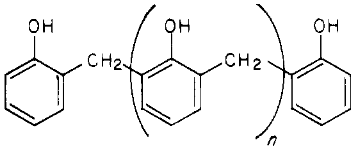
Communications to the Editor

The Design of a Versatile Synthesis of Ortho-Ortho' Methylene-Bridged Polyphenols. ^{13}C NMR Investigation of "All-Ortho" Oligomers

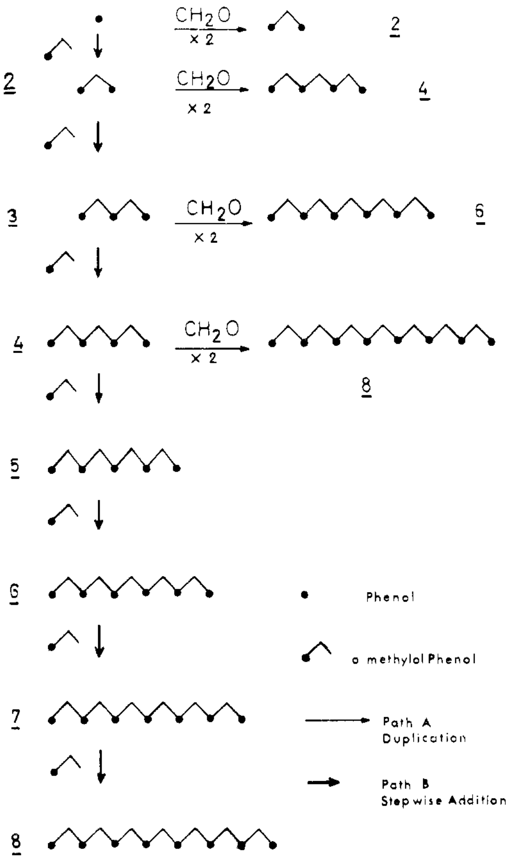
Recent experiments in our laboratory indicate that phenoxymagnesium halides are suitable intermediates for highly selective organic synthesis.[1]

We wish to report here our findings in the field of step-growth phenol–formaldehyde oligomerization,[2] which has been extensively studied, but still requires elucidation for the positional selectivity[3] as well as for the fine-structure constitution of the products.[4] Thus, using bromomagnesium salts of a phenolic substrate, we have developed two general methods for the highly selective synthesis of linear methylene-bridged polyphenols **2–8**.[5]



2, $n = 0$ **6**, $n = 4$
3, $n = 1$ **7**, $n = 5$
4, $n = 2$ **8**, $n = 6$
5, $n = 3$

Chart I



As shown in Chart I, the duplication procedure (A) consists in the insertion of a methylene bridge between two phenolic units by reaction with paraform, producing even oligomers **2**, **4**, **6**, and **8**. Moreover, the stepwise addition of a *o*-hydroxybenzylene unit to the phenolic substrate (B) gives rise to the complete serie of oligomers **2** to **8**.

The reaction is generally accomplished by stirring under reflux a suspension of the bromomagnesium salt of the phenolic substrate[6] (0.04 mol) and paraformaldehyde (Baker 95%, 0.01 mol) or *o*-(hydroxymethyl)phenol (0.02 mol) in dry benzene (150 mL) for 12 h. Aqueous quenching, ether extraction, drying (Na$_2$SO$_4$), and rotary removal of the solvent gave a glassy residue from which the desired oligomer was separated by chromatography on a short silica gel column with hexane/ethyl acetate as eluant and further purified by crystallization from benzene. The results are summarized in Table I.

Table I
Preparation of Oligomers 2–8[a]

compd	mp, °C[b]	method	yield, %[c,d]
2	119.5[e]	A	78 (96)
		B	65 (80)
3	161[f]	B	81 (94)
4	159-160[g]	A	70 (90)
		B	60 (97)
5	208-209	B	40 (80)
6	213	A	55 (94)
		B	60 (91)
7	237-238	B	30 (93)
8	240-242	A	49 (98)
		B	53 (93)

[a] Satisfactory analytical results have been obtained for all new compounds. [b] Recrystallization solvent, benzene. [c] Yield is that of isolated product; not optimized. [d] Values in parentheses refer to yield based on unrecovered starting material. [e] Lit.[10] mp 119.5 °C. [f] Lit.[10] mp 160 °C. [g] Lit.[10] mp 161-162 °C.

Significant spectroscopic data for compounds **2–8** are reported here.[7,8] **2**: mass spectrum (157 °C) *m/e* 200 (66), 107 (100); ^{13}C NMR δ 31.0 (CH$_2$), 115.8 (CH ortho), 121.3 (CH para), 126–131 (aromatic carbons), 152.3 (C–O). **3**: mass spectrum (178 °C) *m/e* 306 (60), 212 (61), 200 (41), 107 (100); ^{13}C NMR δ 31.6 (CH$_2$), 116.1 (CH ortho), 121.6 (CH para), 127–131 (aromatic carbons), 149.6 (C–O internal), 152.0 (C–O external). **4**: mass spectrum (190 °C) *m/e* 412 (45), 318 (16), 306 (18), 212 (60), 200 (21), 107 (100); ^{13}C NMR δ 31.3 and 31.7 (CH$_2$), 115.5 (CH ortho), 121.4 and 121.8 (CH para), 127–131 (aromatic carbons), 149.0 (C–O internal), 152.1 (C–O external). **5**: mass spectrum (230 °C) *m/e* 518 (24), 412 (91), 306 (37), 200 (41), 107 (100); ^{13}C NMR δ 31.5 and 31.7 (CH$_2$), 116.0 (CH ortho), 121.6 and 121.8 (CH para), 127–131 (aromatic carbons), 149.4 (C–O internal), 151.8 (C–O external). **6**: mass spectrum (260 °C) *m/e* 624 (36), 518 (7), 412 (14), 306 (13), 200 (64), 107 (100); ^{13}C NMR δ 31.3 and 31.7 (CH$_2$), 115.7 (CH ortho), 121.1 (CH para), 126–131 (aromatic carbons), 148.8 and 149.0 (C–O internal), 151.3 (C–O external). **7**: mass spectrum (280 °C) *m/e* 730 (7), 624 (11), 518 (12), 412 (12), 306 (25), 200 (50), 107 (100); ^{13}C NMR δ 31.6 and 31.8 (CH$_2$), 115.6 (CH ortho), 121.3 and 121.6 (CH para), 126–131 (aromatic carbons), 148.8 and 149.2 (C–O internal), 151.6 (C–O external). **8**: mass spectrum (320 °C), *m/e* 836 (5), 730 (4), 624 (10), 518 (21), 412 (49), 306 (30), 200 (48), 107 (100); ^{13}C NMR δ 31.5 and 31.8 (CH$_2$), 116.3 (CH ortho), 121.9 (CH para), 127–131 (aromatic carbons), 149.1 and 149.3 (C–O internal), 151.7 (C–O external).

Comparison of analytical and spectroscopic data of compounds **2–4** with authentic specimens prepared ac-

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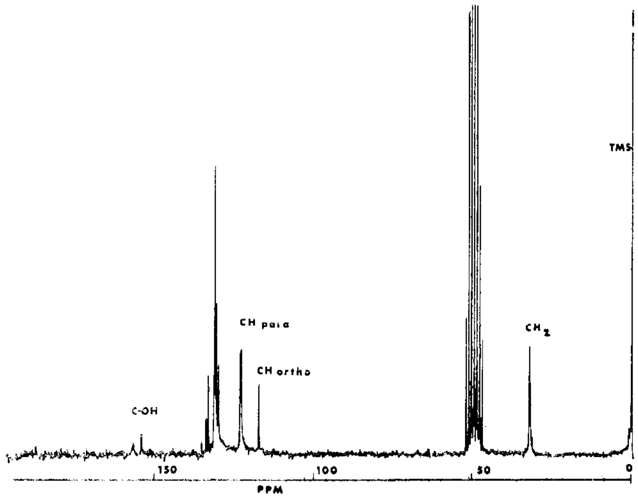


Figure 1. ^{13}C NMR spectrum of octanuclear compound 8 (in CD_3OD).

cording to unequivocal methods[10] permits the identification, without uncertainty, of their ortho-ortho′ substitution pattern. In the oligomers **5**–**8** occurrence of only the ortho-ortho′ sequence of the CH_2 bridges seems quite probable because of the regiospecific nature of this oligomerization. However as, a priori, the CH_2 sequence could also be in ortho-para′ and para-para′ position, a method for the characterization of the three different situations is requested. As the molecular formula is the same for different substituted isomers and slight differences are revealed by ^1H NMR spectra[11] and infrared and ultraviolet analyses, we have studied the ^{13}C NMR spectra which yield more detailed information about the substitution sequence.

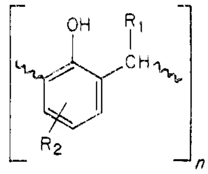
The methylene carbons absorption is the most sensitive to the positional isomerism. The ^{13}C spectra of 2,2′-, 2,4′-, and 4,4′-dihydroxydiphenylmethane prepared according to the literature[10] show three well-distinct resonance peaks for the individual CH_2 units at 31.0, 35.8, and 40.1 ppm, respectively.[12]

The ^{13}C NMR spectra of our oligomers show peaks in two areas (the spectrum shown in Figure 1 was taken in the PFT mode, 3.200 pulses, with a digital resolution of 1.25 Hz/point). The high-field absorption at 31.0 ppm is therefore ascribed to the CH_2's in the ortho-ortho′ ordered sequence. The peaks between 110 and 160 ppm are due to the aromatic moiety. Two shielded peaks of this region at about 115 and 121 ppm were assigned at the resonance of the CH in the ortho positions at the end of the chain and of the CH in the free para positions, respectively, by comparison with the same carbons of *o*-cresol. The presence of only one resonance for the CH ortho also confirms that in these oligomers only the all-ortho-ortho′ bridges occur. The ratio between the integrated intensities of these two peaks gives the molecular size in agreement with the mass spectra determination. The quantitative measurements assume that similar Overhauser enhancements are experienced by the CH ortho and para carbons.[14] Since the experimental ratios correlate with the expected ones, they support the assumption of a constant NOE in the series.[15] The same results were obtained with both no delay and 5 s delay time. The good agreement in our measurement suggests that NOE is not a problem in the limited microstructure range studied, providing that the areas are measured from the two CH (ortho and para) aromatic carbons.

This selective oligomerization is solvent and cation dependent. Use of protic or polar solvents instead of benzene and alkali phenolates rather than phenoxymagnesium bromides causes a lack of selectivity, producing unworkable materials or very complicated randomly substituted mixtures.

This procedure can be a helpful starting point for obtaining directly, on varying the ratio phenol/formaldehyde, a guaranteed all-ortho-linked novolac.[16] Direct condensation of phenoxymagnesium bromide (30 mmol) and paraform (20 mmol), in refluxing benzene (300 mL), afforded a colorless glassy material which was characterized by ^{13}C NMR as a mixture of ortho-ortho′ oligomers.

Finally, we underline the outstanding feature of this synthesis which allows a large choice as far as the starting agents (different aldehydes and variously substituted phenols) resulting in a designing of a variety of mers **9** and



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R_1 = H, alkyl, aryl
R_2 = H, alkyl

even structures with different and/or alternating mers.[18,19]

References and Notes

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(2) M. F. Drumm and J. R. Le Blanc in "Step Growth Polymerization", D. H. Solomon Ed., Marcel Dekker, New York, 1973 chapter 5, pp 172 and 190.

(3) R. Natesan and L. M. Yeddanapalli, *Indian J. Chem.*, **12**, 802 (1974).

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(5) The previous methods for rational synthesis of this class of oligomers suffer from some disadvantages, e.g., multistep procedure and too limited in the substrates; see H. Kämmerer, W. Raush, und I. Söhle, *Makromol. Chem.*, **171**, 1 (1973); N. J. L. Megson in "Phenolic Resins Chemistry", Butterworths, London, 1958, p 161.

(6) The salt is easily obtained from phenolic derivatives with 1 equiv of ethylmagnesium bromide (see ref 1).

(7) IR and ^1H NMR spectroscopic data are in accord with assigned structures. A good linear relationship[9] between ϵ (cm^2/mmol) and the number of phenolic units (n) of the oligomers at 282 nm in 95% EtOH was found: $\epsilon = 2.485n + 0.178$.

(8) Mass spectra were determined with a Varian Mat CH-5 mass spectrometer at 70 eV (source temperature and relative intensities are given in parentheses). ^{13}C NMR spectra were obtained at 25.1 MHz on a Varian XL-100 apparatus in $CDCl_3$ or CD_3OD as solvents; tetramethylsilane (δ = 0 ppm) was used as an internal standard.

(9) R. F. Hunter, R. A. Morton, and A. T. Carpenter, *J. Chem. Soc.*, 441 (1950); H. Kämmerer, J. Pachta, and J. Ritz, *Makromol. Chem.*, **178**, 1229 (1977).

(10) D. A. Fraser, R. W. Hall, P. A. Jenkins, and A. L. J. Raum, *J. Appl. Chem.*, 689 (1957).

(11) T. Yoshikawa and J. Kumanotani, *Makromol. Chem.*, **131**, 273 (1972), and references cited therein.

(12) It is well known[13] that gauche arrangement of a carbon atom with respect to a nonhydrogen substituent in the γ position produces an upfield shift. The magnitude of this steric shift is significantly higher for an ortho-ortho′ link between the phenolic nuclei than for an ortho-para′ link in comparison with the para-para′ substitution (no γ effect). The three kinds of methylene carbons obtained by suitable models are separated by about 5 ppm.

(13) W. R. Woolfenden and D. M. Grant, *J. Am. Chem. Soc.*, **88**, 1496 (1966); D. K. Dalling and D. M. Grant, *ibid.*, **94**, 5318 (1972).

(14) Experimental conditions are as follows: memory used for acquisition, 8K; pulse width, 15 μs; delay between the pulses, from 0 to 5 s; number of pulses, from 1000 to 20000; area

measurements by electronic integration and by planimeter.
(15) J. Schaefer, *Macromolecules*, **5**, 427 (1972); A. Allerhand, D. Doddvell, and R. Komoroski, *J. Chem. Phys.*, **55**, 189 (1971).
(16) No traces of ortho-para' and para-para' linkages were detected. We have examined a number of claimed all-ortho novolacs manufactured according to the reported methods[17] and we have detected significant ortho-para' peaks employing the ^{13}C method.[12]
(17) A. M. Partansky, *Am. Chem. Soc., Div. Org. Coat Plast. Chem., Pap.*, **27** (1), 115 (1967); D. A. Fraser, R. W. Hall, and A. L. J. Raum, *J. Appl. Chem.*, 676 (1957).
(18) Work is in progress to extend the synthesis and to explore the scope and limitations[19] of the reaction. For the present, successful syntheses of "ortho" di, tri, and tetranuclear phenol-acetaldehyde, phenol-benzaldehyde, and *p*-cresol-formaldehyde oligomers were achieved from phenoxymagnesium bromides and the respective aldehyde.
(19) Limitations are due to the inertia of the electron-withdrawing-substituted phenol (R_2 = NO_2, COR) as well as to the unselectivity of reactions involving some etheroaromatic aldehydes.

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Formation of a New Crystal Form (α_p) of Poly(vinylidene fluoride) under Electric Field

Poly(vinylidene fluoride) (PVF_2) is known to have three crystal forms (α, β, and γ) reported up to now.[2] Recently the possibility of transforming the α form PVF_2 into a new crystal form has been considered in relation to the piezo- and pyroelectric properties of polarized PVF_2 films.[3,4] In this communication we present the evidence of another new crystal form of PVF_2 which is formed upon subjecting the α form PVF_2 to high electric field.

PVF_2 films were prepared by melting PVF_2 pellets of M_W = 120000, obtained from Polyscience, in the laboratory press and then cooling rapidly to room temperature. These films were subsequently stretched by ca. four times at 155 °C and then annealed at 145 °C for 1 h at fixed lengths. X-ray diffraction[2] and infrared spectra[5] from these films show that the crystalline phase is predominantly of α form, the content of β form being less than 5%. Aluminum electrodes were vacuum deposited on both sides of the films and then these α-PVF_2 films were subjected to the field of 1500 kV/cm for 3 h at 24 °C. The aluminum electrodes were removed by dissolving in NaOH solutions afterwards.

The infrared spectra taken after the poling process did not show any change other than a minimal decrease in the α-form absorption[5] at 795 cm^{-1} and a little increase in the β-form absorption[5] at 840 cm^{-1}. Hence, the one-dimensional ordering of tg^+tg^- molecular conformations in the α-crystal form of PVF_2 remains unaffected[6] except for the formation of a minimal amount of β-crystal form.

On the other hand, the X-ray diffraction data measured with a conventional diffractometer in the reflection mode exhibited rather significant changes in intensity caused by the poling process as shown in Figure 1. Major changes to be noted are the increase in intensity at (110) and (200) reflections and a significant decrease of (100) and (120) reflection intensities. The contrasting changes at (100) and (200) reflections certainly rule out the orientation or disordering of crystallites as the major cause for the change in X-ray intensities. Also to be noted is the fact that the position of each observed peak remains unchanged within the experimental error. Therefore, only the symmetry of the unit cell seems to have undergone a major change due to the electric field, while the molecular conformations (tg^+tg^-) of α-PVF_2 chains in the unit cell and the dimensions of the unit cell remain the same as in the α form.[2]

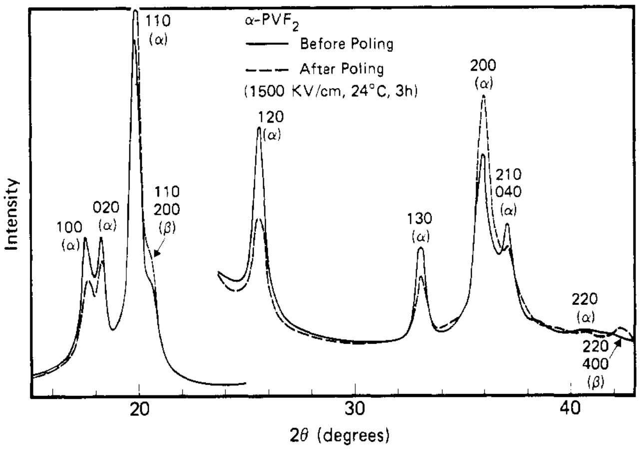

Figure 1. Tracings of X-ray diffraction intensities in the reflection mode from uniaxially oriented α form of PVF_2 before poling (solid line) and after poling with 1500 kV/cm for 3 h at 24 °C (dashed line). Indices of reflection for the peaks are assigned according to ref 2.

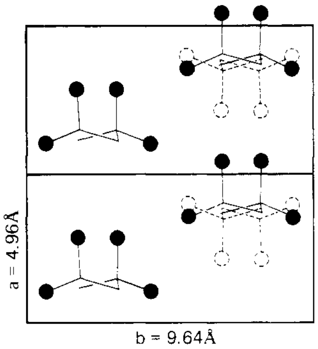

Figure 2. Crystal structure of the proposed α_p form of PVF_2 in the *ab* projection, fluorine atoms being shown by circles, compared with that of the α form; the second chain in the α form is shown by the dashed line. The atomic positions in the *c* coordinate for the α_p form remain the same as in the α form.[2]

Table I
Comparison of Calculated X-ray Intensity Form Factors for the α Form and the α_p Form of PVF_2 Crystals

reflections	form factors in rel units		reflections	form factors in rel units	
	α	α_p		α	α_p
100	76	0	120	49	0
020	74	74	130	45	56
110	133	205	200	103	158

A new crystal form, which is formed upon subjecting the α form PVF_2 to high electric field and is consistent with both the X-ray (Figure 1) and infrared results, is proposed in Figure 2. In this new form, designated α_p hitherfrom, the atomic coordinates for the first chain remain the same as in the α form, but the second chain is now related to the first one by the symmetry operation of screw axis [100] with translation component $a_0/2$. This results in the antiparallel alignment of the two chains along the *c* axis and the displacement of the second chain from the first one by ($a_0/2 + b_0/2$) in the *ab* projection. The projection of atomic coordinates of α_p form on the *bc* plane remains the same as in the α form[2] and, hence, is not shown here. The predicted X-ray intensity form factors at major reflections for this new α_p form are shown in Table I and compared with those for the α form. The observed increase