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Li Di[a]; Bruce M. Foxman[a]
[a] Department of Chemistry, Brandeis University, Waltham, MA, USA

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The Solid-state Polymerization of Styryl Monomers: A Structural Perspective*

LI DI and BRUCE M. FOXMAN[†]

Department of Chemistry, Brandeis University, Waltham, MA 02454-9110, USA

Styryl monomers *p*-acetamidostyrene 1, *p*-benzamidostyrene 2 and *p*-vinylbenzoic acid 3 polymerize upon heating, or under γ- or UV-irradiation. The crystal structures of 1-3 (including two polymorphs of 3) contain short contacts (≈ 4.2 Å) between $-CH{=}CH_2$ groups. Monomer single crystals subjected to heat or irradiation did not diffract X-rays and did not exhibit birefringence. NMR spectra of the polymerized product (at high degrees of conversion) were consistent with the formation of atactic polymer.

Keywords: Solid-state reaction; Crystal structure; Polymerization

INTRODUCTION

Of all solid-state polymerization reactions, those involving topotactic transformations from a monomer single crystal to a polymer single crystal are the most fascinating [1-7]. The solid-state polymerization of vinyl monomers stands in stark contrast to the class of topotactic solid-state polymerizations, which is closely governed by the crystal lattice. For the solid-state polymerization of vinyl monomers, current thinking continues to reflect the view that the geometrical arrangements of the monomer molecules have little influence on the nature of the reaction [8,9], though there are indications that the polymerizability of crystalline vinyl monomers is related to crystal structure [10]. ESR studies suggest that the dimer radical of barium methylacrylate monohydrate retains a preferred orientation in the crystal lattice of the monomer during polymerization [11,12]. X-ray diffraction shows that the aliphatic side chains retain their parallel orientation during the polymerization of vinyl stearate [13]. Infrared spectroscopy shows the retention of the dichroism of the N-H stretching frequency during the polymerization of *p*-benzamidostyrene below the glass transition temperature [14,15]. The retention of dichroism suggested that the polymer retained anisotropy. Highly crystalline poly(*p*-vinylbenzoic acid), which does not lose its birefringence until 350°C, was obtained by heating *p*-vinylbenzoic acid at 100°C for 15 days [16]. The latter two monomers, along with *p*-acetamidostyrene belong to a relatively rare set of molecules that may be readily polymerized in the solid state by thermal treatment, in addition to the more usual methods using UV- or γ-irradiation. The above interesting features suggested that a visit to the

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* In Honor of Professor Fumio Toda on the Occasion of His 67th Birthday.

[†] Corresponding author.

structural chemistry of these compounds, 30–35 years after their initial appearance in the literature, might provide new insight into the reactions of vinyl monomers in the solid state. Before embarking on this study, we carried out a search of the Cambridge Structural Database [17], which revealed the crystal structure of *only one* simple styryl monomer, styrylboronic acid [18]. We report here the crystal structures of *p*-acetamidostyrene **1**, *p*-benzamidostyrene **2** and the structure and polymorphism of *p*-vinylbenzoic acid **3**.

RESULTS AND DISCUSSION

Solid-state Polymerization of Compounds 1–3

Heating compounds **1**–**3** for extended periods leads to the corresponding polymers in good to near-quantitative yield (Tab. I). Compound **1** is also quite sensitive to γ-irradiation, and less to UV. Single crystals of **1** exhibit two kinds of morphology. Morphology I is a large thin plate, with a thickness of ≈ 0.01 mm along the *b* direction. Morphology II has a long rod-like shape with the rod axis along the *b* direction. After heating at 120°C for 7 h, light yellow isotropic polymer (polarizing microscope) was formed on the (010) surface for Morphology I; for Morphology II, the phenomenon observed is exactly the same as that reported previously, that is, isotropic polymer formed on the outside region of a monomer single crystal and proceeded toward the inside region. In both cases, *only* the unreacted monomer remains as a single crystal. The observed physical changes during the reaction suggest that thermal polymerization of **1** begins only at the crystal surface and proceeds inward at the monomer-polymer interface. For the UV and γ-irradiation reactions, the process appears to be physically different from the thermal polymerization. After reaction, based upon observation under a polarizing microscope, the product pseudomorph is isotropic. Solid **Poly-1**, however produced, did not diffract X-rays.

TABLE I Solid-state polymerization of styryl monomers

Compound	Method	Time/Dose	Yield
1	Heating	7 d, 120°C	65%
	γ-irradiation	2520 kGy	90%
	UV	180 d	45%
2	Heating	7 d, 150°C	95%
	γ-irradiation	2520 kGy	25%
	UV	180 d	10%
3b	Heating	10 d, 100°C	90%

Compound **2** was considerably less sensitive to both γ- and UV-irradiation. Previously, Morawetz and coworkers reported that the dichroism of N–H stretching in the IR (3340 cm) remained unchanged even with 80% of **2** converted to polymer (by heating below the glass transition temperature, 120°C) [14]. In the present work the thermal polymerization was followed below the glass transition temperature by using X-ray powder diffraction. Observations included gradual decrease of diffracted intensity and a corresponding increase in the background intensity. All samples of **Poly-2** obtained were amorphous. Examination by polarized light microscopy showed no birefringence. Monomer crystals obtained from triethyl orthoformate solutions polymerized (thermally) more rapidly than those obtained from methanol-methylene chloride solutions. Both samples had the same X-ray powder pattern. Thus, it appears that trace amounts of triethyl orthoformate accelerate the polymerization. A similar phenomenon was observed in the solid state polymerization of propiolaldehyde semicarbazone [19] under γ-irradiation. Sublimed material was not sensitive to γ-irradiation, while samples crystallized from chlorinated solvents reacted upon γ-irradiation.

Compound **3** is polymorphic. Monoclinic polymorph **3a**, space group $P2_1/c$, when heated to 60–70°C, underwent a phase transformation, physically a single crystal to polycrystalline conversion. The product phase (after transformation) was proved to be monoclinic **3b**, space group *C*2, *Cm*, or *C*2/*m*, by powder diffraction. Though both **3a** and **3b** appeared to polymerize at 100 - 120°C, only **3b** will be present at this temperature. Both **3a** and **3b** polymerize upon γ-irradiation (yields were not obtained). There is no indication of a (**3a** → **3b**) phase transformation during the process, as evidenced by powder diffraction patterns. Whether a small, undetectable amount of **3a** transformed to **3b** before polymerization or polymerized directly upon γ-irradiation cannot be addressed at this time, although this seems unlikely. All samples of **Poly-3** are amorphous as evidenced by powder diffraction. Examination of **Poly-3** by polarized light microscopy showed that the polymers exhibit no birefringence.

Polymer sequence determination may be carried out by NMR techniques; polystyrene [20 - 23] is a good model for the identification of the stereosequences of **Poly-1**, **Poly-2** and **Poly-3**. It is difficult to completely assign the ^{13}C NMR spectrum of atactic polystyrene, owing to the long-range sensitivity of the ^{13}C resonances to stereosequence (hexads for CH and heptads for C(1) carbons) [20] and some sensitivity to solvent. Nonetheless, the ^{1}H and ^{13}C NMR spectra of both isotactic and syndiotactic polystyrene have been unambiguously assigned and confirmed by statistical analyses and experimental studies. In the present work, comparison of the spectra of the polymers of **1–3** with those of polystyrene led to the conclusion that the polymers are atactic, rather than either isotactic or syndiotactic [23]. Regrettably, we were unable to reproduce any of the highly interesting anisotropic effects previously observed, and did not observe the formation of isotactic or syndiotactic polymer in these reactions.

Prior Structural Reports

The cell constants and space groups of **1** and **2** were reported in 1964, with partial, incomplete solutions of the structures [14]. Detailed structural information was not reported. For **1**, we found space group *Pbca*, $a = 25.184$, $b = 9.410$, $c = 7.676$ Å (Tab. II). The cell constants previously reported were $a = 7.05$, $b = 9.7$, $c = 25.5$ Å, with a reported space group of *Pbca* (*Pcab* would be expected for this setting). The space group found for **2** is *Cc*, with $a = 28.781$, $b = 5.288$, $c = 8.024$ Å, $\beta = 104.03°$, while the cell

TABLE II Data for the X-ray diffraction studies of **1**, **2** and **3a**

Formula	**1**, $C_{10}H_{11}ON$	**2**, $C_{15}H_{13}ON$	**3a**, $C_9H_8O_2$
Crystal System	Orthorhomibc	Monoclinic	Monoclinic
a, Å	25.184(8)	28.781(5)	8.380(2)
b,Å	9.410(3)	5.288(1)	6.579(1)
c,Å	7.676(2)	8.024(2)	14.844(3)
β,deg	(90)	104.03(2)	110.35(2)
V,Å^3	1819.1	1184.8	767.3
Z	8	4	4
Forumla Wt	161.204	223.275	148.161
Space group	$Pbca[D_{2h}^{15}; No.61]$	$Cc[C_s^4;\mathrm{No.9}]$	$P2_1/c[C_{2h}^5;\mathrm{No.14}]$
T, °C	294(1)	294(1)	294(1)
λ, Å	0.71073	0.71073	0.71073
ρ_{calc}, g-cm^{-3}	1.177	1.252	1.283
ρ_{obs}, g-cm^{-3}	1.18(1)	1.25(1)	1.28(1)
μ, mm^{-1}	0.0714	0.0733	0.0844
R $(I/\sigma(I) \geq 1.96)$	0.0498	0.0449	0.0397
R_w $(I/\sigma(I) \geq 1.96)$	0.0492	0.0554	0.0499

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o$; $R_w = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$.

TABLE III Selected bond lengths (Å) interplanar and bond angles (deg) for **1**, **2** and **3a**

p-Acetamidostyrene 1			
O(1)—C(9)	1.228(3)	C(1)—C(2)	1.283(4)
N(1)—C(6)	1.419(3)	C(2)—C(3)	1.474(4)
N(1)—C(9)	1.345(3)	C(9)—C(10)	1.490(3)
N(1)—H(1)	0.87 (3)		
C(6)—N(1)—C(9)	128.0(2)	O(1)—C(9)—N(1)	123.0(2)
C(6)—N(1)—H(1)	114(2)	O(1)—C(9)—C(10)	121.5(2)
C(9)—N(1)—H(1)	118(2)	N(1)—C(9)—C(10)	115.5 (2)
C(1)—C(2)—C(3)	127.5(3)		
C(1)/C(2)/C(3) — C(3)/C(4)/C(5)/C(6)/C(7)/C(8)			14.1
C(3)/C(4)/C(5)/C(6)/C(7)/C(8) — N(1)/C(9)/C(10)/O(1)			15.1
*p*Benzamidostyrene 2			
O(1)—C(9)	1.224 (4)	C(1)—C(2)	1.244 (7)
N(1)—C(6)	1.421 (4)	C(2)—C(3)	1.477 (5)
N(1)—C(9)	1.357 (4)	C(9)—C(10)	1.499 (5)
N(1)—H(1)	0.89 (4)	C(10)—C(11)	1.382 (5)
C(6)—N(1)—C(9)	125.2 (3)	O(1)—C(9)—N(1)	123.6 (3)
C(6)—N(1)—H(1)	118 (3)	O(1)—C(9)—C(10)	121.4 (3)
C(9)—N(1)—H(1)	115 (3)	N(1)—C(9)—C(10)	115.0 (3)
C(1)—C(2)—C(3)	129.5(5)		
C(1)/C(2)/C(3) — C(3)/C(4)/C(5)/C(6)/C(7)/C(8)			3.9
C(3)/C(4)/C(5)/C(6)/C(7)/C(8) — N(1)/C(9)/O(1)			35.4
N(1)/C(9)/O(1) — C(10)/C(11)/C(12)/C(13)/C(14)/C(15)			29.2
Vinylbenzoic acid 3a			
O(1)—C(9)	1.266 (2)	C(1)—C(2)	1.293 (2)
O(1)—H(1)	0.79 (4)	C(2)—C(3)	1.475 (2)
O(2)—C(9)	1.264 (2)	C(6)—C(9)	1.473 (2)
O(2)—H(2)	0.78 (4)		
C(9)—O(1)—H(1)	119 (3)	O(1)—C(9)—O(2)	122.9 (2)
C(9)—O(2)—H(2)	119 (3)	O(1)—C(9)—C(6)	118.2 (1)
C(1)—C(2)—C(3)	127.2 (2)	O(2)—C(2)—C(6)	118.9 (1)
C(1)/C(2)/C(3) — C(3)/C(4)/C(5)/C(6)/C(7)/C(8)			10.8
C(3)/C(4)/C(5)/C(6)/C(7)/C(8) — C(9)/O(1)/O(2)			2.6

constants reported earlier were $a = 8.04$, $b = 5.3$, $c = 28.0$ Å, space group *Ima*2. Since the cell constants obtained for **2** in the present work are nearly identical to those previously reported, it is reasonable to assume that the two phases are identical, suggesting a revision of the previously reported data [14]. Despite errors in the earlier work, many of the features of the structures of **1** and **2** previously described are consistent with our results. The present work, however, provides a full set of atomic coordinates as well as detailed analyses of the hydrogen bonding and intermolecular contacts.

X-ray Structure Determinations of Compounds 1, 2 and 3a

The structures of compounds **1**, **2** and **3a** were determined in order to provide information on the structural basis for the thermal solid-state polymerization of these materials. Data for the X-ray structure determinations are presented in Table II. *p*-Vinylbenzoic acid was obtained in two polymorphic forms. Polymorph **3a**, which is monoclinic, space group $P2_1/c$, crystallized from (a) HOAc, (b) DMSO, or (c) $HCl/H_2O/EtOH$ solutions. Single crystals of monoclinic polymorph **3b** (space groups *C*2, *Cm* or *C*2/*m*;

$a = 26.29$, $b = 4.00$, $c = 15.64$ Å; $\beta = 96.0°$; $V = 1635.7$ Å^3; $Z = 8$) were obtained by sublimation. The structure of **3b** could not be determined owing to the extremely high mosaicity of all crystals obtained ($\approx 9°$ in ω). X-ray powder diffraction studies showed **3**, as obtained commercially in powder form (Aldrich), to be polymorph **3b**.

The molecular structures of **1**, **2** and **3a** are shown in Figures 1, 2 and 3, respectively. All H atoms were located. Methyl H atoms in **1** were disordered in a 3:1 ratio; only the major component is shown. The acid proton in **3** was disordered in a 1:1 fashion, such that it was observed to be attached to either O(1) or O(2); only the H atom attached to O(1) is shown. Compounds **1** and **2** exhibit weak intramolecular hydrogen bonds of the type C7–H71$\cdots$O1, where C7$\cdots$O1 distances and C7–H71$\cdots$O1 angles are 2.868 Å, 117.8° and 2.904, 108.8° for **1** and **2**, respectively. Bond lengths and angles (Tab. II) lie within normal ranges for all three compounds. The dihedral angles between the phenyl ring and the C(1)/C(2)/C(3) group range from 3.9–14.1°, while the dihedral angles between phenyl groups and amide planes are 15.1° for **1** and 35.4° for **2**. In **2**, the phenyl ring attached to N is twisted by 29.2° from the amide plane. In **3**, the carboxylate group is nearly coplanar with the phenyl moiety (2.6°).

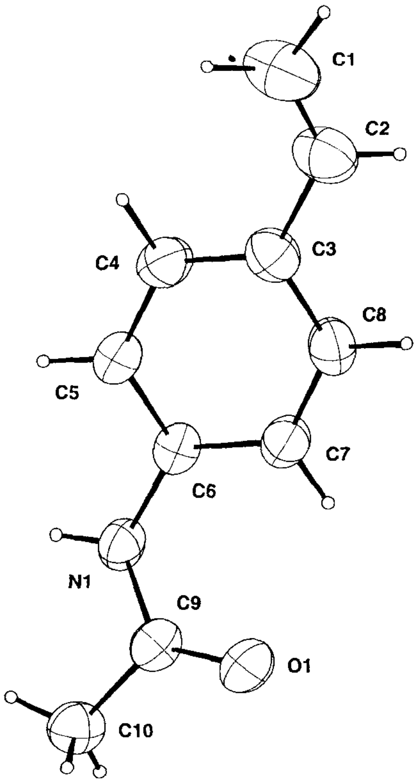

FIGURE 1 Molecular structure of **1**, showing 50% probability ellipsoids for atoms refined using anisotropic displacement parameters.

Hydrogen bonding in **1** and **2** follows the "twofold screw axis motif" and "translation" motif, respectively, as described by Leiserowitz and Tuval [24]. Figure 4 shows that, in **1**, the **C(4)** chains [25] are comprised of N(1)–H(1)$\cdots$O(1)[$1-x$, $y-1/2$, $1/2-z$] hydrogen bonds, with N$\cdots$O = 2.917 Å, N—H$\cdots$O = 176.5°, C═O$\cdots$N = 138.6° and C—N$\cdots$O = 119.9°. As pointed out correctly by Morawetz and coworkers in 1964, the arrangement closely resembles the structure of acetanilide [26]. Figure 5 shows the hydrogen bonding in Compound **2**:**C(4)** chains [25] with N(1)$\cdots$O(1) [$x, y-1, z$] = 3.139 Å, N(1)–H(1)$\cdots$O(1) = 159.6°, C═O$\cdots$N = 172.4° and C—N$\cdots$O = 128.6°. The hydrogen bonding motif is an infinite chain produced by translation along the b axis (5.288 Å); a similar translation-repeat motif (b axis, 5.222 Å) occurs in the crystal structure of *N*-phenyl-2,5-dihydrothiophene-3-carboxamide [27]. In **3**, there are no strong hydrogen bonds except for those forming the usual hydrogen-bonded dimer ($\mathbf{R}_2^2(8)$ graph set) [25].

As discussed earlier, solid-state reactivity was observed for all three compounds *via* both thermal and irradiation procedures. In this context, analyses of the C(1)$\cdots$C(2) intermolecular contacts should reveal possible structure-reactivity relationships. The three structures were examined with regard to the shortest contacts between double bonds. Where appropriate, lower weight was given to contacts

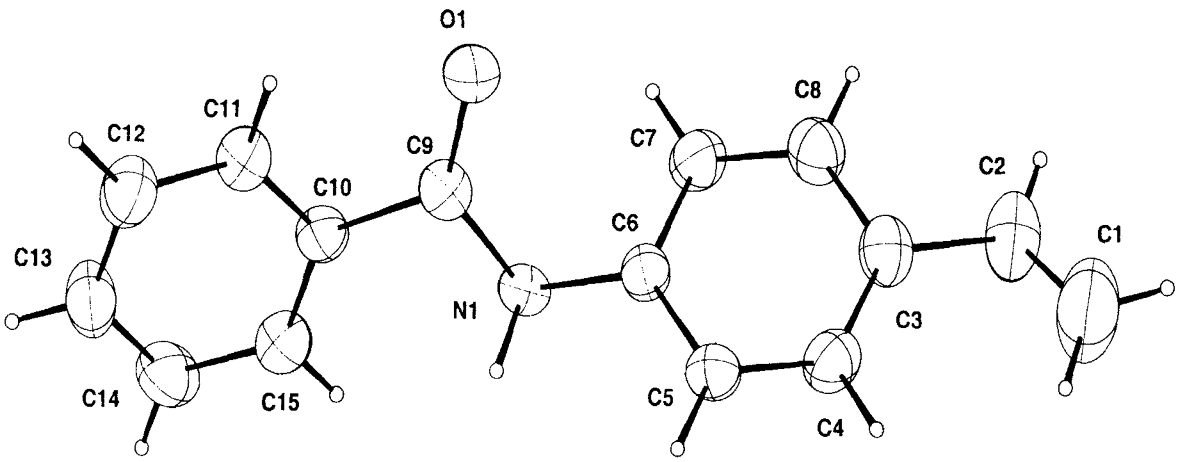

FIGURE 2 Molecular structure of **2** (50% probability ellipsoids).

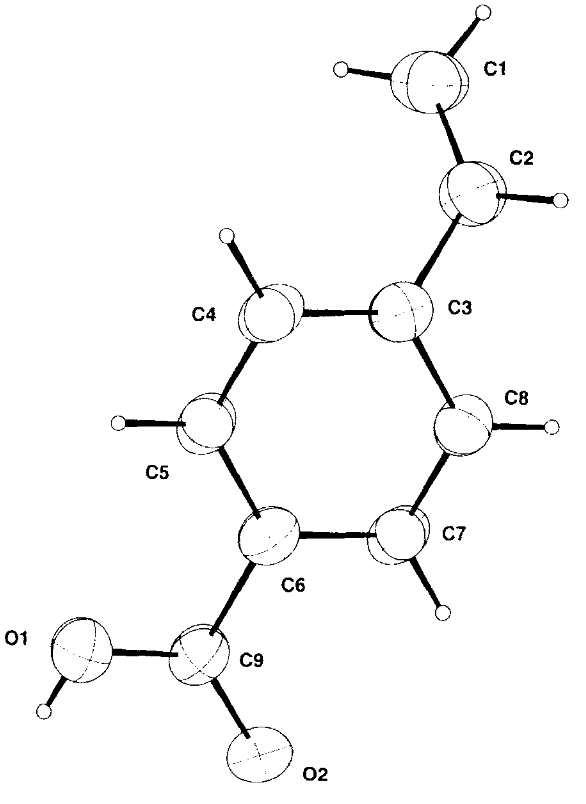

FIGURE 3 Molecular structure of **3** (50% probability ellipsoids).

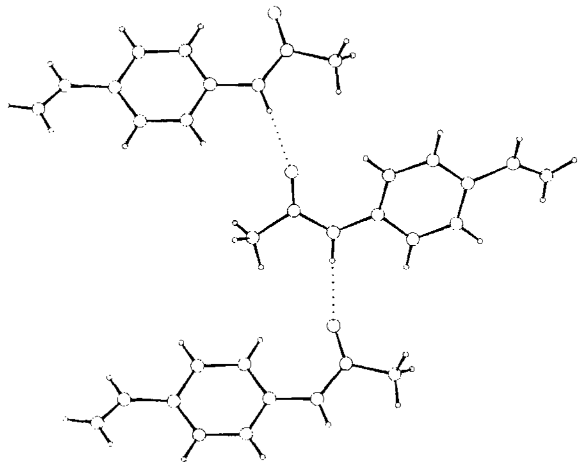

FIGURE 4 Hydrogen bonding in the crystal structure of **1**.

between pairs of —CH=CH$_2$ groups poorly oriented for reactivity (*e.g.*, where φ, the dihedral angle between the two planes in question differed greatly from 0°). For compound **1**, there are three sets of infinite contacts within the usual limit of ca. 4.2 Å. These are C(1)···C(2)[$1/2-x$, $1-y$, $1/2+z$], 4.133 Å, $\phi=86.4°$; C(1)···C(2)[x, $3/2-y$, $1/2+z$], 4.209 Å, $\phi=86.4°$ and C(1)···C(2)[$1/2-x$, $1-y$, $1/2+z$], 4.221 Å, $\phi=1.2°$. Given the orthogonal relationship between the —CH=CH$_2$ groups in the first two cases, only the third set was considered further. A section of the infinite, head-to-tail relationship between molecules at a C1···C2 separation of 4.221 Å is shown in Figure 6. The virtual parallelism, and C(1)···C(2) contacts in the vicinity of 4.2 Å, fit

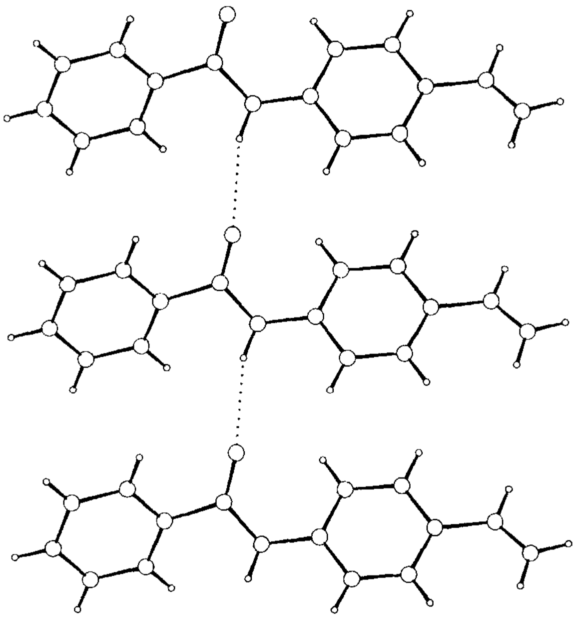

FIGURE 5 Hydrogen bonding in the crystal structure of **2**.

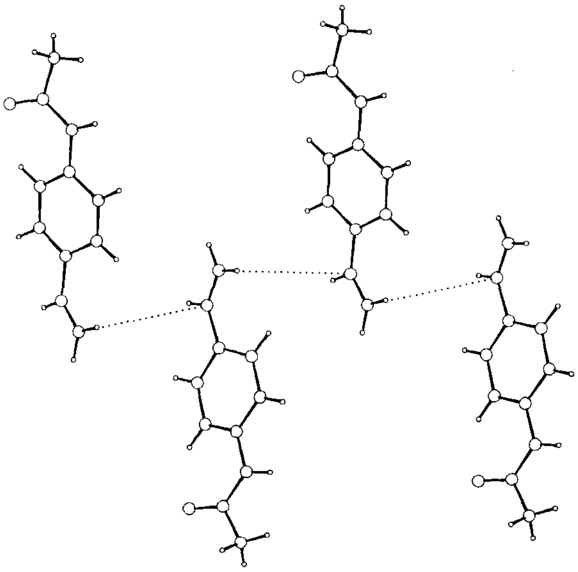

FIGURE 6 C(1)···C(2) contacts in the crystal structure of **1**; the contacts shown are part of an infinite chain propagated along the crystal *b* axis.

the requirements of the topochemical postulate extremely well [28]. The absence of evidence for formation of isotactic or syndiotactic polymer in this or the reactions of **2** and **3** implies that, in all three reactions, topochemical effects are likely responsible only for the initiation step(s) of the reaction. However, in the propagation steps – at a certain stage – topochemical control is lost. At what stage the control is lost no doubt varies from system to system. Without a detailed knowledge of the structure of the polymers and the dependence of structure on molecular weight, such a fine point of topochemical control cannot be addressed.

For compound **2**, there is only one short contact, C(1)···C(2)$[x, -y, 1/2+z]$, 3.996, $\phi = 71.9°$, between nearly orthogonal groups (Fig. 7). The yield of polymer obtained upon heating is nearly quantitative upon heating to within ≈ 16° of the melting point, while the conversion to polymer upon γ- and UV-irradiation is much lower, and is also lower than the observed conversions over a similar time period for **1**. While the high thermal reactivity of **2** may be rationalized by assuming large thermal motion of the vinyl groups at temperatures near the melting point, the reactivity of **2** upon UV- or γ-irradiation was unexpected.

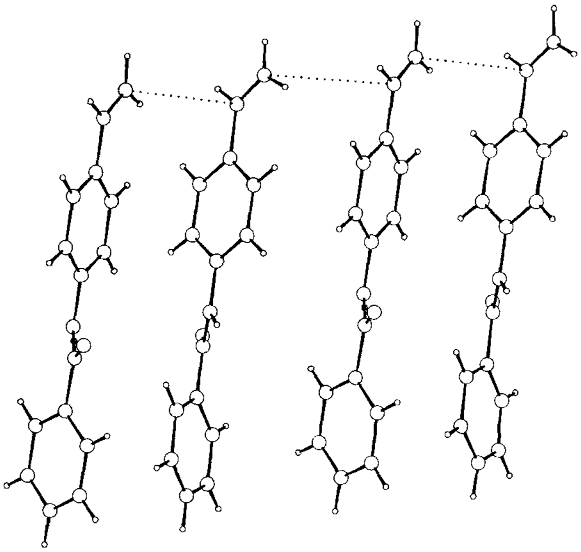

FIGURE 7 C(1)···C(2) contacts in the crystal structure of **2**; the contacts shown are part of an infinite chain propagated along the crystal *c* axis.

For compound **3**, there is again only one short contact, C(1)···C(2)[$-x, y+1/2, 1/2-z$], 4.043 Å, $\phi = 52.6°$, a relatively large deviation from coplanarity (Fig. 8). As discussed earlier, **3** is polymorphic; polymorph **3a** undergoes a transformation to **3b** at 60–70°C. Thus, the structure of **3a** is not relevant to the solid-state polymerization at the experimental temperatures of 100–120°C. Polymorph **3b**, the only phase present at temperatures greater than 70°C, has a short axis ($b = 4.00$ Å), which indicates the presence of parallel molecules in a head-to-head arrangement, separated by this short distance. The β-type packing mode of **3b** is ideal for solid-state polymerization by thermal treatment or irradiation. Once again, the reactivity of **3a** is surprising, as the angular alignment of the C—CH=CH$_2$ moieties is far from ideal.

Beyond the classic cases of 2+2 photocycloaddition reactions and topotactic solid state polymerization, it is becoming increasingly clear that topochemical considerations play – at a minimum – an important role in (at least) the initiation step for many reactions involving C—C bond formation in the solid state. The conditions under which a given reaction affords the "topochemical" or "apparent-nearest-neighbor" product remain poorly defined, although recent experiments suggest that distances greater than 4.2 Å may require significant rotations, and will consequently lead to "unexpected" stereochemistries, as reacting atoms are brought to proximity [29]. Only by increasing the structural database for these reactions, and by studying the stereochemistry of the polymeric products *at all stages of conversion* [30], can we hope to gain further insight into these reactions.

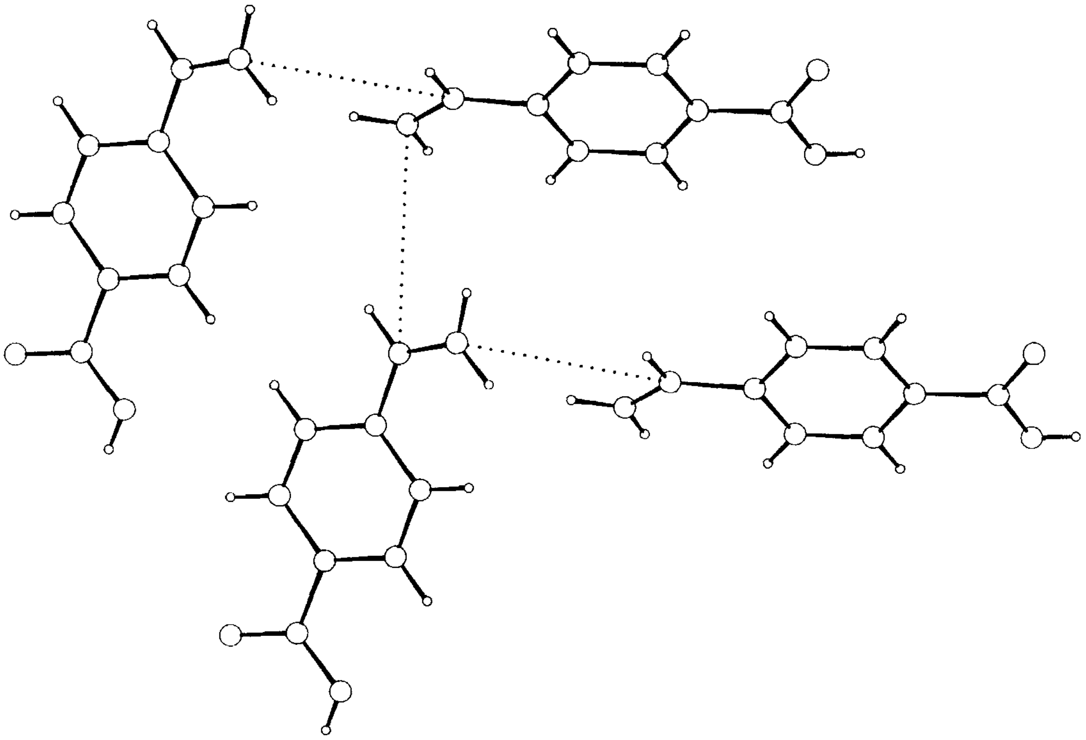

FIGURE 8 C(1)···C(2) contacts in the crystal structure of **3**; the contacts shown are part of an infinite chain propagated along the crystal *b* axis.

MATERIALS AND METHODS

NMR spectra were recorded on a Varian XL-300 spectrometer. A Gammacell 220 Irradiator (Atomic Energy of Canada, Ltd.) equipped with a ^{60}Co source was used for all γ-irradiation experiments. X-Ray powder diffraction, oscillation and Weissenberg photographs were obtained using CuKα radiation, a Philips 12045B generator and Supper Weissenberg and Debye-Scherer cameras.

p-Aminophenylethylene

p-Aminophenylethanol (4.0 g, 0.029 mol, Aldrich) powder was mixed with KOH pellets (4.0 g, 0.071 mol, Fisher) and 3–4 Cu shot [31]. The dehydration reaction was carried out by gradually heating the mixture in a sand bath to 170°C under low pressure (0.1 mm Hg). At the same time, the product was removed by distillation and collected as a colorless liquid (B.P. 84.0°C, 0.1 mm Hg); yield: 2.7 g, 0.023 mol, 78%. p-Aminophenylethylene was very easily oxidized in air and became yellow upon exposure to air.

p-Acetamidostyrene 1

Acetic anhydride (1.0 mL, 0.010 mol) was added dropwise with stirring to 10.0 mL of an acetone solution of *p*-aminophenylethylene (1.0 g, 0.0084 mol) at 0°C. After reaction, acetone was removed under reduced pressure. The slightly yellow powder was washed with water, dried in air and recrystallized with ethyl acetate; yield: 1.3 g, 0.0080 mol, 95%. Colorless thin platelike single crystals of **1** were obtained by slow evaporation of an ethyl acetate solution at room temperature. M.P. 138.0–139.0°C. IR (in part, KBr, cm^{-1}) 1662(C=O) and 905 (terminal double bond). ^{1}H NMR (DMSO/TMS, ppm) δ 2.1(3 H, s, CH), 5.2(1 H, dd, $J = 1.0$, 11.0, H_{trans}), 5.7 (1 H, dd, $J = 1.0$, 17.6, H_{cis}), 6.6 (1 H, dd, $J = 11.0$, 17.6, H_{gem}), 7.5 (4 H, AA′BB′, $J = 8.4$, —C_6H_4—), 10.0 (1 H, s, exchangeable, —NH—).

p-Benzamidostyrene 2

Benzoyl chloride (1.2 mL, 0.010 mol, Aldrich) was added dropwise with stirring to 10.0 mL of an acetone solution of *p*-aminophenylethylene (1.0 g, 0.010 mol) at 0°C. After reaction, acetone was removed under reduced pressure. The slightly yellow powder was washed with water, 10% Na_2CO_3, dried in air and recrystallized from methanol; yield: 2.2 g, 0.0098 mol, 98%. Colorless thin plates of **2** were obtained by slow evaporation of a 1 : 1 MeOH-$CHCl_3$ solution. M.P. 166.0–167.0°C. IR (in part, KBr, cm^{-1}) 1626 (C=O) and 899 (terminal double bond). ^{1}H NMR (DMSO/TMS, ppm) δ 5.2 (1 H, dd, $J = 1.0$, 10.9, H_{trans}), 5.7 (1 H, dd, $J = 1.0$, 17.6, H_{cis}), 6.7 (1 H, dd, $J = 10.9$, 17.6, H_{gem}), 7.5 (5 H, m, —C_6H_5—),7.9 (4 H, AA′BB′, $J = 8.5$, —C_6H_4—), 10.3 (1 H, s, —NH—, exchanged with D_2O).

p-Vinylbenzoic Acid 3

Compound **3** was obtained from Aldrich and used as received. IR (in part, KBr, cm^{-1}) 1678(C=O) and 923 (terminal double bond). Single crystals of polymorph **3a** were grown by slow evaporation of solutions of in either (i) acetic acid, (ii) DMSO, or (iii) HCl/H_2O/ethanol. The single crystal used for the diffraction study was obtained from 1 : 10 37% HCl(aq) : ethanol solution. Single crystals of polymorph **3b** were obtained by sublimation. Solid **3** (powder, 50.0 mg) was placed into a tube, which was then evacuated and sealed. The sample tube was then put into an oven at 70°C. After a few days, large single crystals formed on the top wall of the tube. Compound **3** obtained from Aldrich is polymorph **3b**, as shown by powder diffraction.

Solid State Polymerization of 1–3

Small amounts of **1**, **2** and **3b** were placed into glass tubes and heated in an oven at various temperatures; representative yields are shown in

Table I. For γ-irradiation, small amounts of the same materials were placed in small capped glass vials and irradiated in a Gammacell 220 irradiator (2520 kGy) at room temperature (Tab. I). In UV-irradiation experiments, small amounts of **1** and **2** were placed into polystyrene tubes and irradiated under UV (253.7 nm and 350.0 nm) for 6 months (Tab. I). In all cases, yields were obtained from integration of ^{1}H NMR spectra.

Polyacetamidostyrene(Poly-1)

After thermal polymerization at 100°C, the monomer was extracted with ethyl acetate. The polymer was dried under vacuum. **Poly-1** is light orange in color and is amorphous to X-rays. IR (in part, KBr, cm^{-1}) 1683(C=O). ^{1}H NMR (1 : 1 MeOH(d$_4$): CDCl$_3$, TMS, ppm) δ 1.42(CH, br), 1.72(CH, br), 2.20(CH, br), 6.85(—CH—. br). ^{13}C NMR (1 : 1 MeOH(d$_4$) : CDCl$_3$, TMS, ppm) δ 22.7(s, CH, br), 39.2(s, CH, br), 42.5(m, CH, br), 169.4(s, C=O. br), aromatic ring: 119.5(s, CH, br), 127.2(s, CH, br), 135.2(s, C, br), 140.4(m, C, br). Polymers obtained by UV and γ-irradiation were not subjected to further analysis.

Polybenzamidostyrene(Poly-2)

After thermal polymerization at 120°C, the monomer was extracted with methanol and the polymer was dried under vacuum. **Poly-2** obtained as above is light brown in color and amorphous to X-rays. IR (in part, KBr, cm^{-1}) 1652(C=O). ^{1}H NMR (1 : 1 Py(d$_5$) : CDCl$_3$, TMS, ppm) δ 1.65(CH, br), 1.90(CH, br), 7.0–8.2 (aromatic rings, br). ^{13}C NMR (1 : 1 Py(d$_5$) : CDCl$_3$, TMS, ppm) δ 39(CH, br), aromatic rings: 120.0(br), 127.0(br), 130.0(br); 165.5(br, C=O). Polymers from UV and γ-irradiation were not subjected to further analysis.

Polyvinylbenzoic Acid(Poly-3)

After thermal polymerization of **3b** at 100°C, the monomer was extracted with acetone and the polymer was dried under vacuum. **Poly-3** is colorless and amorphous to X-rays. IR (in part, KBr, cm) 1689(C=O). ^{1}H NMR (1 : 1 Py(d$_5$) : CDCl$_3$, TMS, ppm) δ 1.65(CH, br), 1.95(CH, br), aromatic ring: 6.80(br), 8.10(br). ^{13}C NMR (1 : 1 Py(d$_5$) : CDCl$_3$, TMS, ppm) δ 40.0(s, CH, br), 43.0(m, CH, br), 168.1(s, C=O, br), aromatic ring: 127.0(s, br), 129.0(m, br); other aromatic peaks are obscured by pyridine resonances. Polymer from the γ-irradiation was not subjected to further analysis.

X-ray Structure Determinations of 1, 2 and 3a

After preliminary studies of **1**, **2** and **3a** by oscillation and Weissenberg techniques, fresh crystals of each were mounted on a Pyrex fiber affixed to a brass pin, then transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2$_1$ diffractometer. Routine operations were performed as described previously [32]; other operations are described below. The structures were solved using the heavy-atom method; preliminary computational work was carried out using the Enraf-Nonius MolEN software package [33]. Final refinement was carried out using the Oxford University CRYSTALS package [34]; drawings were produced using CAMERON [35]. For **1** the final refinement (1038 data for which $I > 1.96\sigma(I)$; 115 parameters) included anisotropic displacement parameters for nonhydrogen atoms, and an isotropic displacement parameter for the H atom attached to N. The coordinates of the H atom attached to N were refined, while all other H atoms were fixed at calculated positions. The H atoms attached to the methyl carbon atom were fixed at two orientations, and the occupancy of the major orientation (sum of the sets constrained to add to 1.0) was 0.74(3). The final refinement for **2** (1072 data for which $I < 1.96\sigma(I)$; 159 parameters) was carried out using anisotropic displacement parameters for C, N and O; positional and an isotropic displacement parameter for the H atom attached to N were refined. All other H atoms were included at fixed positions. The final refinement for **3a** was carried out using anisotropic displacement parameters for all C and O atoms (1184 data for which $I < 1.96\sigma(I)$; 109 parameters). Two locations were observed for the acid H atom (one attached to each O). The positional and isotropic displacement parameters of these two atoms were refined with fixed occupancies of 0.5. All other H atoms were included at fixed positions. Coordinates for the structures of **1**, **2** and **3a** have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Crystallographic Characterization of 3b

The space group of the second polymorph of compound **3** (**3b**) was obtained from oscillation and Weissenberg photographs of a crystal grown by sublimation. The only systematic conditions observed were $h+k=2n$ for all hkl. Along with the observed monoclinic metric constants and $2/m$ diffraction symmetry, the possible space groups are $C2$, Cm or $C2/m$. Cell constants: $a=26.29$, $b=4.00$, $c=15.64$ Å; $\beta=96.0°$; $V=1635.7$ Å^3; $Z=8$. Weissenberg photographs indicated that the crystals were highly mosaic (width in ω of an individual reflection $\approx 9°$), and thus further work on the structure determination was discontinued.

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