

A density functional study on dielectric properties of acrylic acid grafted polypropylene

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Influence of acrylic acid grafting of isotactic polypropylene on the dielectric properties of the polymer is investigated using density functional theory (DFT) calculations, both in the molecular modeling and three-dimensional (3D) bulk periodic system frameworks. In our molecular modeling calculations, polarizability volume, and polarizability volume per mass which reflects the permittivity of the polymer, as well as the HOMO–LUMO gap, one of the important measures indicating the electrical breakdown voltage strength, were examined for oligomers with various chain lengths and carboxyl mixture ratios. When a polypropylene oligomer is grafted with carboxyl groups (cf. acrylic acid), our calculations show that the increase of the polarizability volume α' of the oligomer is proportional to the increase of its mass m , while the ratio α'/m decreases from the value of a pure polymer when increasing the mixture ratio. The decreasing ratio of α'/m under carboxyl grafting indicates that the material permittivity might also decrease if the mass density of the material remains constant. Furthermore, our calculations show that the HOMO–LUMO gap energy decreases by only about 15% in grafting, but this decrease seems to be independent on the mixture ratio of carboxyl. This indicates that by doping polymers with additives better dielectric properties can be tailored. Finally, using the first-principles molecular DFT results for polarizability volume per mass in connection with the classical Clausius–Mossotti relation, we have estimated static permittivity for acrylic acid grafted polypropylene, assuming the structural density keeping constant under grafting. The computed permittivity values are in a qualitative agreement with the recent experiments, showing increasing tendency of the permittivity as a function of the grafting composition. In order to validate our molecular DFT based approach, we have also carried out extensive three-dimensional bulk periodic first-principles total-energy calculations in the frameworks of the density functional theory and density functional perturbation theory (DFPT) for crystalline acrylic acid grafted polypropylene. Interestingly, the computed electronic and dielectric properties behave very similarly between the simplified molecular DFT modeling and the more realistic 3D bulk periodic DFPT method. In particular, the static permittivity values $[\epsilon_r(0)]$ from the molecular DFT–Clausius–Mossotti modeling are in excellent agreement with the high-frequency dielectric constant values (ϵ_∞) from the DFPT method. This obviously implies that the chain-to-chain interaction to dielectric and electronic properties of acrylic acid polypropylene, to a first approximation, can be neglected, therefore justifying the usage of molecular DFT modeling in our calculations. © 2011 American Institute of Physics. [doi:10.1063/1.3556704]

I. INTRODUCTION

Because of many beneficial properties such as excellent mechanical and chemical resistance, isotactic polypropylene (IPP) has become one of the most widely used commercial polymer. It is also a widely used insulation material in power engineering products due to excellent dielectric and electrical breakdown strength properties.^{1–6} Since the classical paper by Natta and Corradini⁷ on the structural properties of the IPP the basic properties of pure IPP have been studied extensively experimentally during the past decades,^{1–6} while there are only a few first-principles theoretical studies on the IPP (Refs. 8

and 9) and other polymers.^{10–14} Major improvements in material properties are not expected using conventional material processing techniques. Therefore, new technical approaches are needed. Doping the polymer matrix with selected additives is one such promising approach to make functionalized chemicals with improved properties. For example, the addition of 2 wt.% polyaniline has been measured to increase the alternating-current breakdown voltage of polypropylene by over 30% and the lightning impulse breakdown voltage by almost 20%.¹⁵

Chemical functionalization is used to improve the desired properties of polymeric material for specific uses without adversely affecting the nature of the polymer backbone. When polypropylene is grafted with a water-soluble acrylic acid (AA) monomer, the surface of the material becomes

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hydrophilic improving adhesion, while the bulk properties of the IPP are retained.^{16–20} Acrylic acid provides polar functional groups, for example, the carboxyl group ($-\text{COOH}$), to the IPP chain. Further polarization effects on the dielectric properties of the side chain are of interest, in order to tailor dielectric properties of polymer, e.g., polarizability, permittivity, and dielectric strength for use in high-voltage insulators.

Electrical degradation and breakdown phenomena limit the utility of polymers. For example, it has been observed experimentally¹ that the AC dielectric strength of polypropylene is decreased when blended with flexible polypropylene (Hifax), while the opposite happens when polypropylene is blended with ceresine wax.²¹ Furthermore, even if polarizability and dielectric constant of a material could be increased by grafting, this usually happens at the expense of the decreased dielectric strength. One factor affecting the dielectric strength, at a fundamental level, is the electronic structure of the polymer. Among several microscopical factors, the dielectric strength correlates with the size of the band gap since it requires more energy to excite an electron from an occupied energy level to an unoccupied level when the band gap is larger. Other microscopical factors, e.g., trap states and space charges, and macroscopical factors affecting the dielectric strength, such as the specimen geometry or testing conditions, are not discussed here.^{22–25}

One of the main objectives of polymers research is to study the relationship between the chemical and physical structure and physical properties of polymers. Electronic structure calculations offer atomic level understanding of the dielectric properties of polymers, thus allowing a systematic manner at a fundamental level to develop the desirable properties for new polymer materials. The HOMO–LUMO gap for molecules, or the band gap for solids, can be obtained from quantum mechanical calculations, and allow to estimate the change in the dielectric strength when the polymer is modified by grafting. In addition, polarizability which is directly related to macroscopic dielectric material property of permittivity can be calculated.

In the present study, primarily, calculations based on the density functional theory (DFT) within the molecular modeling framework are performed for IPP oligomers grafted with carboxyl groups ($-\text{COOH}$). Since we are mostly interested in the origin of the polarizability at the molecular level, we choose the molecular approach. Model molecules whose sizes range from 3 to 18 $-\text{C}_3\text{H}_6-$ monomers and acrylic acid content²⁶ from 5.4 to 22.7 wt.% are studied. Polarizability volume and HOMO–LUMO gap changes in IPP oligomers due to grafting are reported. These changes indicate that dielectric properties of polypropylene can be improved by skillful grafting with acrylic acids.²⁶ Finally, in order to justify using the molecular DFT based calculations in our studies, we have also carried out three-dimensional (3D) bulk periodic first-principles calculations in the framework of the density functional perturbation theory (DFPT) for dielectric properties and the band gap and compared and contrasted them with the corresponding molecular modeling based calculations, which is discussed briefly in Sec. III B.

II. COMPUTATIONAL MODELS AND METHODS

A. Models

1. Molecular DFT based modeling

We discuss, in the following, the models used in our molecular DFT based calculations. Model molecules selected for the study comprise a series of IPP chains with the increasing chain length up to 18 propylene (C_3H_6) monomers, the same molecules with one grafted carboxyl group, IPP molecules up to nine monomers with a constant mixture ratio of carboxyl groups, and one 18-monomer molecule with the increasing mixture ratio. These models are used, in order to systematically examine the possible effect of increasing the chain length and varying acrylic acid content, on the dielectric behavior of the molecule. In addition, possible termination effects of the model molecules and interaction between adjacent carboxyl groups could be inspected within this model series.

In the pure IPP oligomer, the methyl groups form a helix structure with a 120° rotation between any two consecutive groups. The helical structure of the IPP molecule is presented in Fig. 1 for an IPP molecule of nine monomers [$-\text{CH}(\text{CH}_3)\text{CH}_2-$] and an IPP molecule of nine monomers grafted with carboxyl ($-\text{COOH}$). The COOH -group is bonded to a carbon atom along with a methyl-group.

Pure and grafted polypropylene molecules of 3, 6, 9, and 18 monomers have been studied in this work. In our previous paper,²⁷ the calculated dielectric properties of pure IPP molecules were already shown to be quite independent on the length of the molecule. In order to see whether this behavior still prevails in the case of acrylic acid grafted polypropylene and how the acrylic acid alloying of polypropylene influences the dielectric properties, we have carried out extensive computational studies with various chain lengths and carboxyl mixture ratios. All the studied grafted IPP molecules are shown in Figs. 2 and 3.

Details related to the permittivity calculation are briefly given in the following (cf. Ref. 27 and references therein). For modeling the permittivity, we assume that our polymer is a

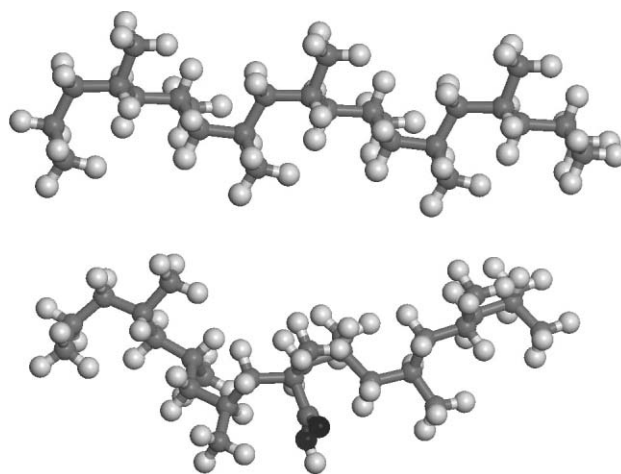


FIG. 1. Polypropylene molecule of nine IPP monomers ($-\text{CH}(\text{CH}_3)\text{CH}_2-$) (above) and polypropylene of nine IPP monomers grafted with carboxyl ($-\text{COOH}$) (below). Gray balls are carbon atoms, white hydrogen atoms, and black oxygen atoms.

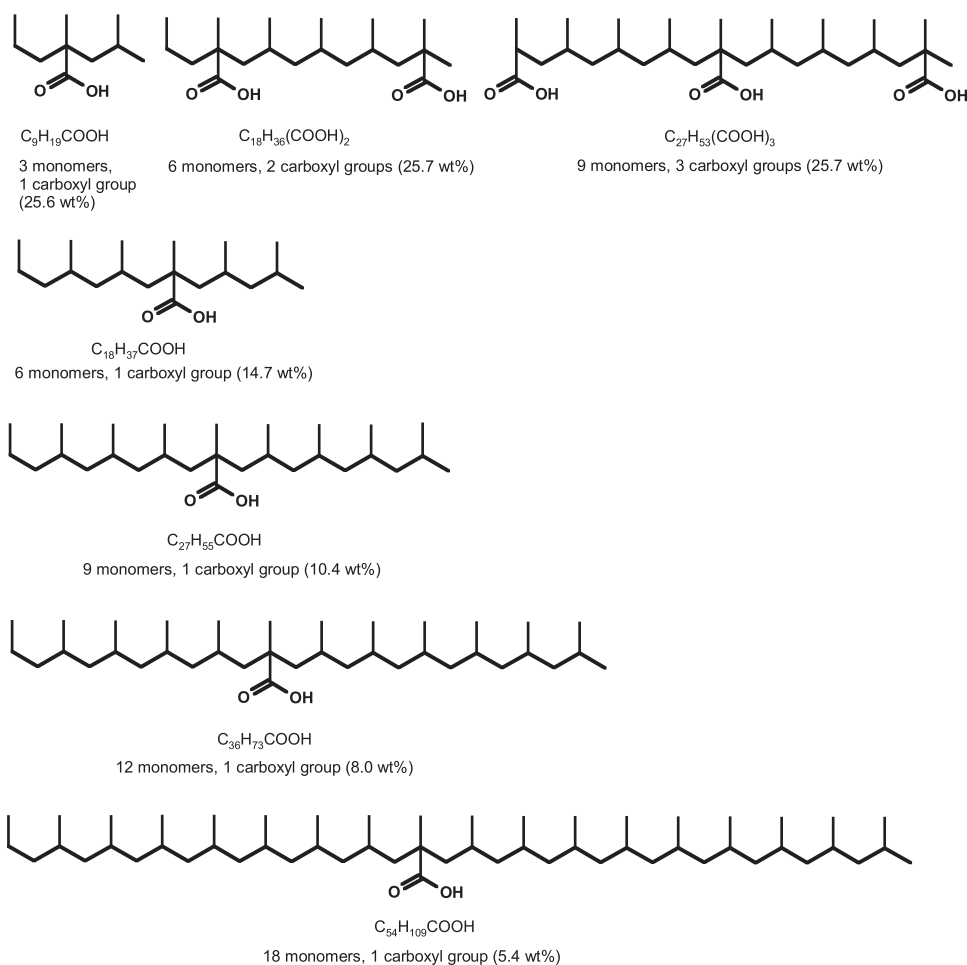


FIG. 2. Carboxyl grafted polypropylene of 3, 6, 9, 12, and 18 monomers with one grafted ($-COOH$) group (at left downward) and 3, 6, and 9 monomers with 1, 2, and 3 grafted groups, respectively (at the top).

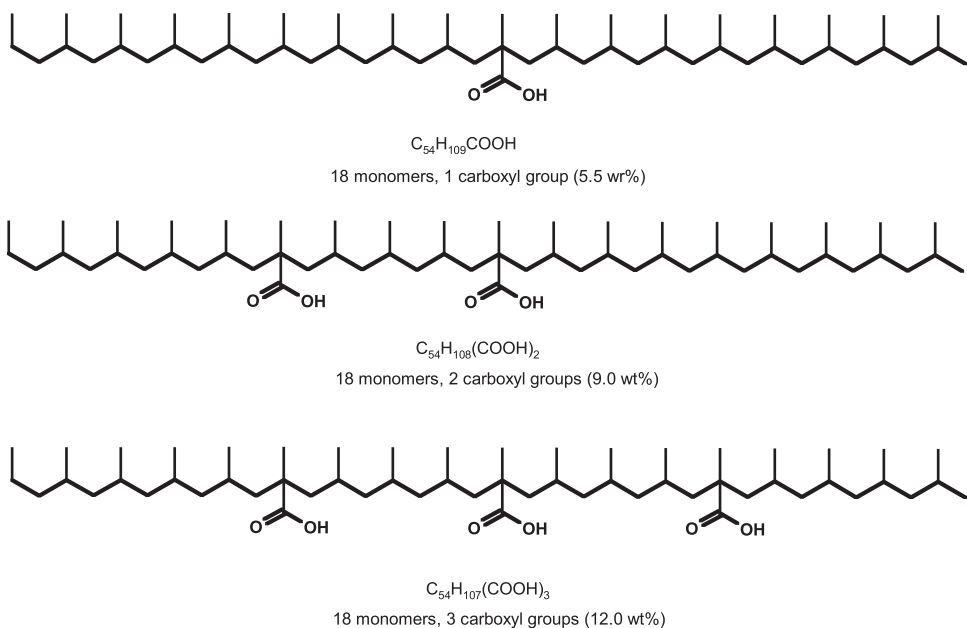


FIG. 3. Carboxyl grafted polypropylene of 18 monomers with 1, 2, and 3 grafted ($-COOH$) groups. Carboxyl mixture ratio for the series of IPP(18)- $COOH$ (1–3) oligomers goes from 5.5 to 12.0 wt.%, respectively.

three-dimensional homogeneous medium, composed of identical, nonpolar and polarizable, molecular chains (oligomers) parallel to each other. Furthermore, in order to simplify the local-field effects, it is assumed that the oligomers are arranged in a lattice with a cubic symmetry. We also assume that the chain–chain interaction has a negligible effect onto the polarization of the medium. Then the Clausius–Mossotti relation²³ gives an approximate relationship between the relative dielectric constant ε_r (permittivity) and the polarizability (α) of the model molecule:

$$\varepsilon_r = \frac{1 + 2K\rho}{1 - K\rho}, \quad (1a)$$

where ρ is the density of the material and the variable K is given by

$$K = \frac{4\pi N_A \alpha'}{3M_W} = \frac{4\pi \alpha'}{3m}, \quad (1b)$$

where N_A is Avogadro's number, M_W is the molar mass of the model molecule, m is the mass of the oligomer, and α' is the polarizability volume defined in terms of the conventional polarizability α as $\alpha' \equiv \alpha/4\pi\varepsilon_0$, where ε_0 is the vacuum permittivity.

2. Bulk DFT based modeling

In order to justify our molecular DFT based calculations on dielectric and electronic properties for acrylic acid grafted polypropylene we present in Sec. III B also calculations on similar properties for acrylic acid grafted polypropylene by using periodic bulk electronic structure methods in the frameworks of the DFT and density functional perturbation theory. These calculations, therefore, should be capable of indicating the crystalline environmental effects, such as chain-to-chain interaction on electronic and dielectric properties not included in our molecular DFT modeling. In particular, the low-frequency dielectric permittivity tensor, $\varepsilon_{\alpha\beta}(\omega)$, in the framework of the DFPT can be calculated by using the following expression derived by Gonze and Lee:²⁸

$$\varepsilon_{\alpha\beta}(\omega) = \varepsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\beta}}{\omega_m^2 - \omega^2}, \quad (2a)$$

where $\varepsilon_{\alpha\beta}^{\infty}$ is the electronic contribution to the dielectric tensor, i.e., the high-frequency dielectric tensor, Ω_0 is the volume of the unperturbed unit cell, ω_m is the m th phonon mode eigenfrequency ω_{mq} at the wave vector $\mathbf{q} = 0$, $S_{m,\alpha\beta}$ is the mode-oscillator strength tensor related to the m th phonon mode with the long-wave (short wave vector) limit $\mathbf{q} \rightarrow 0$, which is given by

$$S_{m,\alpha\beta} = \left(\sum_{\kappa\alpha'} Z_{\kappa,\beta\beta'}^* U_{mq=0}^*(\kappa\alpha') \right) \left(\sum_{\kappa'\beta'} Z_{\kappa',\beta\beta'}^* U_{mq=0}(\kappa'\beta') \right), \quad (2b)$$

where $Z_{\kappa,\beta\alpha}^*$ is the Born effective charge tensor defined in terms of the first-order change in the macroscopic polarization per unit cell ($\partial P_{\text{mac},\beta}$) created along the direction β

under the displacement [$\partial \tau_{\kappa\alpha}(\mathbf{q} = 0)$] of the basis atoms of type κ (belonging to the sublattice κ) along the direction α by the following first-order derivative:

$$Z_{\kappa,\beta\alpha}^* \equiv \Omega_0 \frac{\partial P_{\text{mac},\beta}}{\partial \tau_{\kappa\alpha}(\mathbf{q} = 0)}, \quad (2c)$$

and $U_{mq}(\kappa\alpha)$ are eigendisplacements of a dynamical matrix related generalized eigenvalue problem [see Eq. (12) of Ref. 28].

Starting from the classical electromagnetism equations linking the various macroscopical fields ($D_{\text{mac},\alpha}$ displacement in direction α , $E_{\text{mac},\beta}$ electric field in direction β , and $P_{\text{mac},\alpha}$ polarization in direction α) in connection with the density functional perturbation theory for periodic systems describing the response to a homogeneous and static electric field one can within the long-wave method ($\mathbf{q} \rightarrow 0$) derive the following expression for the electronic contribution to the dielectric permittivity tensor [see Eqs. (36) and (37) of Ref. 28]

$$\varepsilon_{\alpha\beta}^{\infty} = \delta_{\alpha\beta} - \frac{4\pi}{\Omega_0} 2E_{\text{el}}^{E_{\alpha}^* E_{\beta}}, \quad (3a)$$

where $E_{\text{el}}^{E_{\alpha}^* E_{\beta}}$ is the mixed second-order derivative of the total energy with respect to the electric field components E_{α}^* and E_{β} [cf. Eq. (2) of Ref. 28] given by the following stationary expression:

$$\begin{aligned} E_{\text{el}}^{E_{\alpha}^* E_{\beta}} \{u^{(0)}; u^{E_{\alpha}}, u^{E_{\beta}}\} &\equiv \frac{1}{2} \frac{\partial^2 E_{\text{el}}}{\partial E_{\alpha}^* \partial E_{\beta}} \\ &= \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s \left(\left\langle u_{m\mathbf{k}}^{E_{\alpha}} \left| H_{\mathbf{k},\mathbf{k}}^{(0)} - \varepsilon_{m\mathbf{k}}^{(0)} \right| u_{m\mathbf{k}}^{E_{\beta}} \right\rangle \right. \\ &\quad \left. + \left\langle u_{m\mathbf{k}}^{E_{\alpha}} \left| i u_{m\mathbf{k}}^{k_{\beta}} \right\rangle + \left\langle i u_{m\mathbf{k}}^{k_{\alpha}} \left| u_{m\mathbf{k}}^{E_{\beta}} \right\rangle \right) d\mathbf{k} \right. \\ &\quad \left. + \frac{1}{2} \int_{\Omega_0} \frac{dv_{\text{xc}}}{dn} |n^{(0)}(\mathbf{r})| [n^{E_{\alpha}}(\mathbf{r})]^* n^{E_{\beta}}(\mathbf{r}) d\mathbf{r} \right. \\ &\quad \left. + 2\pi\Omega_0 \sum_{\mathbf{G} \neq 0} \frac{[n^{E_{\alpha}}(\mathbf{G})]^* n^{E_{\beta}}(\mathbf{G})}{|\mathbf{G}|^2}, \end{aligned} \quad (3b)$$

where s is the spin degeneracy factor (2 for nonmagnetic materials), $u_{m\mathbf{k}}^{E_{\alpha}}(\mathbf{r})$ is the first-order derivative of the perturbed wave function $u_{m\mathbf{k}}(\mathbf{r})$ with respect to the perturbing electric field along the direction α , $u_{m\mathbf{k}}^{k_{\alpha}}(\mathbf{r})$ is the first-order derivative of the unperturbed wave function $u_{m\mathbf{k}}^{(0)}(\mathbf{r})$ with respect to k_{α} , the component of the electronic wave vector along the α direction. The *periodic* unperturbed wave functions $u_{m\mathbf{k}}^{(0)}(\mathbf{r})$ are defined [cf. Eq. (40) of Ref. 29] in terms of the Bloch functions $\psi_{m\mathbf{k}}^{(0)}(\mathbf{r})$ as

$$u_{m\mathbf{k}}^{(0)}(\mathbf{r}) \equiv (N\Omega_0)^{1/2} e^{-i\mathbf{k}\cdot\mathbf{r}} \psi_{m\mathbf{k}}^{(0)}(\mathbf{r}), \quad (4a)$$

which satisfy the following unperturbed Kohn–Sham eigenequations using the Dirac notation [cf. Eqs. (A8), (A10), and (A11) of Ref. 29 for further details]:

$$H_{\mathbf{k},\mathbf{k}}^{(0)} |u_{m\mathbf{k}}^{(0)}\rangle = \varepsilon_{m\mathbf{k}}^{(0)} |u_{m\mathbf{k}}^{(0)}\rangle, \quad (4b)$$

where the Hamiltonian operator $H_{\mathbf{k},\mathbf{k}}^{(0)}$ can be written as a sum of the kinetic energy, external potential, and Hartree and

exchange-correlation (Hxc) potential terms, respectively, as

$$H_{\mathbf{k},\mathbf{k}}^{(0)} = T_{\mathbf{k},\mathbf{k}}^{(0)} + v_{\text{ext},\mathbf{k},\mathbf{k}}^{(0)} + \left. \frac{\delta E_{\text{Hxc}}}{\delta n} \right|_{n^{(0)}}, \quad (4c)$$

where the last term is the functional derivative of the Hxc functional with respect to density at the unperturbed density $n^{(0)}(\mathbf{r})$. Owing to the definition of the periodic wave function, Eq. (4a), the operators $O_{\mathbf{k},\mathbf{k}}$ in Eq. (4c) are defined in terms of the conventional operators O (related to the standard Bloch function $\psi_{m\mathbf{k}}^{(0)}$ representation) according to the following transformation:

$$O_{\mathbf{k},\mathbf{k}} \equiv e^{-i\mathbf{k}\cdot\mathbf{r}} O e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (5)$$

The lattice-periodic (in the limit $\mathbf{q} \rightarrow 0$) and generally complex quantities $n^{E_\alpha}(\mathbf{r})$ and $n^{E_\beta}(\mathbf{r})$ in Eq. (3b) are related to the first-order derivatives with respect to the electric field components along the α and β directions, respectively, in the perturbation expansion of the perturbed electron density $n(\mathbf{r})$ [cf. Eq. (9) of Ref. 29], and are given by the expression [cf. Eq. (77) of Ref. 29]

$$n^{E_i}(\mathbf{r}) = \frac{2}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s u_{m\mathbf{k}}^{(0)*}(\mathbf{r}) u_{m\mathbf{k}}^{E_i}(\mathbf{r}) d\mathbf{k}, \quad (6)$$

where $i = \{\alpha, \beta\}$, and the band index m and the electron wave vector $\mathbf{k}$ run over the occupied band states only [in the case of insulators $\mathbf{k}$ runs over the whole Brillouin zone (BZ)]. In the Hartree-energy related mixed derivative term [the last term of Eq. (3b)] $n^{E_i}(\mathbf{G})$ [$i = \{\alpha, \beta\}$] is a Fourier component (coefficient) of $n^{E_i}(\mathbf{r})$ at the reciprocal lattice vector $\mathbf{G}$.

Finally, we notice that the electronic contribution to the permittivity could be calculated via a more *conventional* scheme at two stages (cf. Ref. 30). First, the imaginary part (absorption part) of the complex dielectric function of the photon frequency, $\varepsilon_i(\omega)$, is computed using a first-order time-dependent perturbation theory in connection with a 3D bulk DFT method for periodic systems. Second, the real part of the dielectric function, $\varepsilon_r(\omega)$, and therefore the permittivity (in the $\omega \rightarrow 0$ limit) will result when the Kramers–Kronig transformation is applied to the imaginary part of the dielectric function. However, there are a couple of disadvantageous features in this computational scheme. First of all, both occupied (valence) and unoccupied (conduction) band Kohn–Sham states are required in this scheme, while in the DFPT scheme described above only the occupied valence electron states are needed. The second hindering fact in this scheme is that a huge number of $\mathbf{k}$ points (for example, a $15 \times 15 \times 15$ Monkhorst–Pack set of $\mathbf{k}$ points for the dielectric function of GaAs semiconductor with the zincblende crystal structure) is typically required to achieve a well-converged dielectric function for a wide enough range of photon frequencies.

B. Methods

Related to the molecular-modeling based approach in our dielectric studies, we first briefly discuss first-principles computational methods that could be exploited in calculating polarizabilities of the relevant polymer molecules (oligomers),

which are furthermore used to calculate the macroscopic dielectric constant, according to Eq. (1). In our previous paper,²⁷ the reliability and characteristics of different computational methods in predicting dielectric properties of polypropylene using the GAUSSIAN 03 program³¹ were studied. Density functional theory methods were found to offer reliable polarizabilities for saturated polymers with feasible computational time, if a good enough basis set is employed. Further, the HOMO–LUMO energy gap was shown to be less sensitive to the quality of the chosen basis set than the polarizability.

The DFT methods are known to have a general tendency to underestimate the HOMO–LUMO gap for molecules and band gap for solids.^{32–34} However, in our present study we are interested in calculating the changes in electronic (e.g., the band gap) and dielectric (e.g., polarizability) properties of polypropylene under acrylic acid doping. For this purpose, the DFT calculations within the framework of the generalized gradient approximation (GGA), should sufficiently accurately describe these changes and their trends with the doping (grafting) concentration.

For small saturated hydrocarbon molecules such as methane and propane, the best agreement with the experimental polarizabilities is obtained using a hybrid DFT method with Becke’s three-parameter functional^{35,36} combined with Lee *et al.*³⁷ correlation functional, and a meta-generalized gradient approximation (meta-GGA) (functional of Tao, Perdew, Staroverov, and Scuseria (TPSS)) together with a computationally demanding Sadlej’s polarized electric property basis set (Sadlej pVTZ).³⁸ However, this basis set requires too much computational power to be applied for larger oligomers.

A DFT method in the framework of the GGA with Perdew–Wang exchange and correlation functional (PW91) (Ref. 39) together with the split-valence basis set 6–311++G** (Ref. 40) is computationally efficient and proves to give sufficiently accurate polarizabilities for large oligomers of polypropylene. In addition, the optimized geometry of the molecules turns out to be insensitive to the chosen basis set. Consequently, optimization of geometries at the PW91/6–31G** level of the theory, and calculation of polarizabilities then at a more demanding level of GGA-PW91/6–311++G**, proves to be a reliable and computationally efficient way for calculations of large molecules.²⁷

On the basis of the results from the abovementioned study, we have used the same methodology in the present study. The geometries of the oligomers are optimized within the GGA-PW91/6–31G** framework, while single-point total energies to obtain HOMO–LUMO gaps as well as polarizabilities, are computed with the GGA-PW91/6–311++G** scheme. Both the GAUSSIAN 03 (Ref. 31) and TURBOMOLE (Refs. 41 and 42) state-of-the-art *ab initio* program packages have been employed for the molecular DFT calculations in this paper.⁴³

Finally, we briefly comment on the more realistic computational method we use for the three-dimensional bulk periodic system to calculate electronic and dielectric properties of acrylic acid grafted polypropylene. Namely, these calculations are carried out using the first-principles state-of-the-art plane-wave pseudopotential (PWPP) electronic

structure method in the framework of the density functional perturbation theory. We employed the CASTEP (Cambridge Sequential Total Energy Package)^{44–46} computational DFPT scheme in connection with the norm-conserving pseudopotential (NCPP) method⁴⁷ and the GGA with the PW91 exchange and correlation functional.^{48,49} The construction of these pseudopotentials is based on the following atomic valence electronic configurations: H ($1s^1$), C ($2s^2 2p^2$), and O ($2s^2 2p^4$). We found that all CASTEP DFPT calculations carried out were sufficiently converged when using the Monkhorst–Pack $3 \times 3 \times 1$ scheme of $\mathbf{k}$ points and plane wave cutoff energy of 470 eV.

Our DFPT calculations do not incorporate properly the long-range Van der Waals interactions which are known to be important in the geometry optimization of polymers. We are aware that the GGA-PW91 (Perdew–Wang ‘91) exchange and correlation functional that we use in our molecular and bulk DFT calculations, possesses a rather local character and therefore is not capable of treating accurately enough the nonlocal electron correlations required to describe Van der Waals dispersion forces at large distances between the polymer chains. However, in computing the dielectric permittivity for acrylic acid grafted polypropylene (or possibly for any polymer) in the framework of the DFT, it is obvious that the largest contribution to permittivity derives from the electronic polarization along each polymer chain. Furthermore, polarization is mostly governed by the “usual” Coulombic interactions in the effective potential of the Kohn–Sham Hamiltonian: electron–ion and electron–electron Hartree (direct) interactions and many-body quantum mechanics related exchange and correlation potential for which the semilocal GGA-PW91 xc functional seems to work fine. But, of course, it is also obvious that the long-range Van der Waals interaction (cf. long-range electron correlation) would slightly modify the effective potential and consequently the Kohn–Sham orbitals building up the dielectric response function (in our case, the permittivity).^{50–52}

III. RESULTS AND DISCUSSION

A. Molecular DFT based calculations

In our previous study,²⁷ the calculated isotropic polarizabilities of saturated polymers proved to depend linearly on the chain length. We also calculated the relative dielectric constant $\epsilon_r(0)$, i.e., the static permittivity, using the Clausius–Mossotti relation, Eq. (1), for an isotactic polypropylene with a cubic crystal structure. We noticed that the $\epsilon_r(0)$ value first increases slightly with the increasing chain length for small molecules and then becomes saturated when increasing the length of the molecule up to 18 monomers.²⁷ In the case of a grafted polymer, it is not straightforward to use the Clausius–Mossotti relation since the experimentally obtained density of the polymer is needed for this equation. When molecular grafting takes place, the addition of acrylic acid can increase the volume proportional to the molecular size, but the doped molecules may also fit as a complex interstitial defect into the existing polymer structure without a volumetric increase, or the volume can even decrease. Therefore, from the Clausius–Mossotti relation viewpoint [cf. Eq. (1)], the most relevant

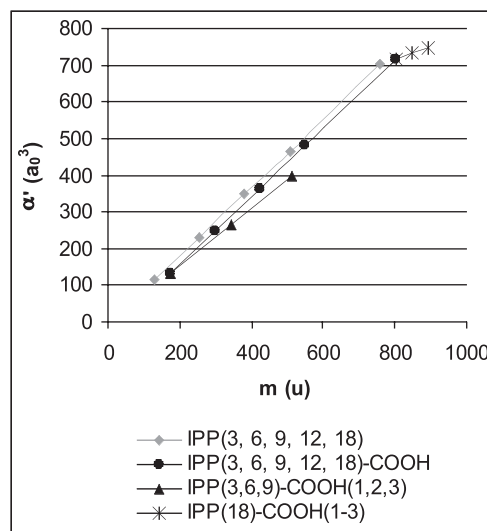


FIG. 4. Polarizability volumes α' as a function of the mass of the molecule for pure IPP chains of 3, 6, 9, 12, and 18 monomers, IPP chains of 3, 6, 9, 12, and 18 monomers grafted with one $-\text{COOH}$ group, IPP chains of 3, 6, and 9 monomers grafted with 1, 2, and 3 $-\text{COOH}$ groups, respectively, and IPP chains of 18 monomers grafted with 1, 2, and 3 $-\text{COOH}$ groups.

quantity of interest in our study, will be the polarizability volume per mass of the molecule (α'/m). We compute this quantity quantum mechanically from first principles.

In Fig. 4 the isotropic polarizability volume α' as a function of the mass of the molecule is presented, for various cases of acrylic acid grafting²⁶ of isotactic polypropylene. As already shown in our previous study,²⁷ the polarizability volume increases linearly with the increasing chain length of the pure IPP. The graph for the IPP molecules grafted with one $-\text{COOH}$ group [series IPP (3, 6, 9, 12, 18)– COOH] is located slightly below the graph for pure IPP molecules, but has essentially the same slope as the pure IPP. Therefore, when viewed as a function of the molecular mass, the polarizability of the carboxyl doped IPP molecule is smaller than that of the IPP molecule. However, the polarizability of any carboxyl grafted IPP molecule is larger than that of the corresponding pure IPP molecule.

The slope of the graph in Fig. 4, in the case of IPP molecules with a constant mixture ratio of $-\text{COOH}$ [series IPP (3,6,9)– COOH (1,2,3)], is clearly smaller than that for pure IPP molecules. The slope of the graph when increasing the mixture ratio for a fixed chain length [series IPP (18)– COOH (1–3)] becomes even smaller. This means that adding $-\text{COOH}$ groups to the IPP chain decreases its polarizability per mass unit.

In Fig. 5 the polarizability volumes per mass of the molecule α'/m are presented as a function of the mass of the molecule for polypropylene and grafted polypropylenes.

It can be seen from Fig. 5 that the ratio α'/m increases only slightly with the increasing chain length both for pure IPP, and for a constant mixture ratio of carboxyl [series IPP (3, 6, 9)– COOH (1, 2, 3)]. The similar trend of a slight increase of permittivity toward saturation with the increasing chain length was observed also in our previous study of pure IPP.²⁷ Thus, the best estimate of α'/m is obtained with the largest model

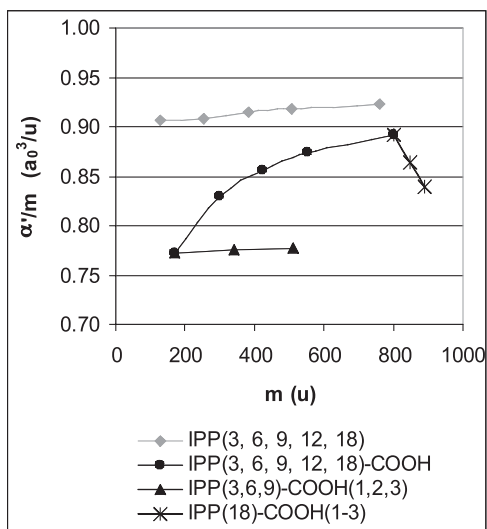


FIG. 5. Polarizability volumes per mass α'/m as a function of mass of the molecule for pure IPP chains of 3, 6, 9, 12 and 18 monomers, IPP chains of 3, 6, 9, 12, and 18 monomers grafted with one -COOH group, IPP chains of 3, 6, and 9 monomers with 1, 2, and 3 -COOH groups, respectively, and IPP chains of 18 monomers with 1, 2, and 3 -COOH groups.

molecule. For the same reason, α'/m is slightly larger for IPP (18)- COOH (2) and IPP (18)- COOH (3) oligomers than for smaller molecules IPP (9)- COOH and IPP (6)- COOH with the same mixture ratio.

Figure 5 also shows the α'/m ratio for IPP molecules with only one grafted acrylic acid with the increasing IPP chain length [series IPP (3, 6, 9, 12, 18)- COOH] for which the mixture ratio of carboxyl goes from 25.6 to 5.5 wt.%, respectively. Due to the local electronic interaction between the carboxyl group and the IPP chain, the α'/m ratio increases first rapidly, then quickly becoming saturated toward the pure IPP value while the mixture ratio goes to zero. Owing to the local interaction between the carboxyl group and the IPP chain and the fact that the polarizability per unit mass is essentially smaller for the formic acid molecule HCOOH (around $0.49a_0^3/\text{u}$) than it is for IPP oligomers (around $0.91a_0^3/\text{u}$), the α'/m values for the carboxyl grafted IPP molecules become smaller than in the case of pure IPP molecules. Also, due to this local interaction it can be understood why the α'/m ratio decreases linearly with the increasing amount of the carboxyl groups grafted to the same IPP molecule [series IPP (18)- COOH (1-3)]. In overall, all the IPP molecules grafted with carboxyl groups have larger polarizability α' , but a smaller α'/m ratio than the corresponding pure IPP molecules.

This trend of the ratio α'/m decreasing with the increasing mixture ratio can be seen more clearly in Fig. 6, where the ratio α'/m is shown as a function of the mass ratio of carboxyl and the whole grafted polypropylene $[m(\text{COOH})/m]$. These findings indicate that although the absolute value of the polarizability volume for any IPP molecule increases when grafting groups are added, the increase in polarizability, due to the local electronic interaction between the carboxyl group and the IPP chain, occurs *linearly* with respect to the number of grafting groups added to the IPP molecule. In other words, the increase in polarizability of the IPP chain, when grafted

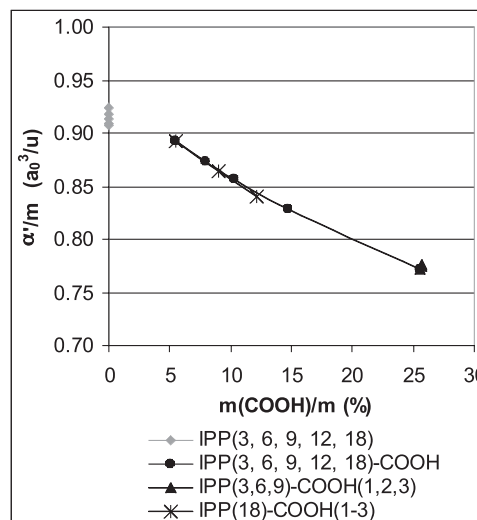


FIG. 6. Polarizability volumes per mass α'/m as a function of the mass ratio of carboxyl and the whole grafted molecule $[m(\text{COOH})/m]$; see Ref. 53] for pure IPP chains of 3, 6, 9, 12, and 18 monomers, IPP chains of 3, 6, 9, 12, and 18 monomers grafted with one -COOH group, IPP chains of 3, 6, and 9 monomers with 1, 2, and 3 -COOH groups, respectively, and IPP chains of 18 monomers with 1, 2, and 3 -COOH groups.

with carboxyl, can be considered solely to be a “mass effect,” because the polarizability of the IPP molecule increases linearly with the mass of carboxyl added to it. However, it is expectable that this linear behavior breaks down when the mixture ratio increases to the limit where the carboxyl grafting groups start to interact with each other.

We now turn the discussion on our first-principles molecular DFT calculations of the electronic HOMO–LUMO gap for the pure and acrylic acid grafted IPP. In Fig. 7 the HOMO–LUMO gap values for the pure and carboxyl grafted IPP oligomers are presented as a function of their mass as well as the mixture ratio. It can be seen that large IPP molecules

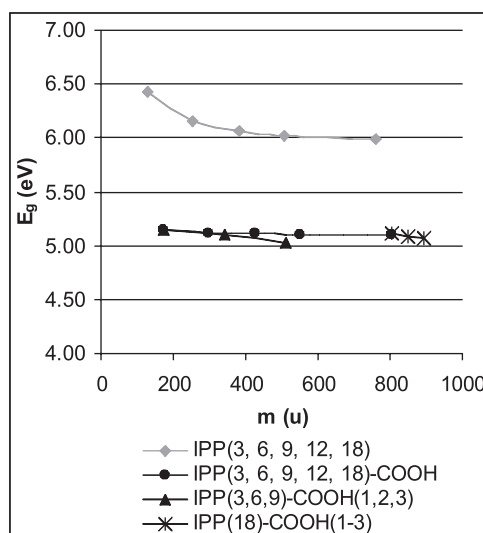


FIG. 7. Calculated HOMO–LUMO energy gaps as a function of mass of the molecule for pure IPP chains of 3, 6, 9, 12, and 18 monomers, IPP chains of 3, 6, 9, 12, and 18 monomers grafted with one -COOH group, IPP chains of 3, 6, and 9 monomers with 1, 2, and 3 -COOH groups, respectively, and IPP chains of 18 monomers with 1, 2, and 3 -COOH groups.

TABLE I. Calculated HOMO–LUMO gap (E_g), isotropic polarizability volume (α'), carboxyl composition (wt.% of COOH), and static permittivity [$\epsilon_r(0)$] from the Clausius–Mossotti relation, Eq. (1), for pure IPP and IPP grafted with COOH groups. Also shown is the change in α' between the grafted IPP oligomers and the corresponding pure IPP oligomers ($\Delta\alpha'$). The model molecules with 3, 6, and 9 IPP monomers, i.e., C_9H_{20} , $C_{18}H_{38}$, $C_{27}H_{56}$, respectively, have been used to represent the infinite IPP chain. In the pure polypropylene cases, density $\rho_{IPP} = 900 \text{ kg/m}^3$ has been used, while in the carboxyl grafted polypropylene cases the density has been evaluated assuming the volume unchanged from the polypropylene material, i.e., $\rho_{\text{grafted}} = (m_{\text{grafted}}/m_{IPP}) \rho_{IPP}$, where m_{IPP} and m_{grafted} are the molecular masses of the IPP and its grafted molecule, respectively.

Molecule	$E_g(\text{eV})$	$\alpha'(a_0^3)$	$\Delta\alpha'(a_0^3)$	$M_W(\text{g/mol})$	wt.% of COOH	$\epsilon_r(0)$
C_9H_{20}	6.43	116		128	0	2.32
$C_{18}H_{38}$	6.16	231		254	0	2.32
$C_{27}H_{56}$	6.06	348		381	0	2.33
$C_{36}H_{74}$	6.02	465		507	0	2.34
$C_{54}H_{110}$	5.99	701		759	0	2.35
$C_9H_{19}COOH$	5.15	133	17	172	26	2.61
$C_{18}H_{36}(COOH)_2$	5.10	265	34	343	26	2.62
$C_{27}H_{53}(COOH)_3$	5.03	398	50	513	26	2.63
$C_{18}H_{37}COOH$	5.11	247	16	298	15	2.46
$C_{27}H_{55}COOH$	5.11	364	16	425	11	2.42
$C_{36}H_{73}COOH$	5.11	481	16	551	8.2	2.41
$C_{54}H_{109}COOH$	5.11	717	16	803	5.6	2.40

have a smaller gap than the smaller ones, in accordance with our earlier results.²⁷ It can be clearly seen that grafting the polypropylene with acrylic acid decreases the HOMO–LUMO gap from the value more than 6 eV down to some 5 eV. Interestingly, we also observe that the carboxyl grafted IPP chain possesses a nearly constant gap value (around 5.1 eV), regardless of the length of the underlying IPP molecule and the mixture ratio of carboxyl. This indicates that the electronic interactions between the carboxyl groups and the polymer backbone are indeed very local, and that there is hardly any interaction between these groups. This is further substantiated by our three-dimensional bulk periodic DFT calculations on acrylic acid grafted polypropylene (see Sec. III B). Therefore, this HOMO–LUMO gap behavior of the carboxyl grafted IPP molecules seems to be in a good agreement with their linearlike polarizability behavior discussed above.

It is important to notice that the behavior of the HOMO–LUMO gap (or the band gap in the bulk case), when polypropylene is grafted, in general, depends strongly on the type of the grafting agent and its concentration along the chain. There is a clear experimental evidence of this, for example, in Ref. 19, where the optical band gap (E_g) of the grafted polypropylene varies in the range of 2–5 eV, depending on the grafting conditions [N-vinyl-pyrrolidone (NVP) grafting, its modified grafting, or irradiated modified grafting]. In parallel with these experimental findings, our calculations show that, when an IPP chain of six monomers is grafted with two NO_2 -groups, the HOMO–LUMO gap experiences a fairly large reduction to 3.59 eV from the value of 6.16 eV of the pure IPP chain of six monomers, while for a similar molecule with $-COOH$ groups the band gap value is 5.10 eV. On the other hand, for an IPP chain of six monomers and two SO_3 -groups, the HOMO–LUMO gap is reduced even less than in the case of $-COOH$ grafting, namely, to 5.58 eV.

Finally, we discuss the permittivity and dielectric strength properties of polypropylene when grafted with

acrylic acid from our molecular modeling calculations viewpoint, and compare and contrast them to our preliminary experimental findings.

First of all, our computational results on static permittivity [$\epsilon_r(0)$], which are based on the combined scheme of the *ab initio* molecular DFT theory of polarizability and the classical Clausius–Mossotti relation [Eq. (1)], are shown in Table I. In our calculations, we have assumed that grafting polypropylene with carboxyl groups keeps structural parameters, in particular the polymer chain-to-chain distance, and therefore the volume of the crystal, unchanged. This assumption is tentatively supported by our ongoing calculations in the framework of the three-dimensional (bulk) DFT methodology for periodic systems (see Sec. III B). From Table I, it can be seen that the computed values of the permittivity depend essentially on the carboxyl composition (wt.% of COOH) along the polypropylene chain, but not on the length of the underlying polypropylene chain molecule, owing to the local carboxyl group interaction with the polypropylene chain mentioned above in the connection with the discussion related to Figs. 5 and 6. Furthermore, when plotting the permittivity as a function of the carboxyl composition in Fig. 8, it can be seen that for lower compositions of carboxyl the permittivity first increases slowly and then for higher compositions more rapidly. However, it is possible that the permittivity values at high carboxyl compositions are overestimated, and consequently the growth of the permittivity curve should slow down, due to the increased distance between the polymer chains at higher carboxyl compositions (see Sec. III B).

In order to further demonstrate the local interaction between the carboxyl group and the polypropylene chain, we have also shown in Fig. 8 a hypothetical permittivity curve calculated from Eq. (1) for an infinite polypropylene chain ($m_{IPP} \rightarrow \infty$) grafted with carboxyl groups, assuming that each added carboxyl group contributes a *constant* value to the polarizability volume α' (it can be seen from Table I that

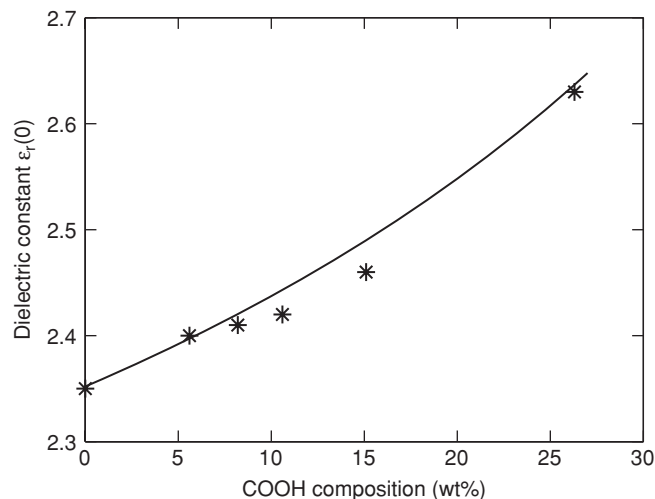


FIG. 8. Static permittivity values [$\epsilon_r(0)$] for various carboxyl compositions (m_{COOH}/m) taken from Table I (stars), along with the hypothetical [$\epsilon_r(0)$] curve (solid line) calculated for an infinite IPP chain grafted with COOH groups from Eq. (7), each added group contributing $\Delta\alpha'_{\text{COOH}} = 16 \text{ a}_0^3$ to the polarizability volume α' , and the $(\alpha'_{\text{IPP}}/m_{\text{IPP}})_{\infty}$ ratio has been estimated using the longest model molecule for isotactic polypropylene in our study, i.e., the 18-monomer oligomer $\text{C}_{54}\text{H}_{110}$.

the values of $\Delta\alpha'$ support well this assumption). In this case, the asymptotic value of $K\rho$ in Eq. (1) can easily be shown to read as

$$K\rho|_{m_{\text{IPP}} \rightarrow \infty} = \frac{4\pi}{3} \left(\frac{\alpha'_{\text{IPP}}}{m_{\text{IPP}}} \right)_{\infty} \rho_{\text{IPP}} + \frac{4\pi x}{3} \frac{\Delta\alpha'_{\text{COOH}}}{m_{\text{COOH}} - xm_{\text{COO}}} \rho_{\text{IPP}}, \quad (7)$$

where $(\alpha'_{\text{IPP}}/m_{\text{IPP}})_{\infty}$ is the polarizability volume to mass ratio of an infinitely long polypropylene chain molecule, $\rho_{\text{IPP}} = 900 \text{ kg/m}^3$ is the mass density of polypropylene, x is the carboxyl composition (wt.%), $\Delta\alpha'_{\text{COOH}} = 16 \text{ a}_0^3$ (estimated from the $\Delta\alpha'$ values of Table I), and m_{COOH} and m_{COO} are the molecular masses of COOH and COO species, respectively. We can see from Fig. 8 that the permittivity curve underlying the abovementioned assumptions, follows rather closely the computed permittivity values for finite model molecules from Table I. This good agreement between the two computational approaches further confirms the local interaction behavior between the carboxyl groups and the polypropylene chain. Finally, our bulk three-dimensional DFT and DFPT calculations discussed in Sec. III B indicate that the locality effect discussed above prevails not only along the acrylic acid grafted IPP chain but also in between different chains. In other words, there is essentially no interaction between the carboxyl groups –COOH belonging to different IPP chains.

Second, concerning the experiments on polypropylene and acrylic acid grafted polypropylene, we notice that Pelto *et al.*⁵⁴ have recently studied the behavior of permittivity and dielectric strength in these materials. Their preliminary experiments show that the static permittivity value increases, from 2.40 to 2.54, i.e., by nearly 6%, when pure polypropylene film is alloyed with only 1 wt.% of acrylic acid. This behavior is in a qualitative agreement with our computed permittivity values from Table I (see Fig. 8).

Finally, concerning the dielectric strength property from theory, our molecular DFT calculations as well as periodic bulk DFT calculations (see Sec. (III B)) show that under the acrylic acid grafting the HOMO–LUMO gap of polypropylene oligomers (see Fig. 7) as well as the electronic band gap of bulk polypropylene decrease, which seems to indicate that the dielectric strength could also decrease.

However, in addition to the electronic energy gap, there may be even more dominant factors not included in our calculations, e.g., trap states which contribute to the behavior of the dielectric strength when polypropylene is grafted with acrylic acid. Furthermore, our DFT molecular modeling and DFT and DFPT bulk calculations have been targeted for a periodic crystal, and therefore special structural features reflecting more realistic materials such as polycrystalline and amorphous phases are not considered in our calculations. In fact, the experiments⁵⁴ show that the dielectric strength will improve when polypropylene is grafted with acrylic acid. However, we are not going to discuss these rather subtle details here as it would go beyond the scope of the present studies.

B. Three-dimensional bulk periodic DFT and DFPT calculations

In order to study the validity and accuracy of our molecular DFT based calculations on dielectric (polarizability and permittivity) and electronic (HOMO–LUMO gap) properties for acrylic acid grafted polypropylene we have also carried out calculations on corresponding bulk-related properties (polarizability per unit cell, permittivity, and band gap). For this we use more realistic three-dimensional (bulk) periodic first-principles methods in the frameworks of the density functional theory and density functional perturbation theory (see Secs. II A 2 and II B). Furthermore, to demonstrate possible differences occurring in these electronic and dielectric properties between the bulk DFT or DFPT calculations and the DFT molecular modeling, we have used the simplest and computationally most efficient testing platform for this, namely the simple tetragonal crystal structure.⁵⁵

In Fig. 9 we show the polarizability volume per mass (α'/m) as a function of the mass m for a 6-monomer polypropylene oligomer grafted with various numbers of –COOH groups, computed with the molecular DFT method. The figure also shows the corresponding α'/m versus m function for acrylic acid grafted polypropylene with a tetragonal crystal structure, computed with the DFPT method, in which case the α' and m quantities are defined *per unit cell*. Interestingly, from Fig. 9 it can be clearly seen that the α'/m quantity as a function of m behaves very similarly between the molecular DFT calculation (in this case m is the mass of the grafted oligomer) and the bulk DFPT calculation (in this case m is the mass per computational unit cell). In particular, the α'/m ratio as a function of m decreases in both of these cases, confirming the *local* carboxyl group-to-IPP chain interaction assertion we discussed in Sec. III A in connection with our molecular DFT based calculations. However, owing obviously to the slight chain-to-chain interaction, the α'/m ratio

TABLE II. Calculated HOMO–LUMO energy gaps ($E_g^{\text{HOMO-LUMO}}$) using the DFT molecular modeling, and band-gap energies (E_g^{bulk}) as well as the electronic total energies per computational unit cell ($E_{\text{tot}}^{\text{bulk}}$) using the three-dimensionally periodic bulk DFT method, for acrylic acid grafted polypropylene. In the molecular DFT modeling n represents the number of –COOH groups grafted onto the isolated 6-monomer IPP oligomer ($\text{C}_{18}\text{H}_{38}$). In the case of the bulk DFT calculations n represents the number of –COOH groups grafted onto the single 6-monomer IPP oligomer ($\text{C}_{18}\text{H}_{38}$) contained in the tetragonal unit cell defined by the lattice parameters a and c (a is set manually, and the length of the c crystallographic axis along which the grafted 6-monomer oligomer is oriented, i.e., the lattice parameter c is determined through the molecular geometrical optimization of the oligomer). The numbers in the parentheses refer to the cases where the terminal hydrogens (one at each end) of the 6-monomer oligomer $\text{C}_{18}\text{H}_{38}$ oriented along the c axis have been removed. The bold faced numbers denote the approximate minimum total energies at particular polymer chain-to-chain distances.

n	Cell [$a, b = a, c$](Å)	$E_g^{\text{HOMO-LUMO}}$ (eV)	E_g^{bulk} (eV)	E_{tot} (eV)
0	[9, 9, 15.55 (13.05)]	6.27	5.43 (5.18)	– 3415.67 (–3383.07)
	[8, 8, 15.55 (13.05)]		5.33 (5.16)	– 3415.70 (–3383.10)
	[7.5, 7.5, (13.05)]		5.31 (5.20)	– 3415.73 (– 3383.17)
	[7, 7, 15.55 (13.05)]		5.34 (5.35)	– 3415.74 (–3383.14)
	[6.5, 6.5, 15.55]		5.39 (5.56)	– 3415.53 (–3382.94)
1	[9, 9, 14.51 (12.16)]	5.13	4.76 (2.90)	– 4430.91 (–4390.53)
	[8.5, 8.5, (12.16)]		4.73 (2.88)	– 4430.85 (– 4390.61)
	[8, 8, 14.51 (12.16)]		4.71 (2.88)	– 4430.94 (–4390.57)
	[7.5, 7.5, (12.16)]		4.78 (2.95)	– 4430.91 (–4390.50)
	[7, 7, 14.51 (12.16)]		4.92 (3.07)	– 4430.57 (–4390.16)
2	[9, 9, 16.38 (13.36)]	5.13	4.68 (2.86)	– 5446.28 (–5404.75)
	[8.5, 8.5, (13.36)]		4.66 (2.85)	– 5446.26 (–5404.85)
	[8, 8, 16.38 (13.36)]		4.65 (2.88)	– 5446.35 (– 5404.88)
	[7.5, 7.5, 16.38 (13.36)]		4.65 (2.97)	– 5446.38 (–5404.79)
	[7, 7, 16.38 (13.36)]		4.69 (3.03)	– 5446.32 (–5404.42)
3	[9.5, 9.5, 16.29]	4.90	4.70	– 6461.45
	[9, 9, 16.29]		4.65	– 6461.47
	[8.5, 8.5, 16.29]		4.62	– 6461.55
	[8, 8, 16.29]		4.59	– 6461.54
	[7.5, 7.5, 16.29]		4.55	– 6461.48

in the bulk DFT calculation seems to decrease a bit faster as a function of m than it happens in the molecular DFT calculation for an isolated grafted IPP oligomer. Furthermore, due to the band-gap energies given by the bulk DFT method, which are systematically smaller than the corresponding HOMO–LUMO gap values (see the discussion below), the α'/m values from the DFT calculation in Fig. 9 become larger than those from the corresponding molecular DFT calculation.

We next compare and contrast the calculated HOMO–LUMO energy gaps based on the molecular DFT modeling with the electronic band gaps calculated using the periodic bulk DFT method. In Table II we present these results as well as the electronic total energy computed per unit cell, for polypropylene (the case $n = 0$) and acrylic acid grafted polypropylene (the cases $n = 1, 2$, and 3). From Table II it can be seen that the electronic energy-gap behavior between the bulk DFT calculation (band gap) and molecular DFT calculation (HOMO–LUMO gap) is very similar in many ways. First of all, the energy gap decreases substantially when a carboxyl group (the case $n = 1$) is grafted onto the IPP oligomer (the molecular DFT calculation) or onto the IPP chain within the tetragonal unit cell (the bulk DFT calculation). As we already mentioned in Sec. III A, in the connection with molecular DFT modeling, grafting more carboxyl groups onto the IPP oligomer (the cases $n = 2$ and 3) would cause hardly any change to the HOMO–LUMO gap energy.

The same clearly happens in the case of the bulk DFT calculations (cf. E_g^{bulk} values in Table II) where the unit cell contains a 6-monomer carboxyl grafted IPP oligomer with or without (the numbers in parentheses) the terminal hydrogen at

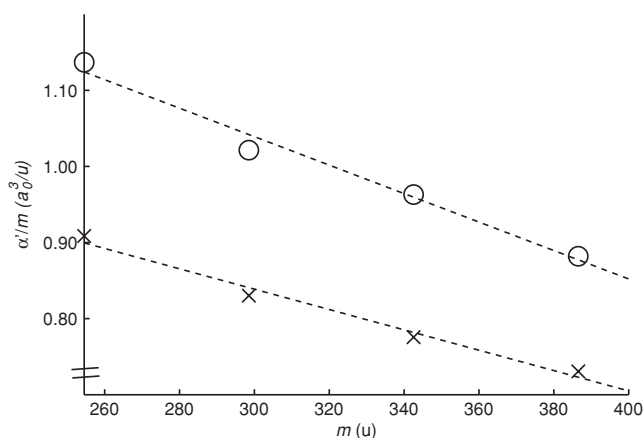


FIG. 9. Polarizability volumes per mass (α'/m) for an isolated 6-monomer IPP oligomer ($\text{C}_{18}\text{H}_{38}$) grafted with n –COOH groups ($n = 0, 1, 2$, and 3) as a function of the grafted oligomer mass m , using the molecular DFT method (marked with crosses). Also shown is α'/m as a function of m for acrylic acid grafted polypropylene with a tetragonal crystal structure, using the DFPT method (marked with circles). In this case, the α'/m and m quantities are defined per unit cell which contains one oligomer, similar to those used in the molecular DFT calculations. The dashed lines indicate the least-squares fitting applied to the computed data.

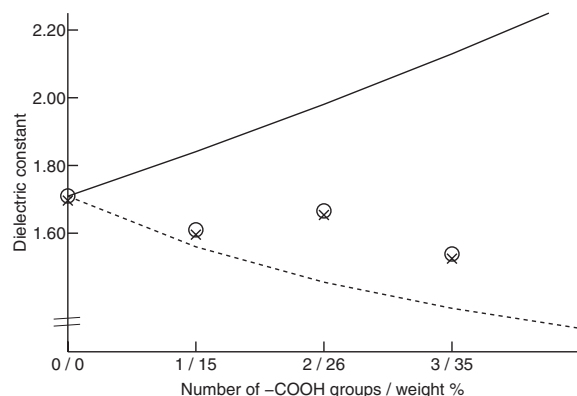


FIG. 10. High-frequency dielectric constant (ϵ_∞) for acrylic acid grafted polypropylene with a tetragonal crystal structure as a function of the number of the carboxyl groups ($-\text{COOH}$) grafted onto the 6-monomer long IPP oligomer ($\text{C}_{18}\text{H}_{38}$, along the c axis of the unit cell) with a 3/1 helical conformation in each unit cell, according to the periodic bulk DFPT calculation (CASTEP) [marked with circles]. Also shown is the static dielectric constant [$\epsilon_r(0)$] computed using the molecular DFT modeling (TURBOMOLE) in connection with the Clausius–Mossotti relation for the same mass densities as the DFPT calculations have been carried out, i.e., for the minimum total-energy metastable states from Table II (marked with crosses). The solid and dashed lines, which are fitted to the data points at $n = 0, 1, 2$, and 3 number of $-\text{COOH}$ groups, are the permittivities calculated from the Clausius–Mossotti relation in two different hypothetical cases. In the first case (solid line) it is assumed that the structural density (cf. the chain-to-chain distance) is constant under the grafting, while in the second case (dashed line) the mass density is assumed to stay constant under the grafting.

each end of the oligomer.⁵⁶ Second, we notice from Table II that the band-gap energies (E_g^{bulk}) and electronic total energies (E_{tot}) for polypropylene (the $n = 0$ case) and acrylic acid grafted polypropylene (the cases $n = 1, 2$, and 3) depend only weakly on the polymer chain-to-chain distance. From these two points it follows that the electronic interactions between the carboxyl groups along a given polymer chain are quite weak and the same is true for interactions between the carboxyl groups belonging to different chains. This further confirms our assertion we stated in Sec. III A in connection with the molecular DFT modeling that the carboxyl group-to-IPP chain interaction is truly local.

Finally, we briefly discuss in the following the calculation of the dielectric constants for polypropylene and acrylic acid grafted polypropylene using the molecular DFT modeling for the static permittivity $\epsilon_r(0)$ [see Eq. (1)] and the three-dimensional bulk DFPT method for the high-frequency dielectric constant ϵ_∞ [see Eq. (3)].

Figure 10 shows the high-frequency dielectric constant (ϵ_∞) computed with the bulk DFPT method along with the static dielectric constant [$\epsilon_r(0)$] computed using the molecular DFT modeling in connection with the Clausius–Mossotti relation. These quantities are calculated at the equilibrium values of the lattice constant a (a and b lattice constants are identical for the tetragonal unit cell) which correspond to the minimum total energy geometry for several compositions of acrylic acid grafted polypropylene according to Table II.⁵⁷ We consider the case where the computational unit cell contains one 6-monomer long grafted oligomer ($\text{C}_{18}\text{H}_{38}$ grafted with $-\text{COOH}$ groups) oriented along the

c axis of the unit cell with the terminal hydrogen atom at each end of the oligomer. Interestingly, in this case the permittivity values for polypropylene and carboxyl grafted polypropylene computed with the molecular DFT modeling in connection with the simple Clausius–Mossotti relation are in excellent agreement with those computed using a more rigorous DFPT method for three-dimensionally periodic systems. It is obvious that this situation can be achieved only through two conditions. Namely that (1) the polymer chain-to-chain interaction must be weak enough and (2) for a given chain the interaction between the oligomers belonging to neighboring unit cells should also be weak. In other words, the orbital overlap within the Bloch electron wave function between neighboring unit cells along a given chain should be small. We have already verified earlier in connection with the discussion about the band-gap (E_g^{bulk}) and electronic total energy (E_{tot}) behavior (see Table II) that the condition (1) is satisfied. Furthermore, using the three-dimensionally periodic DFT method (see Sec. II B) we have calculated the electronic band structure (not shown here) for polypropylene and acrylic acid grafted polypropylene (cf. the cases $n = 0, 1, 2$, and 3 in Table II). These results clearly show that especially the occupied bands $E_{j(\text{occ})}(\mathbf{k})$ are highly dispersive in several high-symmetry directions inside the Brillouin zone, including the Γ – Z direction which corresponds the c -axis direction of the tetragonal unit cell along which the oligomer is oriented. The flatness of the occupied (valence) bands for the isolated (3/1) helical IPP chain and for the IPP material with the monoclinic α crystal structure can also be seen from Figs. 2 and 3, respectively, of the recent DFT studies by Stournara and Ramprasad.⁹ This shows that the condition (2) is also satisfied.

Finally, Fig. 11 shows the behavior of the high-frequency dielectric constant (ϵ_∞) and the static dielectric constant [$\epsilon_r(0)$] as a function of the lattice constant a , i.e., the chain-to-chain distance, computed using the bulk DFPT method, Eq. (1) and molecular DFT modeling in connection with the Clausius–Mossotti relation, Eq. (1), respectively, for acrylic acid grafted polypropylene with several grafting compositions of carboxyl groups ($-\text{COOH}$) onto the IPP chains.

Interestingly, from Fig. 11 it can be seen that the results for the dielectric constants computed with the molecular DFT modeling [$\epsilon_r(0)$] for a range of lattice constant values are nearly identical to those computed with the bulk DFPT method (ϵ_∞) in the case where the oligomer inside the unit cell contains the terminal hydrogens ($\text{C}_{18}\text{H}_{38}$ grafted with $-\text{COOH}$ groups). Consequently, this generalizes the conclusions made in the context of Fig. 10 where $\epsilon_r(0)$ and ϵ_∞ were computed at one particular chain-to-chain distance only corresponding to the minimum total-energy configuration for each $-\text{COOH}$ grafting composition.

Figure 11 also shows ϵ_∞ values from the bulk DFPT calculations as a function of the lattice constant in the case where the terminal hydrogens have been removed from the grafted oligomer inside the unit cell ($\text{C}_{18}\text{H}_{36}$ grafted with $-\text{COOH}$ groups). We can see that the ϵ_∞ values in this case (perfect tetragonal crystal structure with an ordered grafting structure along the IPP chains) are slightly larger than in the case where the terminal hydrogens are included in the oligomer.

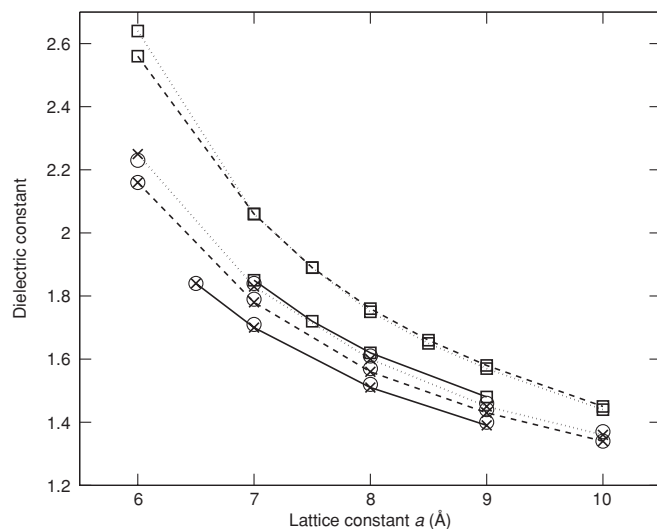


FIG. 11. High-frequency dielectric constant (ϵ_∞) from the bulk DFPT calculation and the static dielectric constant [$\epsilon_r(0)$] from the molecular DFT calculation in connection with the Clausius–Mossotti relation for acrylic acid grafted polypropylene with a tetragonal crystal structure as a function of the polymer chain-to-chain distance, i.e., the a lattice constant. Computational details used are described in the caption to Fig. 10. The ϵ_∞ values from the DFPT calculations with and without the terminal hydrogens at each end of the grafted oligomer are marked with circles ($C_{18}H_{38}$ grafted with $-COOH$ groups) and squares ($C_{18}H_{36}$ grafted with $-COOH$ groups), respectively. The static permittivity [$\epsilon_r(0)$] values from the molecular DFT–Clausius–Mossotti calculations are shown by crosses. The solid, dashed, and dotted lines are acting as guides to the eye for the data points corresponding to $n = 0, 1$, and 2 $-COOH$ groups, respectively, used in grafting the 6-monomer IPP oligomer.

However, as indicated by our molecular DFT modeling of the static permittivity in connection with the Clausius–Mossotti relation as a function of the IPP oligomer length (cf., for example, the behavior of the longitudinal component of the polarizability volume per number of monomers in the IPP oligomer as a function of the number of monomers in Fig. 7 of Ref. 27) it is obvious that when the length of the grafted oligomer (with the terminal hydrogens attached to it) inside the unit cell increases the corresponding values for the high-frequency dielectric constant (ϵ_∞) increase toward the ϵ_∞ value calculated using the DFPT method where the oligomer inside the unit cell does not contain the terminal hydrogens.⁵⁶

We can conclude that on the basis of our computational results on polarizability volume per mass (α'/m) (Fig. 9), electron energy-gap behavior (Table II), and high-frequency and static dielectric constants, ϵ_∞ and $\epsilon_r(0)$, respectively (Figs. 10 and 11), it is obvious that the molecular DFT modeling in connection with the Clausius–Mossotti relation can be successfully used, in place of the more realistic but far more complicated DFPT method, to calculate electronic and dielectric properties of acrylic acid grafted polypropylene. Furthermore, the good agreement between the results from the molecular DFT modeling and the bulk DFPT method can be attributed to the local interaction between the carboxyl groups ($-COOH$) and the IPP chains, and to the weak Coulombic interaction between the polymer chains.

IV. CONCLUSIONS

First, we have carried out first-principles computational studies on dielectric and electronic properties for acrylic acid grafted polypropylene using a molecular based DFT modeling as well as DFT and DFPT methodologies for bulk periodic systems in the framework of the GGA approximation with the PW91 exchange and correlation functional. Our molecular modeling calculations show that when a polypropylene molecule (oligomer) is grafted with carboxyl, the polarizability volume α' is increased linearly, while the ratio α'/m is decreased linearly, from the value of a pure polymer, as a function of the amount, i.e., the mixture ratio, of the added carboxyl groups. This linear behavior can be interpreted to derive from the local carboxyl group interaction with the polypropylene backbone. It is obvious that for the same reason, our computed HOMO–LUMO energy gap, which is decreased by some 15% in grafting, is essentially independent on the mixture ratio of carboxyl.

Second, using the first-principles molecular DFT approach for polarizability in connection with the simple Clausius–Mossotti relation predicts the permittivity of polypropylene to increase when grafting with acrylic acid in agreement with the preliminary experiments.

Third, we briefly comment on the dielectric strength behavior of acrylic acid grafted polypropylene. Our molecular DFT calculations, which show that the HOMO–LUMO gap decreases under the acrylic acid grafting of polypropylene, seem to indicate that the dielectric strength could also decrease. However, the opposite takes place in the experiments, showing the dielectric strength to improve when polypropylene is grafted with acrylic acid. This indicates clearly that in addition to the size of the electronic band gap, there are other more dominant factors, contributing to the improved dielectric strength. Further deviation between the theoretical and experimental results derives from the fact that our calculations have been done for perfect crystalline polymers, therefore not necessarily reflecting realistic materials on which the experiments have been conducted.

Finally, in order to validate our molecular modeling DFT calculations on molecular polarizability, permittivity from Clausius–Mossotti relation and HOMO–LUMO gap to represent dielectric and electronic properties of acrylic acid grafted polypropylene we also have carried out extensive calculations on corresponding bulk related properties using three-dimensional periodic DFT and DFPT approaches with the same exchange and correlation approximation (GGA-PW91). Remarkably, the results between the molecular modeling DFT and bulk (DFT, DFPT) computational schemes behave very similarly, therefore validating our simpler molecular based DFT approach in tackling dielectric properties of acrylic acid grafted polypropylene.

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ingly, it turns out (see discussion below) that the artificial tetragonal crystal structure, which comprises a metastable state, causes only minor changes to these properties. Therefore, within the scope of this paper, we will not carry out rather massive DFT and DFPT computations on these properties for possible realistic phases of acrylic acid grafted isotactic polypropylene (the known phases of isotactic polypropylene are the α -form [monoclinic crystal structure], the β -form [hexagonal crystal structure], and the γ -form [triclinic crystal structure]). However, we have done some calculations (not shown here) for pure isotactic polypropylene with the α -form. Conclusions from these calculations are very similar to those from our present calculations based on the tetragonal crystal structure. For example, the band gap energy and permittivity are quite insensitive to the relative positions of the right- and left-handed helical chains along the chain direction, and the permittivity values computed with the DFPT method and molecular DFT modeling (Clausius–Mossotti relation) are very similar.

⁵⁶In the bulk DFT calculations, the case where the oligomer inside the unit cell contains the terminal hydrogens should be very close to the Clausius–Mossotti DFT molecular modeling where the terminal hydrogens are always attached to the oligomer in order to avoid dangling bonds. On the

other hand, the bulk DFT calculations where the terminal hydrogens have been removed from the oligomer, correspond to a more realistic periodic atomic structure along each infinite grafted polymer chain. However, it is obvious that the results for electronic and dielectric properties from the bulk DFT calculations with the unit cell oligomer containing the terminal hydrogens will approach the results from the bulk DFT calculations where the terminal hydrogens have been removed from the unit cell oligomer, when the length of the oligomer increases (cf., e.g., the HUMO-LUMO gap values in Fig. 7 which decrease for IPP and grafted IPP when the length of the oligomer increases, in connection with the band gap values E_g^{bulk} in Table II).

⁵⁷We have found through our CASTEP DFPT calculations that in the case of polypropylene and acrylic acid grafted polypropylene the atomic lattice vibrational (phonon) contribution, i.e., the second term of Eq. (2a), to the static dielectric constant $\epsilon_0 \equiv \epsilon(0)$ (relative permittivity) shows up only in the second or third decimal place. Therefore, the high-frequency ($\omega_{\text{phonon}} \ll \omega \ll E_g/\hbar$) electronic contribution to the permittivity, i.e., ϵ_∞ , should describe accurately the permittivity behavior in these materials.