	0.67	183	3.0667	4.58		
	0.50	139	2.0889	4.18		
	0.40	114	1.5333	3.83		
	0.33	100	1.2222	3.70		
4	1.00	110	1.4444	1.44	0.94	3.11×10^5
	0.67	83	0.8444	1.26		
	0.50	72	0.6000	1.20		
	0.40	66	0.4667	1.17		
	0.33	61	0.3556	1.08		
5	1.00	130	1.8889	1.89	1.50	5.96×10^5
	0.67	98	1.1778	1.76		
	0.50	83	0.8444	1.69		
	0.40	75	0.6667	1.67		
	0.33	69	0.5333	1.62		

[a] Experimental conditions of each experiment are described in Table VII. [b] t is the efflux time of polymer solution in toluene at 25 °C and, t_0 is the efflux time of toluene at 25 °C ($t_0 = 45$ s). [c] $[\eta]$ was obtained by extrapolation of η_{red} to $C = 0$. [d] Molecular weight was obtained by the Mark–Houwink equation.[15] $[\eta] = K\bar{M}_v{}^a$, where $K = 1.05 \times 10^{-4}\ r$ and, $a = 0.72$ (at 25 °C, toluene).[16] K value (1.05×10^{-2}) in ref 16 was divided by 100 since the dimension of $[\eta]$ in ref 16 is mL/g and we use dL/g for convenience.

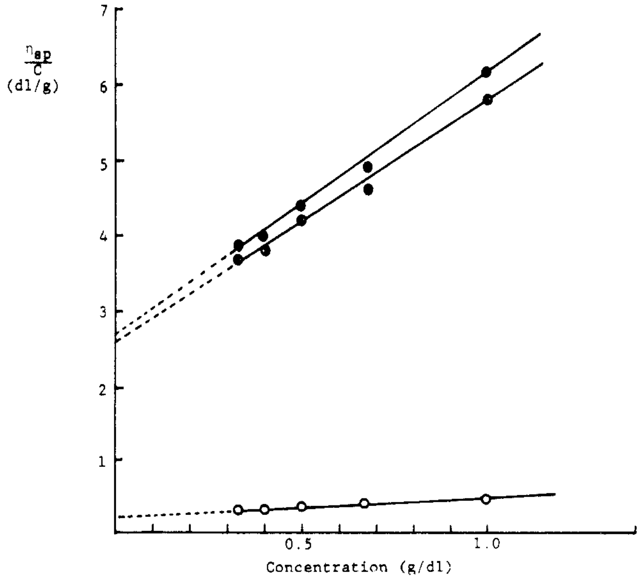


Figure 7. Reduced viscosity–concentration curves for polystyrenes in toluene at 25 °C: (○) expt. 1 in Tables III and IV; (●) expt 2 in Tables III and IV; (⊗) expt 3 in Tables III and IV.

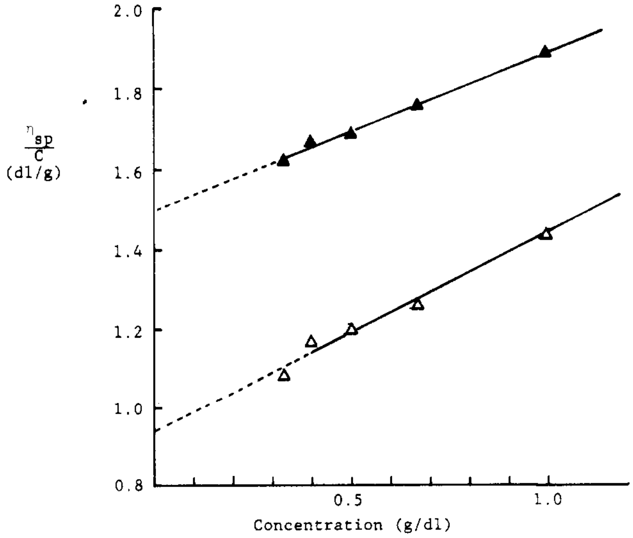


Figure 8. Reduced viscosity–concentration curves for polystyrenes in toluene at 25 °C: (△) expt 4 in Tables III and IV; (▲) expt 5 in Tables III and IV.

as follows: 8 g of ceric sulfate was dissolved in the mixture of 190 mL of concentrated sulfuric acid and 650 mL of water.

The second most common method of visualization was the use of an ultraviolet (UV) lamp. A UV light was used for the visualization of spots in preparative TLC.

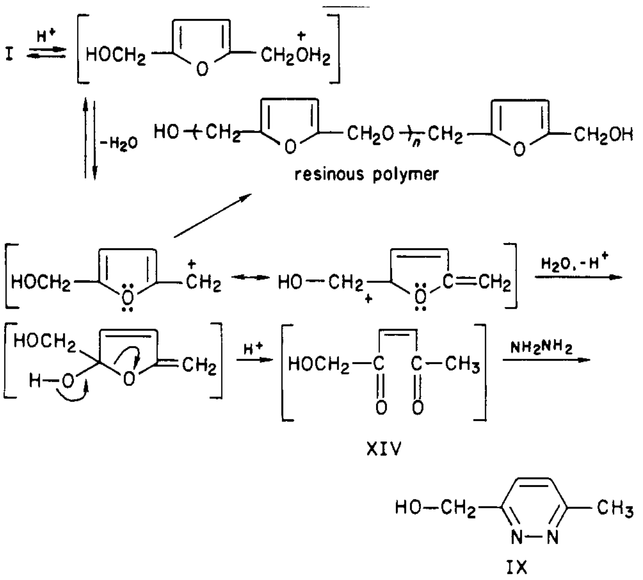
A saturated picric acid solution in methanol was used for the visualization of the spot that corresponds to II and its dibenzoate.

Materials. The silica, GF-254 (Type 60), purchased from EM Laboratories, Inc. (Associate of E. Merck, Darmstadt, West

Germany) was used for the preparation of TLC plates. Uniplates precoated with silica gel GF (20 × 20 cm^2, 1000 μm thickness, Analtech, Inc.) were used in preparative TLC.

Discussion

The formation of IX during the attempted conversion of I to II can be explained on the basis of the Leger and Hibbert mechanism[12] for the transformation of furfuryl alcohol to levulinic acid. Similarly, the formation of IX can be explained to involve the intermediate XIV during the reaction of I with acid and hydrazine together with the observed resinous polymer

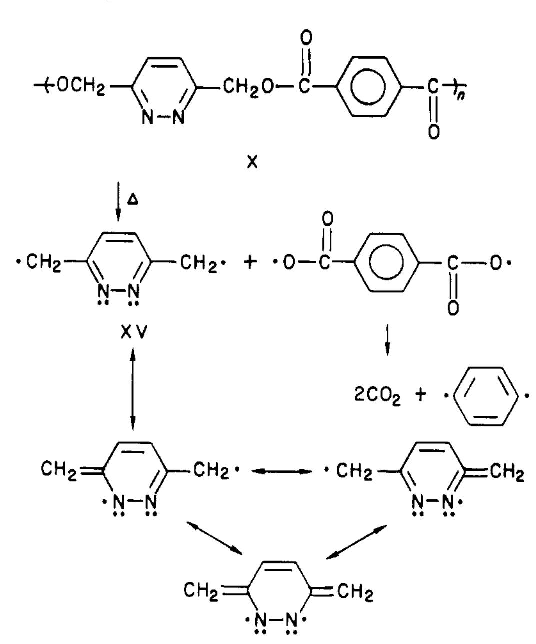


Noviskii and his colleagues[8] have reported the preparation of II from I, on a small scale, in a 56.7% overall yield via III. In our hands, but on a larger scale, the overall yield of II from I was only 33.0%, and the reaction gave byproducts IV, V, and VI, which were not reported previously. Apparently, the latter are produced by the reactions of ammonia formed from the oxidative decomposition of hydrazine[14]

$$4H_2NNH_2 + O_2 \rightarrow 2N_2 + 4NH_3 + 2H_2O$$

In view of the observation that the polymer of interest X readily undergoes thermal decomposition around 310 °C, it was suspected that the 3,6-pyridazinediylbis(methylene) ester moiety is the site of thermal instability, possibly because of the resonance stabilization of the 6-methylene-3-pyridazinylmethyl and the corresponding diradical XV.

In order to test this hypothesis, 3,6-pyridazinediylbis(methylene) dibenzoate (XII) was prepared by means of the Schotten–Baumann procedure[13] and it was found that XII indeed decomposed at about 160 °C, turned brown, evolved a gas at about 300 °C, and turned into a black tar. The apparent formation of free radicals upon thermal decomposition of XII was confirmed by heating styrene in its presence and absence and by comparing the yields and average molecular weights of the resulting polystyrenes. As can be seen from their results summarized in Table III, the polymerization of styrene was not catalyzed by XII at 85–90 °C, but there is definite evidence that XII exerted a catalytic function at 125–135 °C in view of the quadruple yield of polystyrene and the 50% reduction of its molecular weight. Furthermore, polystyrene prepared at 125–135 °C in the presence of 1% by weight of XII was found to contain 0.64% N, and this result corresponds to a polymer with a 42:1 ratio of styrene to pyridazinediylbis(methylene) moieties.



Conclusions

While the pyridazine ring is conducive to strong intermolecular associations because of its builtin polarity, its 3,6-methylene derivatives are homolyzed at relatively low temperatures, presumably because of resonance stabilization of the benzylic-like radicals. Thus, while a polyester of II such as X is not a high-temperature-resistant polymer, analogous monomeric esters such as XII may be useful as high-temperature biradical polymerization initiators.

Acknowledgment. We thank Dow Chemical Co. for a research fellowship award to M.I.C. and M-H-W Laboratories, Phoenix, AZ, for microanalysis reported in this work.

Registry No. I, 1883-75-6; II, 37444-30-7; (II)·(terephthaloyl chloride) (copolymer), 99214-32-1; III, 37444-26-1; VII, 5076-10-8; VIII, 99214-02-5; XII, 99214-03-6; hydrazine, 302-01-2; (1,4-bis(hydroxymethyl)benzene)·(terephthaloyl chloride) (copolymer), 99214-33-2; (1,4-bis(hydroxymethyl)benzene)·(terephthaloyl chloride) (SRU), 26468-49-5; benzoyl chloride, 98-88-4; polystyrene, 9003-53-6.

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Copolymerization of Styrene with *N*-Arylmaleimides

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ABSTRACT: The copolymerization of styrene with (2-chlorophenyl)maleimides was investigated in two solvents. It has been shown that a charge-transfer complex participates in the process of copolymerization. The relative reactivity ratios were found to be solvent-dependent. The initial rate of copolymerization was measured as a function of the monomer molar ratios, and the participation of the charge-transfer complex monomer and the free monomers was quantitatively estimated.

Introduction

In continuation of our interest in investigating the polymerization behavior of the *N*-arylmaleimides,[1-3] styrene was chosen as a comonomer to study their copolymerization behavior. There has been controversial information regarding the copolymerization of *N*-phenylmaleimide (NPMI) and styrene (St).

It was shown that NPMI and St undergo alternating copolymerization in benzene and in chiral solvents;[4,5] however, trials to detect the formation of complexation between the monomers with UV and/or NMR spectroscopy were not successful. On the other hand, Russian reporters have indicated[6,7] that the copolymerization proceeded via the participation of a charge-transfer complex (CTC) in addition to free monomers and that the predominant mechanism was by the addition of CTC monomer to the macroradical. No detailed information is however available.

The large difference in polarity between e values for St ($e = -0.8$) and *N*-arylmaleimide (e.g., *N*-(2-chlorophenyl)maleimide[2,4]) seemed a good enough base for the formation of even a weak CTC between these two monomers. This study attempts to throw more light on this controversial behavior.

Several approaches have been used in the literature to treat the kinetic data of systems with the anticipated participation of CTC in the copolymerization process. Seiner and Litt[8] first derived a mathematical formulation for alternating copolymerization systems. In view of the complexity of the mathematical expressions, they were used under certain restrictions, in most cases not representing the real situation. Farmer et al.[9,10] have analyzed the model in terms of kinetic probabilities and have been able to compare the importance of different models in a few complicated systems. Braun and Czerwinski[11] extended the method of Farmer et al. to describe the kinetic relationship for systems supposed to involve complexes between monomers.

Arnaud, Caze, and Fossey[12] and independently Georgiev and Zubov[13] have used the existence of maxima in the rate vs. feed composition curve in alternating copolymerization in order to analyze the kinetic data and to get values for the different rate constants. However, the exact position of the maxima is usually not well-defined, and the method cannot be applied always with certainity.

A treatment of the data for alternating copolymerization was also proposed by Shirota et al.[14,15] The treatment is based on the view that a 1:1 alternation in the resulting copolymer is brought about by the stabilization of the transition state in the cross reactions of the free monomers and the complex. The treatment of Shirota et al. has been adapted by us in the present study.

Recently, Deb and Meyerhoff[16,17] presented a scheme for the copolymerization of styrene and maleic anhydride that included the participation of a charge-transfer complex between monomers in the propagation. They derived an equation for the rate of copolymerization that is resolvable into two parts signifying the influence of propagation via free monomer and by complex.

Experimental Section

Monomers. *N*-(2-Chlorophenyl)maleimide (2CMI) was prepared by the method of Searle[18] and recrystallized several times from ethanol. The purity of 2CMI was checked by TLC and NMR in order to make sure that it was free from unreacted maleic anhydride and the uncyclized maleamic acid. The latter acts as a moderate inhibitor for free radical polymerization of the maleimide. Melting points and elemental analysis agreed well with literature values.[1,4]

Styrene was distilled under reduced pressure after removal of the inhibitor by the usual method. It was kept cold and redistilled again directly before use.

Solvents. Dioxane (BDH) was refluxed over sodium wire for 24 h and distilled before use. DMF (prolabo) was used as received. Chloroform, methanol, ethanol, and acetone, pure for analysis (Fluka), were distilled before use.

Initiator. 2,2-Azobis(isobutyronitrile) (AIBN) (BDH) was recrystallized twice from methanol.

Rates of Copolymerization and Monomer Reactivity Ratios. Rates of copolymerization were measured dilatometrically. Dilatometers filled with initiator (AIBN), monomer mixture, and solvent were connected to a high-vacuum line and freed of oxygen by three freezing–thawing cycles. The dilatometers were then placed in transparent Dewar s flasks connected to a thermostat. The volume contraction was recorded as a function of time. The reaction was terminated by vacuum suction of the contents and precipitation in excess cold methanol. After filtration and washing, the copolymers were dried under vacuum to constant weight. The conversion was determined gravimetrically. Since

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