Inner-Shell Excitation Spectroscopy of Polymer and Monomer Isomers of Dimethyl Phthalate

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The C 1s X-ray absorption spectra (XAS) of poly(diallyl phthalate), poly(diallyl isophthalate), and poly-(ethylene terephthalate) (PET) have been recorded using transmission detection. The phthalate segments of these polymers are isomers with different patterns of substitution (ortho, meta, para) of the methyl carboxylate groups on the phenyl ring. The C 1s and O 1s electron energy loss spectra (EELS) of the corresponding isomeric monomers, dimethyl phthalate, dimethyl isophthalate, and dimethyl terephthalate, have also been recorded in the gas phase using inelastic electron scattering under conditions dominated by electric dipole transitions. Good agreement is found in overall shape and in the energies of the spectral features of the same isomer in monomeric (EELS) versus polymeric (XAS) form. *Ab initio* calculations are used to provide a detailed interpretation of the spectra, in particular the origin of the isomeric variations. The analytical potential for using inner shell excitation spectroscopy to identify isomeric character and to map spatial distributions of polymer isomeric substitution is assessed.

1. Introduction

This work extends earlier studies¹⁻³ of the core excitation spectroscopy of poly(ethylene terephthalate) (PET), a ubiquitous polymer often found in packaging applications, and its small molecule analogue, 1,4-dimethyl terephthalate (1,4-DMP), which is the repeat unit of PET. Core excitation, using either synchrotron-based X-ray absorption (XAS) in a scanning transmission X-ray microscope (STXM) or electron energy loss spectroscopy (EELS) in a transmission electron microscope (TEM), is finding increasing applications in chemical speciation at a microscopic scale.⁴ We are interested in determining if isomeric polyphthalates can be analytically differentiated by changes in their C 1s and/or O 1s near edge spectra. Such a capability could be of use in tracking isomeric selectivity in phase segregation phenomena in polymers of mixed polyphthalates. To investigate the sensitivity of inner-shell excitation spectroscopy to the ring substitution pattern in phthalate-based polymers, we have studied both monomer standards and isomeric phthalate polymers.

Investigation of the degree of correspondence of the core spectra of monomers and polymers is a further motivation for this study. The validity of the use of small molecule (in this case monomer) species as standards for polymer spectra has been discussed and demonstrated previously.^{5–8} The combination of several experimental techniques, along with semiempirical extended Hückel (EHMO) calculations of 1,4-DMP, has helped elucidate assignments of the spectral features of both polymer and monomer.³ Other monomer—polymer comparisons include comparisons of phenylurethane to polyurethane,² and phenylurea to polyurea.⁹ In many cases there is a close correspondence between the core spectra of monomer and polymer. This is true especially when there is no difference in degree of saturation between the monomer and the polymer and when there is minimal interaction among adjacent monomer units of a single polymer chain or among adjacent chains.

In this paper, we report the C 1s X-ray absorption spectra of poly(diallyl phthalate) (1,2–PDP), poly(diallyl isophthalate) (1,3-PDP), and poly(ethylene terephthalate) (1,4-PET or PET) and the C 1s and O 1s inner-shell electron energy loss (ISEELS) of the three isomeric monomers: dimethyl phthalate (1,2-DMP), dimethyl isophthalate (1,3-DMP), and dimethyl terephthalate (1,4–DMP) (see Chart 1). ISEELS is particularly suited for gas phase studies, while XAS in the STXM is exactly the technique for which this work is helping to develop quantification capabilities. Strictly speaking only two of the three polymers are isomers because of the different alkyl linkage. However, because the saturated fragment in which the polymers differ has no effect on π^* conjugation, the π^* aspect of the polymers were isomers.

Semiempirical EHMO methods have proven useful for assignment of spectral features, even though EHMO does not give accurate absolute core excitation energies. Typically orbital eigenvalues (ϵ) in a "Z+1" calculation are interpreted as relative term values ($-\epsilon \approx TV = IP - E_{ex}$) which are placed on an absolute scale using experimental core level ionization potentials (IPs). In the case of 1,4-DMP, the quality of the agreement between the experimental and the EHMO calculated spectrum is poor⁷ when compared to that found in other applications of EHMO to core excitation. EHMO was never able to reproduce important aspects of the experimental C 1s spectrum of 1,4-DMP, particularly the splitting of the lowest energy $\pi^*_{C=C}$ band, even when a range of plausible geometries were explored. For this reason we have used ab initio calculations based on Kosugi's "GSCF3" methodology¹⁰ to provide improved theoretical results upon which to base our spectral interpretations. We report the results of GSCF3 calculations of the C 1s and O 1s absorption spectra of 1,4-DMP, 1,3-DMP, and 1,2-DMP.

2. Experimental Section

X-ray absorption measurements were made using the scanning transmission X-ray microscope (STXM) at the X-1A beamline

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CHART 1



at the National Synchrotron Light Source (NSLS). Details of the apparatus and operating procedures have been provided elsewhere.^{3,12,13} The polymer samples were obtained from Scientific Polymer Products (PET density 1.385; 1,3-PDP density 1.256, degree of polymerization 20; 1,2-PDP density 1.267, degree of polymerization 10). The PET sample was microtomed at room temperature to prepare ~0.1 μ m thick sections for the C 1s spectrum. The 1,3-PDP and 1,2-PDP polymer samples were prepared by evaporating a 0.1 wt % solution of the polymer in acetone to form thin polymer films on carbon-coated TEM grids.

Spectra were acquired with an atmosphere of He gas in the microscope enclosure.¹¹ The energy resolution was about 0.3 eV. Spectral acquisition time was less than 1 min per energy scan, which represents approximately 5% of the critical dose in the case of PET. We assume that the critical dose of 1,2-PDP and 1,3-PDP is similar to that measured for PET.³ In addition, the spectra for 1,2-PDP and 1,3-PDP were acquired under defocused beam conditions.

The energy scales of the C 1s spectra were determined by simultaneously measuring the C 1s spectrum of the polymer

and CO₂ gas mixed with He gas in the microscope enclosure. The C 1s \rightarrow 3s Rydberg peak at 292.80 eV¹⁴ is used for calibration. The derived position of the main $\pi^*_{C=C}$ peak of PET is 284.8(1) eV. The estimated 0.1 eV uncertainty is largely associated with the uncertainties in a small correction for nonlinearity of the energy scale, which was variable in time but which amounted to as much as 0.2 eV in the 8 eV difference between the energies of the π^* peaks in PET and CO₂. The π^* energy for PET is in agreement with that of the main peak in the ISEELS of 1,4-DMP (284.86(6) eV).

The gas phase energy loss spectrometer has been described previously.¹⁵ Spectra were recorded using a final electron energy of 2.5 keV, a scattering angle of 2° , and a resolution of 0.6 eV fwhm. Under these conditions electric dipole transitions dominate. Small angle rather than zero-degree scattering is used in order to prevent the main electron beam from entering the analyzer and creating a large background. The solid 1,4-DMP and 1,3-DMP samples and the liquid 1,2-DMP sample were introduced directly in a small metal cell directly attached to the collision cell. This normally provided adequate intensity, although gentle heating of the collision cell and sample to ~40

TABLE 1: Calculated Geometries of 1,4-DMP, 1,3-DMP,and 1,2-DMP^a

	1,4-DMP	1,3-DMP	1,2-DMP	crystal ²⁹	PET ³⁰							
	Bond	Lengths (A	Å)									
C-C(ring) average	1.383	1.383	1.384	1.385	1.35							
C-H (ring)	1.069	1.070	1.069	1.070	1.07							
$C-(CO_2Me)$	1.480	1.475	1.487	1.486	1.49							
C=0	1.207	1.207	1.205	1.23	1.27							
(CO)-O	1.346	1.347	1.342	1.331	1.34							
O-Me	1.454	1.453	1.453	1.450	1.44							
C-H(Me)	1.078	1.078	1.078	0.93								
	Bond	Angles (de	g)									
C(Ph)-C(O)-OMe	112.6	112.5	113.0									
C(Ph)-C=O	124.9	125.0	126.4									
(OC)-O-Me	118.2	118.2	118.4									
Ph-CO ₂ Me	planar	planar	nonplanar									
1.2-DMP Dihedral Angles												
(See	(See Chart 1 for Atom Labeling) (deg)											
2-1-7-8	-19.5											
3-2-11-12			-41.5									

^{*a*} The molecular structures were obtained from an *ab initio* selfconsistent-field (SCF) geometry optimization (3-21G* basis set). Harmonic frequency calculations were performed to verify that these structures represent the minima on the potential energy surface. Conformations are presented in Chart 1. The total energies for the minimum energy conformations are -680.185, -680.187, and -680.167au for 1,4-DMP, 1,3-DMP and 1,2-DMP, respectively. In a fully planar geometry the total energy for 1,2-DMP is -680.156 au.

°C was used in some cases to obtain higher vapor pressure. All three DMP isomers were obtained from Aldrich (stated purity >99%). Absolute energy scales were determined by recording spectra of a mixture of the molecule and CO_2 .

The spectra of the gas phase monomer and solid polymer were converted to an absolute oscillator strength scale using standard methods¹⁶ that are based on background subtraction and normalization of the far continuum to atomic oscillator strengths.¹⁷

3. Calculations

The ground state structures of 1,4-DMP, 1,3-DMP, and 1,2-DMP were provided from an *ab initio* geometry optimization performed with a 3-21G* basis set using the program SPAR-TAN.¹⁸ The effect of the methyl carboxylate conformation on the total energy was explored. For example, the C_{2h} configuration of 1,4-DMP has a lower energy than the C_{2v} configuration. Similar determinations were made for the 1,2-DMP and 1,3-DMP structures. Harmonic vibrational frequencies were calculated (3-21G* basis) to verify that the lowest energy optimized structures indeed represent minima in the potential energy surface. The lowest energy conformation is planar for 1,4-DMP and 1,3-DMP, but in 1,2-DMP the methyl carboxylate groups are forced out of plane by steric effects. These geometries are listed in Table 1. Chart 1 presents the atom numbering used to identify atomic-specific contributions to the calculated core excitation spectra.

The core-ionized and core excited states of 1,4-DMP, 1,3-DMP, and 1,2-DMP were obtained by *ab initio* self-consistent-field (SCF) calculations with explicit consideration of the core hole¹⁹ and with the localized core hole picture. These calculations were performed using the *ab initio* program "GSCF3".¹⁰ The basis set used is the extended basis set taken from (63/6) and (53/5) contracted Gaussian-type functions for C and O and (6) for H of Huzinaga et al.,²⁰ where the contraction scheme was (311121/21111/1*) for atoms with a core hole, (521/31) for heavy atoms with no core hole, and (31) for H. The core excited states were obtained with the improved virtual orbital



Figure 1. Comparison of C 1s oscillator strengths derived from x-ray absorption spectra of 1,2-PDP, 1,3-PDP, and 1,4-PET polymers, recorded by transmission through a solid thin film in a scanning transmission X-ray microscope (STXM) at X-1A of NSLS. The solid state IPs³¹ are indicated by hatched lines. The inset shows an expansion of the π^* region.

(IVO) method.²¹ The relaxed Hartree–Fock (HF) potential is essential in accurately considering large electronic reorganization upon inner-shell hole creation; therefore, the IVO method based on the relaxed HF potential is superior to the method using the ground state orbitals. This method has been shown to be quite accurate in predicting term values and intensities of core \rightarrow Rydberg excitations,^{22,23} and provides a good first-order approximation to the energies and intensities of core \rightarrow valence excitations.²⁴ Gaussian line widths used in generating the simulated spectra from the *ab initio* results were 0.6 eV fwhm for orbitals of eigenvalue (ϵ) –15 < ϵ < 0, 1.2 eV for 0 < ϵ < 4 in the C 1s simulation; and 0.8 eV fwhm for orbitals of eigenvalue (ϵ) –15 < ϵ < 0, 1.2 eV for 0 simulation. These widths were chosen to be similar to the experimentally observed line widths.

Molecular orbital diagrams of the LUMO and (LUMO+1) π^* states of the C 1s(C–H) core excited states of 1,4-DMP, 1,3-DMP, and the ground state of benzene and 1,3-DMP have also been prepared. The orbital energies and wave functions for 1,3-DMP and 1,4-DMP were taken from the above calculations. The ground state of benzene was calculated using an identical basis set and the experimental geometry.²⁵

4. Results and Discussion

4.1. C 1s Spectra. Figure 1 compares the C 1s X-ray absorption spectra of the 1,2-PDP, 1,3-PDP and 1,4-PET polymers. Figure 2 presents the corresponding C 1s spectra of the gas phase monomers 1,2-DMP, 1,3-DMP, and 1,4-DMP,



Figure 2. Comparison of the C 1s oscillator strength spectra of monomeric 1,2-, 1,3-, and 1,4-DMP, derived from gas phase, innershell electron energy loss measurements carried out in the electric dipole scattering regime (2° scattering angle, 2.5 keV final electron energy, 0.6 eV fwhm resolution). The inset shows an expansion of the π^* region. The hatched lines indicate estimated gas phase C 1s IPs.

all recorded by energy loss spectroscopy. Figure 3 presents the O 1s spectra of the monomers. In all cases the spectra are converted to absolute oscillator strength scales, after subtraction of underlying valence and lower energy core excitation signal. Note the oscillator strength scale refers to that of the repeat unit or full molecule as opposed to a per-atom basis, which has been used in some earlier work. The repeat units of 1,2-PDP, 1,3-PDP, and 1,4-PET have 14, 14, and 10 carbon atoms, respectively, whereas all of the DMP monomers have only 10 carbon atoms. This is why the continuum intensity in the 1,2-PDP and 1,3-PDP C 1s spectra is larger than that in all of the other species.

Tables 2, 3, and 4 summarize the energies, estimated term values (TV = ionization potential (IP) - transition energy (E)), and proposed assignments for the C 1s and O 1s spectra of the three isomeric monomers and polymers. The C 1s spectra predicted from the GSCF3 ab initio calculations of 1,4-DMP, 1,3-DMP, and 1,2-DMP are presented in Figure 4, in comparison to the experimental spectra of the related polymers. Since the monomer and polymer spectra are generally similar, the calculations are compared to the polymer XAS spectra instead of the more appropriate monomer spectra because of the added information provided by the higher resolution. The relative positions of the calculated component spectra are set using the calculated C 1s ionization energies. The full spectrum was generated by summing the components in stoichiometric proportion. The calculated energies are higher than the absolute experimental energies, with the energy difference between calculated and experimental features increasing for transitions that occur at higher energy, such as the C 1s(C=O) $\rightarrow \pi^*_{C=O}$



Figure 3. Comparison of the O 1s oscillator strength spectra of monomeric 1,2-, 1,3-, and 1,4-DMP, derived from gas phase EELS (see caption to Figure 2 for experimental details). The hatched lines indicate estimated gas phase O 1s IPs.

transition. For the lowest energy $1s \rightarrow \pi^*$ transition, the energy difference is ~2 eV for the C 1s spectra and ~1 eV for the O 1s spectra. The calculated energies, term values, oscillator strengths, and ionization potentials for the C 1s and O 1s spectra are presented in Tables 5 and 6, respectively.

In general the assignments follow those proposed for PET in our earlier studies.^{1–3} Here we focus the discussion on some of the differences among these three species, in particular the change in shape of the lowest energy π^* band in the C 1s spectrum and the energy shifts that are found in both the C 1s and O 1s spectra. On the basis of the effect of substitutional pattern on relative stability and chemical reactivity, one might expect that the electronic structure of the 1,2 and 1,4 isomers should be similar, while that of the 1,3 isomer might differ. However, because steric interactions cause the geometry of 1,2-DMP to be nonplanar, its orbital interactions are expected to be quite different and thus the expected correspondence with the para isomer should be reduced. Overall the spectra of the three isomers are quite similar, although there are some notable differences. The energy of the main C 1s $\rightarrow \pi^*_{C=C}$ shifts upward by 0.26 eV, while the main O 1s $\rightarrow \pi^*_{C=O}$ peak shifts upward in energy by 0.47 eV between 1,4-, and 1,2-DMP. These isomeric shifts of the energy of the main π^* transitions are reproduced by the ab initio calculations. In addition, the lowest energy C 1s $\rightarrow \pi^*$ band in 1,4-DMP has a different shape than that for the 1,3- and 1,2-DMP isomers (see inset of Figures 1 and 2). Finally, the energy of the weak band at 290 eV in the higher energy end of the $\pi^*_{C=O}$ region is dependent on the isomer. All of the energy shifts are real since the calibration precision of the energy loss scale is better than 0.05 eV (with an accuracy of better than 0.1 eV). It is likely that the isomeric shifts in the $\pi^*_{C=C}$ and $\pi^*_{C=O}$ peak positions arise mainly from

TABLE 2: Experimental Energies (*E*, eV) and Assignments for Features in the C 1s Spectra of Polymers: Poly(ethylene terephthalate) (1,4-PET), Poly(diallyl isophthalate) (1,3-PDP), and Poly(diallyl phthalate) (1,2-PDP)

					a	ssignment	
	1,4-PET	1,3-PDP	1,2-PDP	С-Н	C-R	CH_x	C=0
IP^b	284.7	284.6	284.6	IP			
1	284.8^{a}	284.87^{a}	285.05^{a}	$\pi^*_{C=C}$	$\pi^*_{C=C}$		
\mathbf{IP}^{b}	285.2	285.1	285.1		IP		
2	285.43			$\pi^*_{C=C}$			$\pi^*_{C=C}$
\mathbf{IP}^{b}	286.2	286.2	286.2			IP	
3 (sh)	287.4	287.5	287.6			$\sigma^*_{\rm C-H}$	
4	288.27	288.21	288.38				$\pi^{*}_{C=0}(+)$
\mathbf{IP}^{b}	288.7	288.7	288.7				IP
5	289.0	289.2	289.4	$\pi^*_{C=C/C=O}$			
6	290.1	290.3	290.3				$\pi^{*}_{C=0}(-)$
7 (sh)	291.6	291.6					
8 (sh)	292.8	293.0	293.1	$\sigma_{1}^{*}(Bz)$			$\sigma^*_{C-O}/\pi^*_{C=O}(mix)$
9	296.4	296.3	296.2	$\sigma^{*}(Bz)$			
10	303.3	303.2	302.8				$\sigma^*_{C=0}$

^{*a*} Calibration: Energy scales were determined by simultaneously measuring the C 1s spectrum of the polymer and CO₂ (admixed with He in the microscope enclosure). The C 1s \rightarrow 3s Rydberg peak at 292.80 eV¹⁴ is used for calibration. ^{*b*} From XPS.³¹

TABLE 3: Experimental Energies (*E*, eV), Term Values, and Assignments for Features in the C 1s Spectra of Dimethyl Terephthalate (1,4-DMP), Dimethyl Isophthalate (1,3-DMP), and Dimethyl Phthalate (1,2-DMP)

	dimethyl terephthalate (1,4-DMP				DMP)	dimethyl isophthalate (1,3-DMP)				dimethyl phthalate (1,2-DMP)									
	energy	term value			energy	term value			energy	term value			assignment						
	(eV)	T_{C-H}	T_{C-R}	T_{Me}	$T_{C=0}$	(eV)	T_{C-H}	T_{C-R}	$T_{Me} \\$	T _{C=0}	(eV)	T_{C-H}	$T_{C-R} \\$	T_{Me}	T _{C=0}	С-Н	C-R	Me	C=0
1	284.86^{a}	5.6	6.1			284.95^{b}	5.6	6.1			285.12^{c}	5.4	5.9			$\pi *_{C=C}(a)$	$\pi^*_{C=C}$		
2	285.7	4.8														$\pi^{*}_{C=C}(b)$			
3	287.4			5.2							287.2			5.2				$\sigma^*_{\rm C-H}$	
4	288.2		2.8		6.7	288.4		2.6		6.5	288.5		2.5		6.4		$\pi^*_{C=C/C=O}$		$\pi^{*}_{C=O}(+)$
5	289.1	2.4														$\pi^*_{C=C/C=O}$			
6	289.9				5.0	289.9				5.0	289.9				5.0				$\pi^{*}_{C=O}(-)$
\mathbf{IP}^d	290.5					290.5					290.5					IP			
\mathbf{IP}^d	291.0					291.0					291.0						IP		
\mathbf{IP}^d	292.6					292.6					292.6							IP	
\mathbf{IP}^d	294.9					294.9					294.9								IP
7	292.8	-2.3	-1.8		2.1	293.0	-2.5	-2.0		1.9	293.3	-2.8	-2.3		1.6	$\sigma_{1}^{*}(Bz)$	σ^*_{C-O}		$\pi^*_{C=O}(mix)$
8	296.3	-5.8				296.4	-5.9				296.3	-5.8				$\sigma^{*}_{2}(Bz)$			
9	304				-9	304				-9	304				-9				$\sigma^*_{C=0}$

^{*a*} Calibration: -5.88(6) eV relative to π^* of CO₂ (290.74 eV). ^{*b*} Calibration: -5.79(3) eV relative to π^* of CO₂. ^{*c*} Calibration: -5.62(3) eV relative to π^* of CO₂. ^{*d*} The IPs were estimated from those of related species.³² Note that the underscore in the following indicates the site of core ionization. C₆H₆, 290.3 eV; CH₃CO₂CH₃, 291.3; CH₃CO₂CH₃, 292.6; CH₃CO₂CH₃, 294.9 eV.

 TABLE 4: Experimental Energies (E, eV), Term Values, and Assignments for Features in the O 1s Spectra of Dimethyl Terephthalate (1,4-DMP), Dimethyl Isophthalate (1,3-DMP), and Dimethyl Phthalate (1,2-DMP)

	1,4-DMP			1,3	-DMP		1,2	-DMP			
		TV			Т	V		TV		assignment	
	energy (eV)	$T_{C=0}$	$T_{\rm C-O}$	energy (eV)	$T_{C=0}$	$T_{\rm C-O}$	energy (eV)	$T_{C=O}$	$T_{\rm C-O}$	С=0	С-О
1	531.5 ^a	5.5		531.53 ^b		5.5	531.77 ^c		5.2	$\pi^*_{C=0}(+)$	
2	534.0	3.0		534.3	2.7		534.5	2.5		$\pi^{*}_{C=0}(-)$	$\pi^{*}_{C=0}(+)$
3	536.4		4.1	536.8		3.7	536.5		4.0	$\pi^*_{C=O,C=C}$	$\pi^*_{C=0}(-)$
IP^d	537.0			537.0			537.0			IP	
IP^d	540.5			540.5			540.5				IP
4	540.3		0.2	540.5		0	540.4		0.1		$\sigma^*_{\rm C-O}$
5	546	9		546	9		546	9		$\sigma^*_{\rm C-O}$	

^{*a*} Calibration: -3.9(1) eV relative to π^* of CO₂ (535.4 eV). ^{*b*} Calibration: -3.87(2) eV relative to π^* of CO₂. ^{*c*} Calibration: -2.34(4) eV relative to π^* of CO (534.11(8) eV). ^{*d*} Estimated from the XPS IPs of related species:³² CH₃CO–OCH₃, 537.0; CH₃O–OCH₃, 540.5 eV.

the changing nature of $\pi^*_{C=C}$ and $\pi^*_{C=O}$ mixing. Similar changes were observed recently in the 1s spectra of nitro-anilines.²⁶

The *ab initio* calculations (Figures 4 and 5) mirror the isomerrelated changes in the core excitation spectra. The energy and width of the first C 1s $\rightarrow \pi^*_{C=C}$ transition changes between 1,4-DMP and 1,2-DMP, as found experimentally. The width of this transition in the 1,3 and 1,2 species is a consequence of the overlap of multiple phenyl ring (C-H) contributions. The energy shift occurs because some of the C 1s(C-H) $\rightarrow \pi^*_{C=C}$ and C 1s(C-R) $\rightarrow \pi^*_{C=C}$ components in 1,3-DMP and in 1,2-DMP are shifted to higher energy and overlap (note that C-R refers to the ring carbon to which the methyl carboxylate is attached). The isomeric changes observed in the C 1s(C=O) $\rightarrow \pi^*_{C=O}$ transition are also reproduced, although there is a clear "stretching" of the calculated energy scale relative to the experimental one. The *ab initio* results show that the increase in the energy of the main $\pi^*_{C=O}$ transition between 1,4-DMP and 1,2-DMP arises from a competition between a small decrease in the C 1s binding energy and a larger increase in the



Figure 4. *Ab initio* calculations for the C 1s spectra of 1,4-DMP, 1,3-DMP, and 1,2-DMP, in comparison to the experimental C 1s X-ray absorption spectra of 1,4-PET, 1,3-PDP, and 1,2-PDP. Each component spectrum corresponds to an IVO calculation at a specific site (see Chart 1 for atom numbering). The excitation energy is the sum of the calculated term values for individual transitions and the calculated absolute IPs. *Note there is a 2.0 eV difference in the energy scales used to plot the experimental and calculated results.* The peak areas are the calculated absolute oscillator strengths. The sum is weighted by stoichiometry.

TABLE 5: Calculated Energies, Term Values, and Oscillator Strengths for C 1s $\rightarrow \pi^*$ Transitions of 1,4-DMP, 1,3-DMP, and 1,2-DMP

								1	,4-DMP									
	С	1s C−H	1(2,3,5,6)		C 1s	C-R(1,4	4)		(C 1s C=O(7,11)				C 1s CH ₃ (10,14) ^a			
	<i>E</i> (eV)	TV ((eV)	OS	<i>E</i> (e	V) '	TV (eV)	(OS	<i>E</i> (eV)	TV	(eV)	OS	E	(eV)	TV (eV)	OS
IP	290.842				291.2	212				295.711				29	2.990			
1	286.73	4	.12	0.0619	286.8	82	4.39 0.0304		290.97	4.	75	0.0933	29	0.67	2.32	(0.0000	
2	288.02	2	.82	0.0317	289.1	16	2.06 0.0000		294.63	1.	.08	0.0420	29	1.72	1.27	(0.0083	
3	290.96	-0	.11	0.0058	291.1	12	0.10	0.0	0011	294.81	0.	.90	0.0000	29	2.45	0.54	(0.0343
								1	,3-DMP									
	C 1s C-H(4,6) C 1s C-H(2) C 1s CH(5)					(5)	C 1s	s C-R(1	1,3)	C 1s	C=O(=O(7,11) C 1s CH),14) ^a			
	Е	TV		E	TV			ΤV		E	TV		E	ΤV		E	TV	
feature ^a	(eV)	(eV)	OS	(eV)	(eV)	OS	E (eV)	(eV)	OS	(eV)	(eV)	OS	(eV)	(eV)	OS	(eV)	(eV)	OS
IP	291.091			290.986			290.826			291.112			295.659			292.968		
1	286.74	4.35	0.0436	286.84	4.15	0.0252	287.33	3.50	0.0196	287.17	3.94	0.0283	291.09	4.57	0.1002	291.00	1.97	0.0001
2	288.46	2.63	0.0015	287.86	3.13	0.0000	287.58	3.25	0.0000	288.38	2.73	0.0011	293.90	1.76	0.0027	291.71	1.26	0.0083
3	291.26	-0.17	0.0074	291.46	-0.48	0.0000	290.81	0.01	0.0069	291.29	-0.18	0.0044	295.26	0.40	0.0333	292.28	0.69	0.0003
								1	,2-DMP									
	C 1s C-H(3,6)			C	ls C−l	H(4,5)		C 1s C-R(1,2)				C 1s C=O(7,11)			C 1s CH ₃ (10,14) ^b			

	C 1s C-H(3,6)			C 1s C $-H(4,5)$			C Is C - R(1,2)			C I	S C=O(7,1)	1)	C 1s CH ₃ $(10,14)^{p}$		
	$E(\mathrm{eV})$	TV (eV)	OS	E (eV)	TV (eV)	OS	E (eV)	TV (eV)	OS	E (eV)	TV (eV)	OS	E (eV)	TV (eV)	OS
IP	290.898			290.95			291.240			295.551			292.533		
1	287.26	3.64	0.0448	286.89	4.06	0.0387	287.12	4.12	0.0373	291.28	4.27	0.1053	290.58	1.95	0.0024
2	287.78	3.12	0.0073	288.47	2.48	0.0014	288.77	2.47	0.0033	293.79	1.77	0.0187	291.69	0.84	0.0018
3	291.62	-0.72	0.0099	291.63	-0.67	0.0153	291.35	-0.11	0.0073	294.62	0.93	0.0189	291.94	0.60	0.0133

^{*a*} For C 1s(C–H) and C 1s (C–R) excitation; feature 1 is mainly $\pi^*_{C=C}$ (lower energy component from the $1\pi^*(e_{1u})$ orbital of benzene); 2 is the higher energy component of the $1\pi^*(e_{1u})$; and 3 is the main $\pi^*_{C-O}(+)$ orbital. For excitation at the other carbon sites, these are the 3 lowest energy virtual orbitals. ^{*b*} Tabulated C 1s(CH₃) \rightarrow final state transitions for methyl carbons include π^* and σ^* final states.

 $\pi^*_{C=0}$ term value. The dominant term value change indicates the important role of π^* mixing in these molecules, especially the mixing of the two carbonyl π^* orbitals.

In 1,4-DMP, there is a second, relatively intense transition at 285.7 eV that is absent in the spectra of both 1,3-DMP and 1,2-DMP. The *ab initio* calculations clearly show that the 285.7

eV peak is associated with C 1s(C–H) excitation to the second component of the $1\pi^*$ orbital, i.e. the higher energy of the two orbitals that correlate with the e_{1u} orbital of benzene (see Figure 6). Extended Hückel molecular orbital (EHMO) calculations previously performed for 1,4-DMP also predicted that the second transition originated from the C–H carbons.⁷ However, the



Figure 5. Ab initio calculations for the O 1s spectra of 1,4-DMP, 1,3-DMP and 1,2-DMP. Each component spectrum corresponds to an IVO calculation of core excitation at a specific site (see Chart 1 for atom numbering). The excitation energies are the sum of the term values for individual transitions and the calculated absolute IPs. Note there is a $\sim 1 \text{ eV}$ difference in the presentation of the energy scales for the experimental and calculated energy scales. The peak areas are the calculated absolute oscillator strengths.

TABLE 6: Calculated Energies, Term Values, and Oscillator Strengths for O 1s $\rightarrow \pi^*$ Transitions of 1,4-DMP, 1,3-DMP, and 1,2-DMP

	O 1s	s(C=O) (8,	12)	O 1:	13)	
feature ^a	<i>E</i> (eV)	TV (eV)	OS	<i>E</i> (eV)	TV (eV)	OS
			1,4-DMP			
IP	536.854			538.583		
1	532.44	4.30	0.0155	535.28	3.30	0.0047
2	536.10	0.76	0.0005	538.13	0.45	0.0002
3	536.33	0.53	0.0072	538.65	-0.07	0.0033
			1,3-DM	Р		
IP	536.708			538.547		
1	532.65	4.06	0.0166	535.54	3.06	0.0051
2	535.11	1.60	0.0001	537.27	1.28	0.0007
3	536.79	-0.08	0.0066	538.83	-0.28	0.0123
			1,2-DM	Р		
IP	536.662			538.137		
1	532.89	3.77	0.0179	535.36	2.77	0.0040
2	535.18	1.49	0.0028	536.94	1.20	0.0014
3	536.14	0.53	0.0057	538.09	0.04	0.0043

^{*a*} Feature 1 is $\pi^*_{C=0}(+)$, feature 2 is $\pi^*_{C=0}(-)$, and feature 3 is $\pi^*_{C=0}(-)$ in character.

EHMO calculation did not reproduce correctly the relative intensity of the first and second transition. In particular, the second transition was predicted to be significantly larger than the first.⁷ The *ab initio* result confirms the EHMO attribution of the origin of the second transition and, in addition, reasonably reproduces the relative intensity of the first two transitions.

As EHMO calculations have had a good track record at reproducing the C 1s $\rightarrow \pi^*$ transitions,^{1,2} we have made further comparisons with the *ab initio* results in order to determine if the error in the relative intensities of the first two transitions in 1,4-DMP is related to assumptions made in our implementation of EHMO to core excitation or whether it is simply a reflection of the limitations of EHMO wave functions. Two assumptions that might be questioned are the use of the Z+1 approximation

to correct for core hole relaxation and the use of N 2p coefficients to estimate spectral intensities. In the improved virtual orbital method of the GSCF3 ab initio package the core hole is included explicitly and the transition matrix element integrals are evaluated in full. However, it is possible to use GSCF3 in modes similar to the way we use EHMO, i.e. using orbital coefficients from Z+1 ground state calculations to approximate transition intensities. The EHMO Z+1 (EICVOM) result for 1,4-DMP has been compared to the result from the ab initio Z+1 calculation, as well as to an IVO-ab initio calculation in which the orbital coefficient is used to approximate intensities. All of the ab initio calculations used the same basis set, with the same level of expansion. The three ways of carrying out the GSCF3 calculation are compared to the EHMO result for 1.4-PET in Figure 7. Only the first two transitions are presented. While the term value differs with the calculation technique, all of the *ab initio* results qualitatively reproduce the relative intensity of the first and second transition, while the EHMO-EICVOM result does not. From Figure 7, we conclude that the shortcomings of EHMO are not simply a matter of limitations of the EICVOM model or the approximation in which $\sum c^2(2p)$ is used as the relative intensity, but rather they are associated with inadequacies of the EHMO wave functions themselves.

The prominent second peak in 1,4-DMP and its absence in the 1,2- and 1,3-DMP isomers suggest that a unique pattern of orbital mixing occurs in 1,4-DMP that does not exist in 1,3-DMP or 1,2-DMP. The nature of this mixing can be determined by examining the molecular orbitals corresponding to these final states. Figure 6 presents an orbital correlation diagram illustrating the relationships of the LUMO and (LUMO+1) π^* MOs of the ground state and the C 1s(C-H) core excited state of 1,4-DMP and 1,3-DMP and the ground state of benzene. The first π^* transition is to a final state similar to one of the $\pi^* e_{2u}$ MOs of benzene, mixed with a positive combination (same phase on each methyl carboxylate group) of $\pi^*_{C=0}$ orbital



Figure 6. Orbital correlation diagram of the LUMO and (LUMO+1) π^* orbitals of the ground state and the C 1s(C-H) core excited states of 1,4-DMP and 1,3-DMP and of the ground state of benzene. The diameter of the circles is proportional to the $2p\pi$ orbital density on each atom in the molecular orbital. For visibility, the diameters of the circles on the methyl carboxylate group have been increased by a factor of 5. The "*" designates the site of the core hole.



Figure 7. Comparison of the C 1s(C-H) spectrum of 1,4-DMP evaluated by extended Hückel molecular orbital calculations using the equivalent ionic core virtual orbital model (EICVOM, Z+1); *ab initio* EICVOM (Z+1) calculation; the IVO–*ab initio* (GSCF3) calculation with intensities approximated by 2p coefficients; and the IVO calculation using the full transition matrix element.

density. The second peak is evolved as well from the benzene $\pi^* e_{2u}$ MO mixed with $\pi^*_{C=0}$ orbital density of the methyl carboxylate group on the opposite side of the molecule from the core excited center. Typically, the second lowest e_{2u} -derived level (LUMO+1) in a substituted benzene ring has no orbital density on the core excited carbon (see Figure 6 for MOs of C 1s excited and ground state 1,3-DMP). As the core hole is

moved to different sites on the phenyl ring, the spatial distribution of this orbital changes so that there is no $2p\pi^*$ density at the site of the core hole. This trend has been observed in several other recent EHMO studies of substituted aromatic systems.^{1,2} However, in 1,4-DMP, the para substitution of the two methyl carboxylate group appears to "pin" the electron distribution in the (LUMO+1) level, such that a portion of the e_{2u}-derived orbital density remains at the site of the C 1s(C-H) core excited atom. Examining the (LUMO+1) MO of 1,3-DMP, we observe that the corresponding pinning does not occur, so that there is no $2p\pi^*$ density at the C 1s(C-H) core excited atom in the higher energy of the two e_{2u} -derived MOs. In the (LUMO+1) of 1,3-DMP, the methyl carboxylate group has the same phase relationship to the ring as it has in 1,4-DMP, but the core excited carbon site now has no $2p\pi^*$ orbital density. This picture of a systematic influence of para substitution on the spatial distribution of the higher of the two e_{2u}-derived MOs is a recurring theme in core excitation in disubstituted phenyl groups.^{1,2} In the absence of other perturbations, such as a ligand-ring delocalization which is dependent on the pattern of isomeric substitution, one may expect to see a second C 1s $\rightarrow 1\pi^*_{C=C}$ signal in para species, but not in the meta or ortho species. A distinct ~0.5 eV splitting of the main $\pi^*_{C=C}$ feature in p-xylene has been observed in recent studies of the C 1s spectra of the isomeric xylenes, supporting this outlook.²⁷

The features in the region above the C 1s(C-H) $\rightarrow 1\pi^*_{C=C}$ transitions are less well resolved because this region has contributions from all of the carbon atoms in the polymer or monomer. In the spectra of the polymers and monomers there is a shoulder at \sim 287.5 eV. This shoulder is approximately of equal height in the monomer spectra, but is more than twice as large in the spectra of 1,3-PDP and 1,2-PDP than in the spectrum of 1,4-PET. This intensity difference provides a basis for assigning this feature to C 1s(CH_x) $\rightarrow \sigma^*_{C-H}$ transitions, since the intensity trends correlate well with the different alkyl bridge structure of the polymers. The ab initio calculations (Figure 4) predict that the C 1s(CH₃) $\rightarrow \sigma^*_{C-H}$ transitions occur at somewhat higher energy. This is an example of an energy scale "stretching" that occurs in the GSCF3 calculations at the level of basis set we are using. The effect is particularly clear for the C 1s(C=O) $\rightarrow \pi^*_{C=O}$ transitions. For transitions at higher energy, more caution is required for interpretation, and the use of empirical observations is especially helpful.

The 288–292 eV region is dominated by a mixture of C $1s(C=O) \rightarrow \pi^*_{C=O}$ and C $1s(C-H) \rightarrow 2\pi^*_{C=C}$ transitions (the $2\pi^*_{C=C}$ orbital is derived from the π^* b_{2g} orbital of benzene). In general these features involve excitation to delocalized upper levels of mixed $\pi^*_{C=C/C=O}$ character (see Figure 5 of ref 3). The intense feature at ~288.3 eV in the spectra of the monoms and polymers is assigned to the C $1s(C=O) \rightarrow \pi^*_{C=O}(+)$ transition, where "+" refers to the in-phase relationship of the two contributing $\pi^*_{C=O}$ portions. The transition at ~289 eV is assigned as a C $1s(C=H) \rightarrow \pi^*_{C=C/C=O}$ transition, and the transition at ~290 eV is assigned as the C $1s(C=O) \rightarrow \pi^*_{C=O}(-)$ transition. All of these transitions are superimposed on a broad background from C $1s(CH_x) \rightarrow \sigma^*_{C-C}$ transitions.

With the exception of the effect of resolution and a few key differences outlined below, the polymer C 1s spectra are very similar to the monomer spectra. In 1,4-PET orientational effects are possible because 1,4-PET has a propensity to be crystalline. However polarization dependent XAS of our 1,4-PET sample showed less than 5% variation between grazing and normal incidence. A small difference is expected between 1,4-PET and 1.4-DMP because the monomer model represents the ethyl bridge as two terminal methyl groups. In principle the spectra of methyl and ethyl groups differ,²⁸ but since the features from saturated sites are broad and masked by the sharper spectral features of the saturated carbon sites, this difference is not observed in these systems. The 1,3-PDP and 1,2-PDP polymers have a substantially different alkyl bridge structure, with more carbons per repeat unit than 1,4-PET. The associated spectral changes are small, although the longer alkyl group does increase the spectral cross section in 1,2- and 1,3-PDP. Another possible source of differences between polymer and monomer spectra is electronic interactions between neighboring repeat units in the polymer. However, in these phthalate polymers the alkyl bridge acts as a barrier to π^* delocalization between polymer repeat units. Thus the π^* electronic environment of the polymers is expected to be very similar to that of the corresponding monomer. The considerable degree of similarity of the C 1s spectra of monomer and polymer (compare Figures 1 and 2) supports this interpretation. A significant difference between the polymer and monomer spectra exists in the relative intensities of the $\pi^*_{C=0}$ region (288–290 eV), with that for the polymer being larger than that for the monomer. This can be seen by comparing the total oscillator strength of the $\pi^*_{C=0}$ region in the polymers (Figure 1) with that of the monomers (Figure 2). A large part of this difference is likely the larger contribution of the saturated alkyl linkages in the polymer than in the monomer. Finally there is a clear difference in the intensity of the 289 eV feature between polymer and monomer, with the polymer signal being in all cases more intense than that of the corresponding monomer. This difference may be a signature of an unexpected degree of delocalization between adjacent repeat units of the polymer. It is interesting that this feature is most intense in 1,4-PET, the species in which interunit interactions might be expected to be strongest.

4.2. O 1s Spectra. In the experimental (Figure 3) and calculated (Figure 5) O 1s spectra of the isomeric phthalate molecules the π^* energies evolve as a function of isomerism in a manner similar to that observed in the C 1s spectra. The energy of the first O 1s $\rightarrow \pi^*$ peak increases between 1,4-DMP and 1,2-DMP. The *ab initio* calculations predict that the first peak is a O 1s $\rightarrow \pi^*_{C=O}(+)$ transition in each phthalate. The increase in the energy of this transition from 1,4- to 1,2-DMP is the result of a larger decrease in term value (~virtual level

binding energy) than a simultaneous increase in O 1s(C=O) binding energy, as the two methoxy carboxyl groups are brought closer to each other. This balancing effect (i.e. the opposite isomeric influence on the 1s binding energy and the π^* term value) is very similar to that observed in the calculated C 1s excitation spectrum. The second O 1s spectral feature is assigned as a combination of O 1s(C=O) $\rightarrow \pi^*_{C=O}(-)$ and O $1s(C-O) \rightarrow \pi^*_{C=O}(+)$ transitions, although the *ab initio* calculation predicts that these two transitions should be resolved. The third feature is assigned as the O $1s(C-O) \rightarrow \pi^*_{C=O}(-)$ transition, on the basis of the calculations. The main continuum signal at 540 eV is attributed to O 1s(C–O) $\rightarrow \sigma^*_{C-O}$ transitions, while the shoulder at 545 eV is attributed to O $1s(C=O) \rightarrow$ $\sigma^*_{C=0}$ transitions. The shift in the position of the main $\pi^*_{C=0}$ peak is clearly the feature with the most analytical potential for monitoring isomeric character at the O 1s edge.

5. Summary

We have shown that 1,2-, 1,3-, and 1,4-substitution of two ester functionalities on a single benzene ring results in characteristic differences in both C 1s and O 1s spectra that are detectable in the X-ray absorption spectra of polymers and the inner-shell electron energy loss spectra of monomers. Differences arise from the nature of π^* delocalization between the $\pi^*_{C=O}$ orbitals of the methyl carboxylate groups and the $\pi^*_{C=C}$ orbitals of the phenyl ring. In 1,4-DMP, an unusual pinning of the normally silent (LUMO+1) level produces an added feature in the C 1s spectra. This suggests that symmetry and orbital mixing considerations can play an otherwise unexpected role in determining the C 1s spectra of phenyl systems. The major features of the C 1s and O 1s spectra of 1,4-DMP, 1,3-DMP, and 1,2-DMP have been reproduced through *ab initio* GSCF3 calculations.

This study has shown that small but measurable differences in energy and shape exist in the core excitation spectra of the phthalate isomers. These characteristics could provide the basis for mapping phase segregation in phthalate-based polymers prepared from mixed 1,2- and-1,4-substituted precursors. For example, imaging at 285.4 eV could be used to map the spatial distribution of 1,4-PET in a mixed 1,2/1,4 system. Accurate energy scales and good energy resolution will be required.

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