Linear Free Energy Relationships among Substituted Phenol Condensation Products

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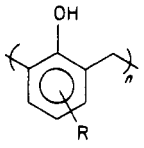
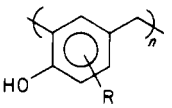
ABSTRACT: A diverse series of meta- and para-substituted poly[(1-hydroxy-2,6-phenylene)methylenes] and ortho-substituted poly[(1-hydroxy-2,4-phenylene)methylenes] has been synthesized and acidity constants have been determined by computerized slope analysis. Two discrete acidity constants exist for all substituted poly[(1-hydroxy-2,6-phenylene)methylenes]. Ortho-substituted poly[(1-hydroxy-2,4-phenylene)methylenes] also demonstrated this dual acidity when the ortho substituent was not too bulky. Linear free energy correlations were performed by using the first and second acidity constants and the Hammett and extended Hammett equations for meta- and para-substituted poly[(1-hydroxy-2,6-phenylene)methylenes], while ortho-substituted poly[(1-hydroxy-2,4-phenylene)methylenes] were assessed only by the extended Hammett equation. Correlations indicate that the resonance contribution for all polymers is best approximated by that for monomeric phenols and that the steric contributions for ortho-substituted polymers are best described by those for ortho-substituted phenols.

Introduction

Well-ordered and well-characterized phenol condensation products have been synthesized in this laboratory. The enhanced and multiple acidities for these polymers, i.e., poly[(1-hydroxy-2,6-phenylene)methylenes] (*o,o*-PHMP (I)) and poly[(1-hydroxy-2,4-phenylene)-methylenes] (*o,p*-PHMP (II)), are well documented in the



I



II

literature.[1,2] Indeed, it is this heightened acidity that others have exploited for use in polymer miscibility studies[3] and polymer-supported polypeptide synthesis,[4] to name a few.[5] Surprisingly, however, little quantitative information on the nature of the condensation reaction or acidities of the polymer is available. Only recently have reactivity ratios of substituted phenols been examined for this condensation reaction.[6] In an attempt to provide quantitative information on the acidities of substituted *o,o*- and *o,p*-PHMP's, a wide variety of these materials were synthesized and pK_a's determined according to techniques established for very weak acids. Computerized slope analysis was performed on all titration curves for end point determination.

Linear free energy correlations involving the Hammett equation (eq 1) and the first acidity constants from meta- and para-substituted *o,o*-PHMP's were performed. In eq 1 σ represents the substituent constant, ρ is the reaction constant, and h is the intercept. Our fundamental assumption was that the ortho,ortho methylene appendage would have a "constant" effect so that monomeric phenols could serve as acidity models. Meta and para substitutions were chosen as prototypes. σ values were obtained by using two strategies: (a) restrictive and (b) nonrestrictive. The nonrestrictive mode meant that σ values were calculated by using the acidity data of meta- and para-substituted phenols in 95% ethanol as described by Schwarzenbach.[7] In this design substituents with extensive ±I and ±R characteristics were included in our original calculations.

$$\log (k_X/k_H) = \sigma\rho + h \quad (1)$$

In the restrictive design, however, σ values were obtained directly from the van Beekum compilations.[8]

More quantitative information was obtained by using variations of a multiple linear regression analysis (eq 2 and 3). In eq 2 and 3 L, D, and S represent localized ("field"),

$$Q_X = L\sigma_I + D\sigma_R^- + h \quad (2)$$

$$Q_X = L\sigma_I + D\sigma_R^- + S^\gamma + h \quad (3)$$

delocalized ("resonance"), and steric parameters, respectively, while σ_I, σ_R^-, and γ represent substituent constants for inductive, resonance, and steric effects, respectively. Q_X represents the measurable parameter, the acidity constants. Other than the demarcation of σ values into their electrical and nonelectrical components, eq 3 permits direct assessment of ortho-substituted polymers.

Experimental Section

Condensation polymerizations were performed by using well-established synthetic procedures. With a single exception, all meta- and para-substituted *o,o*-PHMP's were synthesized by using a group 2 basic catalyst according to the procedure of Shepherd and McNaughton.[10] *p*-Acetyl-*o,o*-PHMP was synthesized by using an acid catalyst according to the procedure of Burke[11] without a Carius tube. The *o*-fluoro-, *o*-chloro-, *o*-bromo-, and *o*-methoxy-*o,p*-PHMP's as well as nonsubstituted *o,p*-PHMP were obtained from the corresponding 3-substituted-4-hydroxybenzyl alcohols by using an acid catalyst according to the procedure of Mackey[12] since higher overall conversions were obtained than when the ortho-substituted phenol was reacted directly with formaldehyde. The *o*-methyl- and *o*-ethyl-*o,p*-PHMP's were obtained from the corresponding 3-alkyl-4-methoxybenzyl chloride precursors. Demethylation of the oligomer was cleanly effected by using hydriodic acid. The remaining *o*-alkyl-*o,p*-PHMP's were obtained from the corresponding *o*-alkylphenols by using the acid catalyst route of Burke.[11] NMR characterization was performed with a Bruker 250-MHz spectrometer and by FTIR using an Analect FX6250. ^{1}H NMR was used primarily to monitor curing of the prepolymers at 165 °C (Figure 1). All number-avarage molecular weights were obtained with a Perkin-Elmer 115 osmometer and were run in acetone. The degree of polymerization (DP) for meta- and para-substituted *o,o*-PHMP's was typically 6; for ortho-substituted *o,p*-PHMP's DP was 4.5. Acid dissociation constants were determined with a glass/calomel electrode pair in 95% ethanol according to the procedure of Harlow.[13] Neutralization studies were performed by using a 0.10 M alcoholic solution of each condensation product since model neutralizations involving 2,4-di- and 2,4,6-trialkyl-substituted phenols gave the

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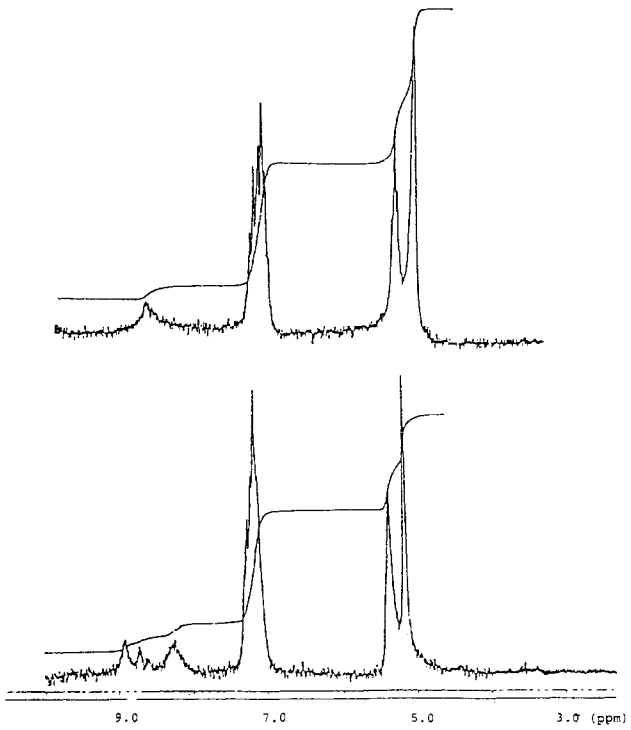

Figure 1. ^{1}H NMR spectra of *o,o*-PHMP before curing (bottom) and after curing (top) at 165 °C for 7 h.

Table I
σ Values Obtained from Schwarzenbach and van Beekum Used in the Hammett Equation for pK_{a_1} Values for *o,o*-PHMP's

substituent	σ_S	σ_{vB}
H	0	0
p-Cl	0.372	
p-Br	0.415	
p-I	0.448	
p-MeO	−0.140	
p-OH	−0.271	
p-MeCO	0.943	0.502
p-NO_2	1.290	0.778
m-Cl	0.516	0.373
m-Br	0.550	0.391
m-I	0.563	0.352
m-Me	−0.072	−0.069
m-NO_2		0.710
m-MeCO	0.419	0.376

least ambiguous inflection points at this concentration. Computerized slope analysis was used to determine inflection points and subsequent acidity constants. Calculations performed for acid constant determinations are reflective of macroscopic inflection points. Microscopic end points, i.e., those contributing less than 15% to the bulk first or second neutralization, were not utilized in any computations. Finally, substitutent constants were available from the extensive compilations of Charton.

Results

The structural characterization of all phenol condensation products was supportive of linear polymers with high regularity as proposed by structures I and II. No evidence for the oxymethylene linkage was detected in any condensation product. In cases where an ortho-substituted phenol was reacted directly with formaldehyde, no evidence for polymeric quinone methines was found.[15] An ortho,ortho content of greater than 96% for para-unsubstituted *o,o*-PHMP's was revealed by ^{13}C NMR, using calcium hydroxide as the catalyst.

Table I summarizes σ values used in the single-parameter correlation, where σ_S and σ_{vB} refer to derived substituent values obtained by using the Schwarzenbach data and values obtained from the van Beekum compilations, respectively. A linear least-squares analysis was performed by using pK_{a_1} acidity constants from meta- and para-substituted *o,o*-PHMP's and results are provided in Figure 2. Results of these correlations, in conjunction with the original phenolic data, are provided in Table II.

Table II
Results of a Single-Parameter Correlation Using Meta- and Para-Substituted *o,o*-PHMP pK_{a_1} Acidity Constants and Corresponding Phenolic Correlations in 95% Ethanol

system	category	ρ	r^a	CL^b	n^c
o,o-PHMP	nonrestrictive	1.72	0.97	99.90	17
o,o-PHMP	restrictive	2.19	0.96	99.99	17
phenol	nonrestrictive	2.36	0.98	99.90	14
phenol	restrictive	3.14	0.98	99.90	6

[a] Correlation constant. [b] Confidence level. [c] Number in set.

Table III
Summary of *L*, *D*, and *S* Values for a Variety of Substituted Phenols

system	solvent, temp	−*L*	−*D*	*S*
p-SP	H_2O, 25 °C	2.84	2.51	
p-SP	H_2O, 25 °C	2.80	2.25	
p-SP	H_2O, 25 °C	2.90	2.33	
p-SP	33.2% aqueous EtOH, 25 °C	3.76	2.47	
p-SP	52.0% aqueous EtOH, 25 °C	3.78	2.52	
p-SP	38.4% aqueous EtOH, 25 °C	3.45	2.46	
p-SP	EtOH, 25 °C	3.23	2.56	
p-SP	H_2O, 20 °C	3.64	2.89	
p-DMP[18a]	50.0% aqueous EtOH, 25 °C	10.04	4.99	
p-DMP[18a]	50.0% aqueous EtOH, 25 °C	9.98	6.14	2.72
p-DBP[18b]	50.0% aqueous EtOH, 25 °C	14.98	6.17	
p-DBP[18b]	50.0% aqueous EtOH, 25 °C	13.99	6.04	5.47
p-DCP[18c]	50.0% aqueous EtOH, 25 °C	11.26	4.70	
p-DCP[18c]	50.0% aqueous EtOH, 25 °C	11.26	4.69	3.14
o-SP	H_2O, 25 °C	4.52	2.48	0.44

Table IV
Acidity Constants for Meta- and Para-Substituted *o,o*-PHMP's and Correlation Parameters Used with Eq 2 and 3

substituent	pK_{a_1}	pK_{a_2}	σ_I	σ_R^-	γ
H	7.34	7.44	0	0	0
p-F	7.51	7.99	0.54	−0.58	0.27
p-Cl	6.50	6.88	0.47	−0.30	0.55
p-Br	7.40	7.52	0.47	−0.28	0.65
p-Me	7.37	7.83	−0.01	−0.09	0.52
p-Et	6.80	8.05	−0.01	−0.07	0.56
p-*t*-Bu	7.94	8.02	−0.01	−0.11	1.24
p-Ph	7.56	7.75	0.12	−0.04	0.57
p-MeCO	5.49	5.86	0.30	0.41	0.50
p-NO_2	5.39	5.63	0.67	0.37	0.35
m-F	7.18	7.60	0.54	−0.58	0.27
m-Cl	6.41	6.51	0.47	−0.30	0.55
m-Br	6.20	6.58	0.47	−0.28	0.65
m-Me	7.46	7.58	−0.01	−0.09	0.52
m-Et	8.63	8.93	−0.01	−0.07	0.56
m-*t*-Bu	6.70	6.86	−0.01	−0.11	1.24
m-NO_2	5.57	6.30	0.67	0.31	0.35

A series of model correlations involving acid dissociation constants for symmetrical 2,6-disubstituted phenols and eq 2 and 3 were undertaken in order to assess the monomeric phenolic system that best describes the *L*, *D*, and *S* coefficients of *o,o*- and *o,p*-PHMP's. The paucity of phenolic acidity data, however, restricted us to the following: para-substituted phenols (*p*-SP),[14] para-substituted 2,6-dimethylphenols (*p*-DMP),[16] para-substituted 2,6-dichlorophenols (*p*-DCP), para-substituted di-*tert*-butylphenols (*p*-DBP),[17] and ortho-substituted phenols (*o*-SP).[9] Results of these correlations are provided in Table III. Summaries of the dissociation constants and correlation results for *o,o*- and *o,p*-PHMP's appear in Tables

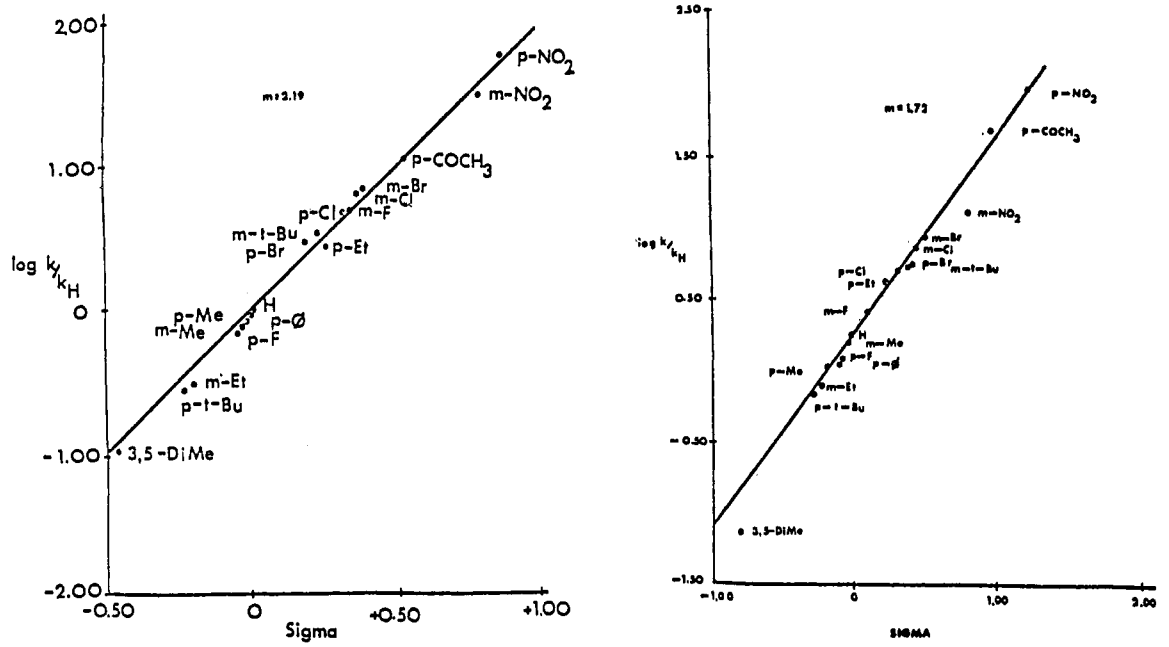

Figure 2. Hammett plot using meta- and para-substituted *o,o*-PHMP pK_{a_1} acidity constants and σ values obtained from van Beekum (left) and Schwarzenbach (right).

Table V
Acidity Constants and Correlation Parameters for Ortho-Substituted *o,p*-PHMP's

substituent	pK_{a_1}	pK_{a_2}	σ_I	σ_R^-	γ
H	7.41	8.94	0	0	0
F	7.64	7.79	0.54	−0.58	0.27
Cl	7.31	7.65	0.47	−0.30	0.55
Br	7.40	7.85	0.47	−0.28	0.65
MeO	6.35	6.91	0.30	−0.65	0.36
Me	7.35	7.49	−0.01	−0.09	0.52
Et	6.54	6.85	−0.01	−0.07	0.56
i-Pr	7.33	none	−0.01	−0.09	0.76
t-Bu	8.26	none	−0.01	−0.11	1.24

IV and V, respectively. The order of magnitude obtained for the *L*, *D*, and *S* coefficients suggests that as a good first approximation para-substituted *o,o*-PHMP's are best described by para-substituted phenols. The excellent agreement of *D* values seems intuitive since resonance effects through the methylene linkage are not expected. The high variability of confidence levels for meta-substituted *o,o*-PHMP's reflects structural irregularities within the polymer. Specifically, group 2 catalysts direct methylene linkages into the ortho,ortho position of the aromatic ring with approximately 95% efficiency. Our models have indicated that minor structural irregularities of this type severely disrupt the capacity of the polymer to generate intramolecular hydrogen bonding, crucial to thermodynamic-enhanced acidity. Neither para- nor meta-substituted *o,o*-PHMP's demonstrated any significant steric contribution as reflected in the overall correlations. This is consistent with the observation that substituents located in either the meta or para position of the aromatic ring are sufficiently removed from the reaction site to exert little steric interference. Table VI summarizes the results of these correlations.

The relatively weak correlations for dissociation constants of ortho-substituted *o,p*-PHMP's is somewhat reflective of our inability to accurately determine end points for this series. Generally inflection points were considerably broader and much less defined. In cases where a bulky ortho substituent was attached, a second inflection point could not be detected. Models have indicated that only alternate hyroxyl groups are spatially available for intramolecular hydrogen bonding. Additionally, intramolecular hydrogen bonding is severely impeded if the ortho substituent is too bulky since the cavity becomes unmanageably large.

Table VI
Summary of Correlations Involving the First and Second Acidity Constants of Substituted *o,o*- and *o,p*-PHMP's Using Eq 2 and 3

system	eq	acidity constant	−*L*	−*D*	*S*	*r*	CL	*n*
p-o,o	2	1	1.83	2.28		0.9020	99.90	10
p-o,o	2	2	2.20	2.26		0.9607	99.90	10
m-o,o	2	1	2.34	1.04		0.7796	95.00	8
m-o,o	2	2	1.84	0.69		0.6513	90.00	8
p-o,o	3	1	1.71	2.18	0.33	0.9039	99.90	10
p-o,o	3	2	2.08	2.30	0.10	0.9639	99.90	10
m-o,o	3	1	2.59	1.15	0.85	0.8410	90.00	8
m-o,o	3	2	2.10	0.80	0.90	0.7461	90.00	8
o-o,p	3	1	1.24	1.46	0.70	0.5925	90.00	9
o-o,p	3	2	2.36	2.20	1.51	0.9140	95.00	7

Since the methylene groups are sterically nonequivalent, the steric parameter of ortho-substituted *o,p*-PHMP's must be somewhat greater than that of ortho-substituted phenols. Localized electrical effects play a less dominant role after the first neutralization since greater bond polarization is expected by the intramolecular hydrogen bonding with the phenoxide ion. As in the case of *o,o*-PHMP's, good agreement of delocalized values for ortho-substituted *o,p*-PHMP's and ortho-substituted phenols is expected since delocalization is restricted to individual aromatic rings.

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*-Cl), 89551-75-7; I (R = *p*-Br), 89551-76-8; I (R = *p*-I), 98330-83-7; I (R = *p*-MeO), 98330-84-8; I (R = *p*-OH), 98330-85-9; I (R = *p*-MeCO), 89551-80-4; I (R = *p*-NO_2), 89551-81-5; I (R = *m*-Cl), 89590-68-1; I (R = *m*-Br), 89590-67-0; I (R = *m*-I), 98360-69-1; I (R = *m*-Me), 89590-71-6; I (R = *m*-NO_2), 89590-70-5; I (R = *m*-MeCO), 98360-70-4; I (R = *p*-F), 89551-74-6; I (R = *p*-Me), 31958-47-1; I (R = *p*-Et), 89551-77-9; I (R = *p*-*t*-Bu), 89551-78-0; I (R = *p*-Ph), 89551-79-1; I (R = *m*-F), 89590-69-2; I (R = *m*-Et), 89590-72-7;

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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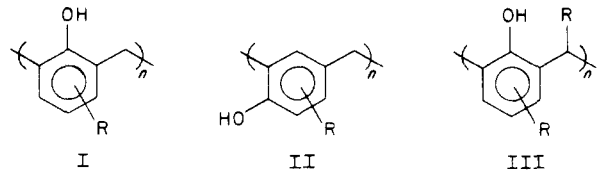
ABSTRACT: A wide variety of meta- and para-substituted poly[(1-hydroxy-2,6-phenylene)methylenes] and ortho-substituted poly[(1-hydroxy-2,4-phenylene)methylenes] were synthesized and the glass transition temperatures were obtained. A two, three, and four multiple correlation analysis using localized, 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]



I II III

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

$$Q_X = L\sigma_I + D\sigma_R^- + h \quad (1)$$

$$Q_X = L\sigma_I + D\sigma_R^- + S\gamma + h \quad (2)$$

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