I (R = *m*-*t*-Bu), 89590-73-8; II (R = H), 88608-20-2; II (R = *o*-F), 89551-66-6; II (R = *o*-Cl), 89551-67-7; II (R = *o*-Br), 89551-68-8; II (R = *o*-MeO), 89551-69-9; II (R = *o*-Me), 89551-70-2; II (R = *o*-Et), 89551-71-3; II (R = *o*-*i*-Pr), 89551-72-4; II (R = *o*-*t*-Bu), 89551-73-5; DMP, 576-26-1; F-*p*-DMP, 2338-56-9; Br-*p*-DMP, 2374-05-2; MeCO-*p*-DMP, 5325-04-2; CN-*p*-DMP, 4198-90-7; NO_2-*p*-DMP, 2423-71-4; Me-*p*-DMP, 527-60-6; MeO-*p*-DMP, 2431-91-6; DBP, 128-39-2; Br-*p*-DBP, 1139-52-2; MeCO-*p*-DBP, 14035-33-7; CI_3-*p*-DBP, 98464-61-0; *t*-Bu-*p*-DBP, 732-26-3; MeO-*p*-DBP, 489-01-0; NO_2-*p*-DBP, 728-40-5; DCP, 87-65-0; Br-*p*-DCP, 3217-15-0; Cl-*p*-DCP, 88-06-2; MeCO-*p*-DCP, 17044-70-1; Me-*p*-DCP, 2432-12-4; NO_2-*p*-DCP, 618-80-4; CN-*p*-DCP, 1891-95-8.

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(18) Ionization constants used for correlations and regression (*F*) and multiple correlation coefficient (*r*) with confidence level (CL) for symmetrically substituted phenols are herein provided.

(a) p-X-2,6-dimethylphenol: H (10.59), F (10.46), Br (9.81), MeCO (8.22), CN(8.19), NO_2 (7.07), Me(10.86), OMe (10.84)

(2- parameter)	r 0.995	CL 99.90
	F 0.203 E03	CL 99.90
(3- parameter)	r 0.996	CL 99.90
	F 0.119 E06	CL 99.90

(b) p-X-2,6-di-t-butylphenol: H (14.22), Br (13.23), MeCO (10.27),CJ_3 (14.77), t-Butyl(14.75 OMe (14.82), NO_2 (7.49)

(2- parameter)	r 0.986	CL 99.90
	F 0.884 E02	CL 99.90
(3- parameter)	r 0.987	CL 99.90
	F 0.512 E02	CL 99.50

(c) p-X-2,6-dichlorophenol: H (6.81), Br (6.21), C_1 (6.23), MeCO (4.60), Me (7.19), NO_2 (3.59), CN (4.38)

(2- parameter)	r 0.998	CL 99.90
	F 0.420 E03	CL 99.90
(3- parameter)	r 0.998	CL 99.90
	F 0.187 E03	CL 99.90

Correlations Using Glass Transition Temperatures for Well-Ordered Substituted Phenol Condensation Products

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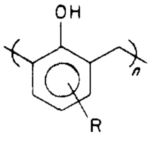
ABSTRACT: A wide variety of meta- and para-substituted poly[(1-hydroxy-2,6-phenylene)methylenes] and ortho-substituted poly[(1-hydroxy-2,4-phenylene)methylenes] were synthesized and the glass transition temperatures were obtained. A two, three, and four multiple correlation analysis using localized, delocalized, steric, and polarization parameters with the glass transition temperature was then performed. No overall correlation for either meta- or para-substituted poly[(1-hydroxy-2,6-phenylene)methylenes] was obtained. Ortho-substituted poly[(1-hydroxy-2,4-phenylene)methylenes] yielded moderately good correlations with these parameters. In addition, alkyl substituents of varying length placed in the α position of poly[(1-hydroxy-2,6-phenylene)methylene] systematically reduced the glass transition temperature.

Introduction

As a result of their high acidities, phenol condensation products are finding wide application in polymer miscibility studies.[1] Recently we began directing our research efforts to the quantification of acidity characteristics of these polymers. Several isomeric orientations of these are known. Poly[(1-hydroxy-2,6-phenylene)methylene] (*o*,*o*-PHMP (I)), poly[(1-hydroxy-2,4-phenylene)methylene] (*o*,*p*-PHMP (II)), and polymers III were synthesized by using known routes, and glass transition temperatures (T_g) were obtained. We recently reported that linear free energy relations exist for the acidities of these oligomers as a consequence of the type and position of a substituent in a polar solvent.[2] To determine whether other correlations exist for each polymeric series, similar correlations were performed by utilizing the T_g's and localized, delocalized, steric, and polarization constants for the substituents.[3]



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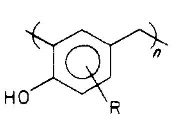

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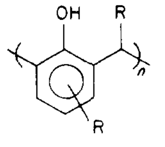

III

A systematic variation of the correlation equations (1)–(4) was used so that critical parameters could easily be identified.

$$Q_X = L\sigma_I + D\sigma_R^- + h \tag{1}$$

$$Q_X = L\sigma_I + D\sigma_R^- + S\gamma + h \tag{2}$$

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$$Q_X = L\sigma_I + D\sigma_R^- + P\varphi + h \qquad (3)$$

$$Q_X = L\sigma_I + D\sigma_R^- + S\gamma + P\varphi + h \qquad (4)$$

In these correlations, σ_I, σ_R^-, γ, and, φ represent substituent constants for localized ("field"), delocalized ("resonance"), steric, and substituent polarizations, respectively, and are readily available from extensive compilations by Charton.[4] L, D, S, and P represent contributions from localized, delocalized, steric, and polarization components, respectively, while h and Q_X represent the intercept and the quantity of interest, respectively.

Finally, since others have determined that α-substituted and α,α-disubstituted *o,o*-PHMP dimers exhibit conformational rigidity in solution,[5] the overall qualitative effect on T_g in the solid state was examined.

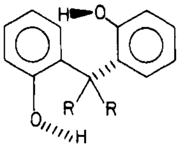
Experimental Section

All *o,o*-PHMP's were synthesized by utilizing a group 2 catalyst to ensure high ortho,ortho content according to the procedure of Shepherd and McNaughton.[6] Ortho-substituted *o,p*-PHMP's were synthesized by utilizing an acid catalyst according to the procedure of Mackey.[7] Structural assignment was made with a Bruker 250-MHz NMR spectrometer and by FTIR using an Analect FX6250. Number-average molecular weights were determined by vapor phase osometry with a Perkin-Elmer Model 115 in acetone. For meta- and para-substituted *o,o*-PHMP the average degree of polymerization (DP) was about 6, for ortho-substituted *o,p*-PHMP's DP was about 4.5, and for α-substituted PHMP DP was 3. Thermal characterization of all materials was performed on a Du Pont 1090 thermal analyzer. All samples were first heated to 150 °C at 10 °C/min and quenched in powdered dry ice. For T_g determination the sample interval was 0.2 at a heating rate of 5 °C/min.

Results

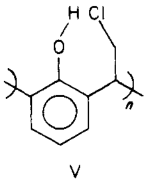
Table I summarizes T_g's and substituent constants used in eq 1–4. T_g's for α-substituted *o,o*-PHMP's are reported in Table II; linear free energy correlations were not performed since the substituent type was too restrictive.

The most dramatic effect on T_g's occurs when an α substituent is present. In the solution state, Elington[5] reported that bulky α substituents reduce the degree of intramolecular hydrogen bonding and induce aromatic π/phenolic hydrogen bonding in PHMP dimers. In this spatially restricted orientation, the molecule is conformationally rigid (IV).



IV

The T_g's for nonpolar α-substituted *o,o*-PHMP suggest that as the α substituent size increases, inter- and intramolecular hydrogen bonding is impeded since unique spatial conformations result. When a polar α substituent is present, however, the phenolic intra- and intermolecular hydrogen bonding is enhanced, resulting in a more rigid oligomer (V).



V

Table I
Summary of Glass Transition Temperatures for Meta- and Para-Substituted *o,p*-PHMP's and Ortho-Substituted *o,p*-PHMP's and Substituent Constants Used for Correlations

	T_g, °C						
substituent	para	meta	ortho	σ_I	σ_R^-	γ	φ
H	82.2	82.2	79.8	0	0	0	0
F	72.1	127.1	64.5	0.54	–0.58	0.27	–0.001
Cl	124.6	79.4	56.2	0.47	–0.30	0.55	0.050
Br	129.2	109.2	44.9	0.47	0.28	0.65	0.079
Me	149.5	122.6	95.2	–0.01	–0.09	0.52	0.046
Et	133.3	137.1	49.4	–0.01	–0.07	0.56	0.093
t-Bu	67.6	70.9	63.6	–0.01	–0.11	1.24	0.186
Ph	121.7			0.12	–0.04	0.57	0.243
MeCO	90.0			0.30	0.41	0.50	0.102
NO_2	97.6	83.6		0.67	0.37	0.35	0.063
i-Pr			61.6	–0.01	–0.09	0.76	0.140
MeO			96.6	0.30	–0.65	0.36	0.063

Table II
Summary of Glass Transition Temperatures for α-Substituted *o,p*-PHMP's

α substituent	T_g, °C
H	72.2
Me	72.1
CH_2Cl	123.0
Et	38.2
n-Pr	48.7

Neither meta- nor para-substituted *o,o*-PHMP demonstrated any regularity in T_g as a function of substituent type. Moderately good correlations (R = 0.8294) were obtained from ortho-substituted *o,p*-PHMP's with localized, delocalized, and polarization parameters (eq 3). Charton[9] has previously shown that both (1) the effect of ortho substituents is independent of steric effects and that (2) vastly different linear combinations for σ_I and σ_R occur when the ortho effect is operational. Thus moderately successful correlations involving ortho-bond polarization is envisioned to be a result of enhanced/diminished intra- and intermolecular hydrogen bonding in the bulk state.

Acknowledgment. We appreciate the support, in part, for this research by the Polymers Program of the Materials Division of the National Science Foundation.

Registry No. I (R = H), 77222-49-2; I (R = *p*-F), 89551-74-6; I (R = *m*-F), 89590-69-2; I (R = *p*-Cl), 89551-75-7; I (R = *m*-Cl), 89590-68-1; I (R = *p*-Br), 89551-76-8; I (R = *m*-Br), 89590-67-0; I (R = *p*-Me), 31958-47-1; I (R = *m*-Me), 89590-71-6; I (R = *p*-Et), 89551-77-9; I (R = *m*-Et), 89590-72-7; I (R = *p*-*t*-Bu), 89551-78-0; I (R = *m*-*t*-Bu), 89590-73-8; I (R = *p*-Ph), 89551-79-1; I (R = *p*-MeCO), 89551-80-4; I (R = *p*-NO_2), 89551-81-5; I (R = *m*-NO_2), 89590-70-5; II (R = H), 88608-20-2; II (R = *o*-F), 89551-66-6; II (R = *o*-Cl), 89551-67-7; II (R = *o*-Br), 89551-68-8; II (R = *o*-Me), 89551-70-2; II (R = *o*-Et), 89551-71-3; II (R = *o*-*t*-Bu), 89551-73-5; II (R = *o*-*i*-Pr), 89551-72-4; II (R = *o*-OMe), 89551-69-9; III (R = Me), 98330-79-1; III (R = CH_2Cl), 98330-80-4; III (R = Et), 98330-81-5; III (R = Pr), 98330-82-6.

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