

Broadband terahertz characterization of the refractive index and absorption of some important polymeric and organic electro-optic materials

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We report broad bandwidth, 0.1–10 THz time-domain spectroscopy of linear and electro-optic polymers. The common THz optical component materials high-density polyethylene, polytetrafluoroethylene, polyimide (Kapton), and polyethylene cyclic olefin copolymer (Topas) were evaluated for broadband THz applications. Host polymers polymethyl methacrylate, polystyrene, and two types of amorphous polycarbonate were also examined for suitability as host for several important chromophores in guest-host electro-optic polymer composites for use as broadband THz emitters and sensors. © 2011 American Institute of Physics. [doi:10.1063/1.3549120]

I. INTRODUCTION

Recent advances in air plasma terahertz (THz) generation have revitalized broadband THz time-domain spectroscopy (TDS),^{1,2} bringing the THz community one step closer to broadband imaging, standoff detection, materials identification and analysis. As such, it becomes increasingly important to catalog the optical properties of materials across the so-called THz gap, spanning 0.1–10 THz. This will allow for more accurate modeling of THz transmission through layered media or improved optical components for THz systems.

In particular, polymeric materials have found numerous uses in the THz regime as lenses, windows, beam-blocks, waveguides,³ and photonic structures⁴ as well as emitter and sensor materials.^{5,6} The appeal of amorphous materials for THz applications is their lack of the transverse optical phonons that are present in crystalline materials that give rise to strong absorption in the THz regime.

Electro-optic (EO) guest-host polymers have been utilized as broadband THz emitters and sensors for a number of years, owing to their tunable properties, high nonlinearity, and lack of phonon absorptions.⁷ Free-space EO sampling (FSEOS) in poled polymers represents a simple alternative to THz field-induced second harmonic generation (TFISH)^{1,2} for broadband THz sensing. These applications require knowledge of the THz refractive index to address phase matching requirements and the THz absorption to guide the selection of appropriate material composition and device geometry.

Several neat polymers have been studied over the 0.1–2 THz range,⁸ typically available through the use of ZnTe emitters and sensors or photoconductive dipole antennae. Many materials that appear transparent between 0.1 and 2 THz have absorption resonances at higher THz frequencies. So as broadband THz work becomes more ubiquitous, the optical properties of polymers must be elucidated at higher frequencies.

Here we report the optical properties of several technologically important polymers from 0.1–10 THz. These materials include polyimide (Kapton), poly[bisphenol A carbonate-co-4,4'-(3,3,5-trimethyl cyclohexylidene) diphenol carbonate] (APC), poly[bisphenol A carbonate] (BPC), polymethyl methacrylate (PMMA), polystyrene (PS), poly(styrene-co-methyl methacrylate) (PS-PMMA), polyethylene cyclic olefin copolymer (Topas), polytetrafluoroethylene (Teflon), and high-density polyethylene (HDPE). Guest-host EO polymers composed of a guest dye in a polymer host: AJLZ53 in a PS-PMMA copolymer, AJLZ53 in BPC, AJLP131 in BPC, AJTB203 (Ref. 9) in BPC, Lemke (Ref. 10) in APC, and DCDHF-6V (Ref. 10) in APC, are also examined.

II. RESULTS AND DISCUSSION

Details of our THz-TDS experimental setup based on air-plasma THz generation and FSEOS in EO polymers are reported elsewhere.² Neat polymer samples were prepared by taking commercially available polymer pellets from chemical distributors (PMMA, BPC, and APC from Sigma-Aldrich; Topas from Advanced Polymers), heating them above their glass transition temperature, and pressing them to the desired thickness in a hydraulic press (Carver 3850). The Kapton was received as a sheet from Dupont while the Teflon and HDPE were slabs of engineering quality materials obtained from McMaster-Carr. Guest-host EO polymers

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were mixed in solution, drop cast onto slides, and baked to remove the solvent, and individual drop cast films were stacked and pressed to the desired thickness in a hydraulic press. These methods resulted in uniform monolithic films that exhibit low birefringence.

Assignments of molecular motions for the THz absorption features we see in the spectra of these polymers and chromophores were made by performing density functional theory (DFT) calculations using the Gaussian 09 suite of programs.¹¹ Calculations on the chromophores were done on single molecules using the 6-31G(d,p) basis set and the B3LYP functional. The polymer calculations used the 6-31G(d) basis set and the B3LYP functional. The polymers were modeled as oligomers containing eight monomers for Teflon, PMMA, and Topas and four monomers for BPC, APC, and Kapton. Because exactly reproducing the experimental spectra from theoretical calculations is beyond the scope of this paper, we aim, merely, to qualitatively identify the important modes for a given THz feature, which for these low energy vibrations nearly always involves the collective motion of almost all the atoms in the molecule. The assignments we list here reflect those modes that have the greatest amplitudes within a given band.

The refractive index, n , and absorption coefficient, α , of common materials for THz optics are shown in Figs. 1 and 2. The HDPE sample is a 90 μm thick black garbage bag, commonly used to block residual infrared, visual, and ultraviolet light while transmitting THz radiation. HDPE is known to have a nearly constant THz refractive index and a low THz absorption⁸ and is commonly used as a binder material when making pellets for spectroscopy.¹² HDPE is also used for THz lenses, windows, and polarizers.¹³ The featureless, nearly linear absorption trend persists across the THz regime and is also observed in Fourier transform infrared spectroscopy (FTIR).¹⁴ Though it is listed here as absorption, it is better thought of as attenuation and could have contributions from scattering. At higher frequencies, the losses through a black HDPE beam block will be significant. Where possible, high resistivity silicon (HRSi) placed at Brewster's angle would make a better choice for a beam block, owing to its very low THz absorption.¹⁴ This may not be possible in time-resolved THz studies as free-carriers in photoexcited HRSi will absorb at THz frequencies.

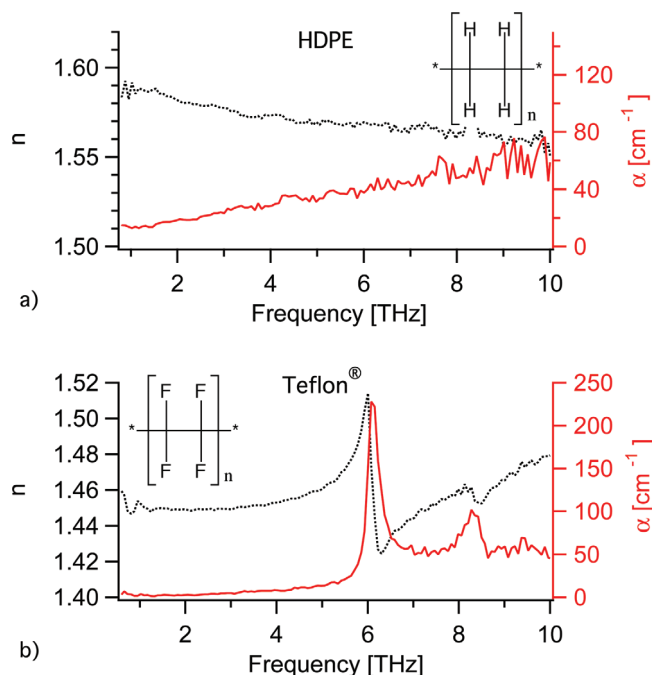


FIG. 1. (Color online) The refractive index (dotted) and absorption coefficient (solid) of (a) a black HDPE garbage bag and (b) Teflon. The chemical structures are included as insets.

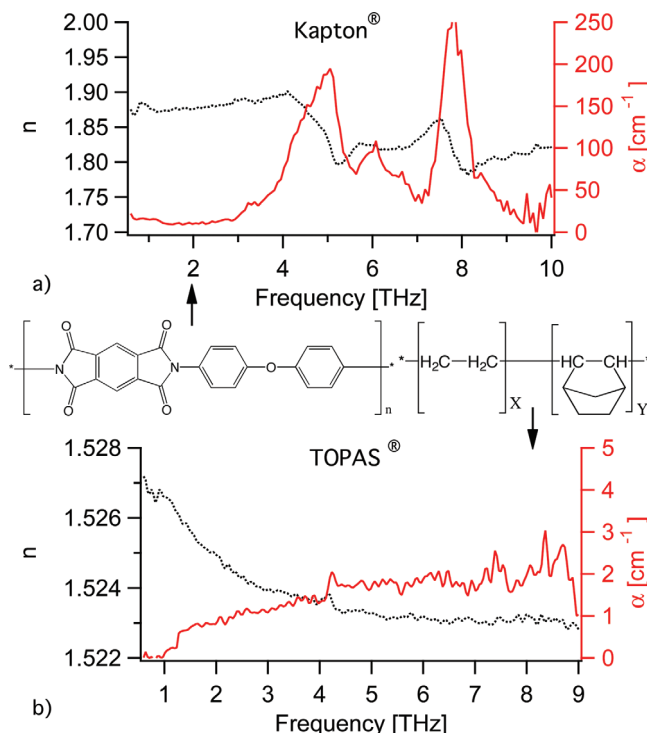


FIG. 2. (Color online) The refractive index (dotted) and absorption coefficient (solid) of (a) Kapton and (b) Topas. The chemical structures are pictured between the graphs. Note the fine scale for the Topas refractive index, emphasizing the precision of the measurement and the nearly constant value of the index for this material over the THz band.

copy (FTIR).¹⁴ Though it is listed here as absorption, it is better thought of as attenuation and could have contributions from scattering. At higher frequencies, the losses through a black HDPE beam block will be significant. Where possible, high resistivity silicon (HRSi) placed at Brewster's angle would make a better choice for a beam block, owing to its very low THz absorption.¹⁴ This may not be possible in time-resolved THz studies as free-carriers in photoexcited HRSi will absorb at THz frequencies.

Teflon has the same backbone chemical structure as HDPE but differs in the substitution of fluorine for all the hydrogens. It has low absorption for THz frequencies below ~ 3 THz and good mechanical properties, making it a potentially desirable material for THz lenses and windows¹³ in that frequency band. However, broadband spectroscopy shows strong absorption features at 6.1 and 8.3 THz, Fig. 1(b), which have previously been assigned to the CF_2 twisting and scissor motion, respectively.¹⁵ These features have been previously seen using wideband THz spectroscopy based on a tunable DAST source¹⁶ as well as FTIR.¹³ Near these features, the index of refraction shows expected derivativelike frequency dependence consistent with the Lorentz oscillator model. The refractive index of the 258 μm thick sample agrees with previous reports less than 2 THz.¹⁷ These strong absorption features make Teflon a poor choice for broadband THz optical components.

Polyimides are a class of polymers with good mechanical properties that are resistant to most solvents and frequently are used for electrical and thermal insulation. Kapton polyimide is thought to have low THz absorption,

making it a desirable material for optical cryostat windows for THz applications. The 125 μm Kapton sample shows strong absorption features at 4.9, 6.1, and 7.8 THz, Fig. 2(a). The 4–5.5 THz band is associated with out-of-plane butterfly motions of the rings, while the band centered at 7.5 THz is associated with a combination of in-plane twisting of the rings and longitudinal stretching of the imide rings relative to the central six-membered ring. These features make Kapton a poor choice of window material for broad bandwidth THz applications.

Topas is a cyclic olefin/ethylene copolymer. Due to very low absorption, it has found applications in THz waveguiding.⁴ Broadband THz spectroscopy of a 3.2 mm thick sample shows an index of refraction between 1.52 and 1.53 and absorption $< 3 \text{ cm}^{-1}$ across the THz band, Fig. 2(b). These properties make Topas ideal for broadband THz optical components, including waveguides and window materials. Topas is also resistive to most acids and solvents, making it a good choice for a substrate material for broadband THz spectroscopy.

Typical THz spectroscopy substrates include z-cut quartz and fused silica. Although quartz substrates show low absorption over narrow bands, the crystalline structure will lead to phonon absorptions. Fused silica, an amorphous glass typically manufactured from quartz, shows significant losses at higher frequencies.¹⁴

Common host materials for EO guest host polymers include PS, PMMA, PS-PMMA, BPC, and APC, Fig. 3. These are also common construction materials and may also be useful for THz optical components. The THz refractive index and absorption coefficients are summarized in Fig. 4, where Topas is included for comparison. To achieve good velocity matching between the optical and THz beams involved in optical rectification or FSEOS, the refractive index should be constant throughout the THz regime.

While the refractive indices of BPC, APC, and PS are relatively flat, PMMA shows several features. There are corresponding absorption features centered at 2.7 and 6.6 THz. They have previously been assigned to the rotor motion of the methyl groups on the side-chain and the wagging of the carboxylic groups, respectively.¹⁸ Both n and α of the 306 μm PMMA sample agree with previous measurements at $< 1.2 \text{ THz}$.⁸ The observed features will lead to poor phase matching and

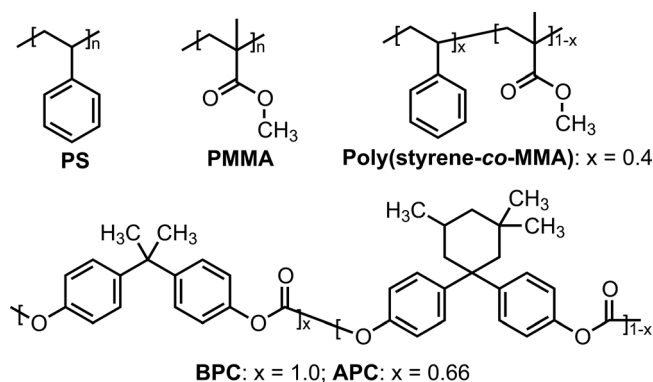


FIG. 3. The chemical structures of common EO polymer hosts PS, PMMA, Poly(styrene-co-MMA), BPC, and APC.

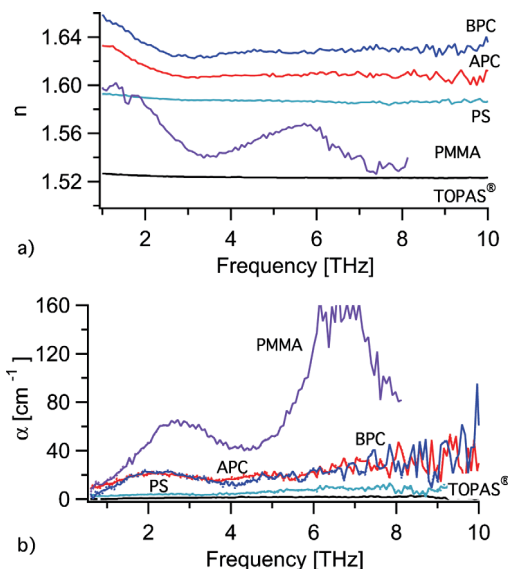


FIG. 4. (Color online) The (a) refractive index and (b) absorption coefficient of BPC (solid), APC (dotted), PS, PMMA, and Topas.

strong THz absorption in EO polymers used for THz emission or detection resulting in spectral gaps.

On the other hand, PS shows very low THz absorption and a relatively constant refractive index, similar to Topas. These properties could make PS a good host material for THz EO polymers. Unfortunately the low glass transition temperature of PS would allow chromophores to re-orient more easily, leading to an optical nonlinearity that decays with time. The measured n and α of the 388 μm thick PS sample are similar to previous measurements in the literature $< 1 \text{ THz}$.¹⁹

Both n and α of the 316 and 335 μm thick BPC and APC samples are also similar to previous measurements in literature $< 1.5 \text{ THz}$.⁸ The relatively constant refractive index and low absorption have led to EO polymers based on these hosts that are capable of broadband THz emission and detection.^{7,9} The higher refractive index of these hosts will also contribute to higher sensitivity in FSEOS, as the detected signal is proportional to the index cubed. However, given that each 1 cm^{-1} of absorption coefficient corresponds to an optical loss of 4.3 dB/cm, EO polymers based on APC and BPC may exhibit too much absorption for waveguide applications.

Numerous chromophore dye molecules have been incorporated in guest-host EO polymers for THz applications.^{5,7,9,10,20} The chromophores we chose to examine are Lemke, DCDHF-6-V, AJTB203, AJLP131, and AJLZ53,^{21–23} Fig. 5. The short Lemke and DCDHF-6-V chromophores have been successfully used in broadband THz emitters and sensors for Ti:Sapphire laser based systems operating at 800 nm wavelengths. The longer phenyltetraene chromophores have red shifted absorption and are capable of achieving larger non-linearity. For this reason, they are desirable for THz emitters and sensors operating in the infrared near telecom laser wavelengths.

The addition of Lemke and DCDHF-6-V to APC leads to an increase in both the refractive index and absorption,

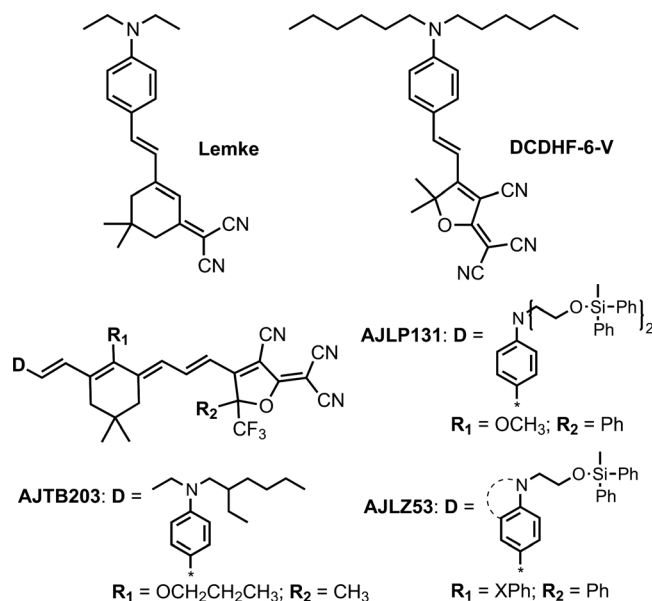


FIG. 5. The chemical structures of chromophores Lemke, DCDHF-6-V, AJTB203, AJLP131, and AJLZ53.

Fig. 6. Both n and α reported here for a 238 μm 40% Lemke/60% APC and 315 μm DCDHF-6-V/APC sample are consistent with previous reports.⁷ Absorption features can be identified at 4.2, 5.9, and 8 THz in Lemke/APC that have also been previously observed in spectra of Lemke/PS and can be attributed to molecular motions of the Lemke dye.¹⁸ The feature at 4.2 THz is associated with a scissor motion of the CN end groups, the 5.9 THz band with a general flexing of the vinyl bridge, and the 8 THz feature with a butterfly motion of the CN group and the conjugated vinyl bridge.¹⁸ The absorption features at 4.9 and 5.7, in DCDHF-6-V/APC are due to similar atomic motions as found in the Lemke

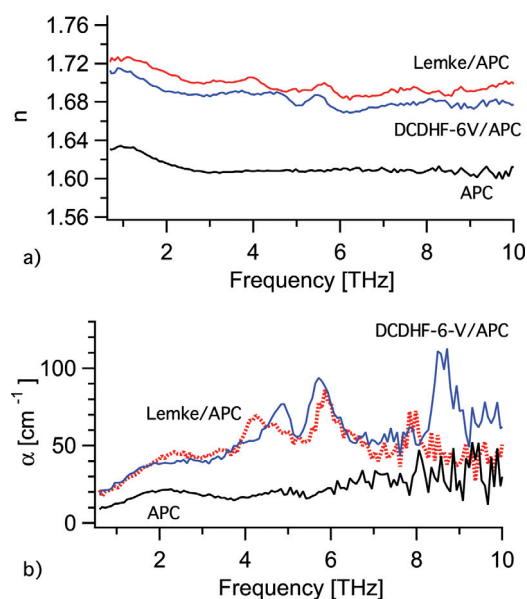


FIG. 6. (Color online) The (a) refractive index and (b) absorption coefficient of Lemke/APC (dotted) and DVDHF-6-V/APC compared to pure APC.

molecule while the 8.6 THz band is due to a combination of two modes, one of which is an out-of-plane wagging of the lone CN group attached to the dihydrofuran ring and the other is due to an in-plane oscillation of the hexyl tails and phenyl group attached to the lone N atom.

Similarly, the addition of chromophores to BPC leads to an increase in both the refractive index and absorption coefficient, Fig. 7. The 217 μm thick 25% AJTB203/75% BPC displays absorption features at 4.4, 5.5, 7.1, and 8.6 THz. The band at 4.4 THz is due to symmetric and asymmetric scissor motions of the three CN groups. The 5.5 THz band is due to an in-phase butterfly motion of the CN groups and a corresponding flexing of the vinyl bridge. The band near 7.1 THz is due to a flexing of the alkyl groups attached to the N atom. The band near 8.6 THz is due to general oscillations of the ring and vinyl bridge in the center of the molecule. The 286 μm thick 25% AJLP131/75% BPC sample shows absorption features at 4.5, 5.5, 7.9, and 8.6 THz. The molecular motions accounting for the main THz bands in AJLP131 are qualitatively the same as those in AJTB203. The 324 μm thick 25% AJLZ53/75% BPC sample has absorption features at 4.5 and 5.5 THz with molecular origins similar to those in AJTB203 and AJLP131 and a broad band centered near 7.3 THz that represents several modes associated with rotor motions associated with the various methyl groups distributed about the molecule coupled to a general, low amplitude twisting of the vinyl bridge. The similarity in many of the absorption features of the chromophore molecules is clearly related to the similarity in the chemical structure of these chromophores. These modest absorption features do not significantly affect the emitted or detected spectra for a typical film thickness between 50 and 100 μm . However, they may significantly limit the length of a THz emitting waveguide structure.

Although PMMA has large absorption features in the THz regime, a copolymer of PMMA and PS may show significantly less absorption. The copolymer would also have a

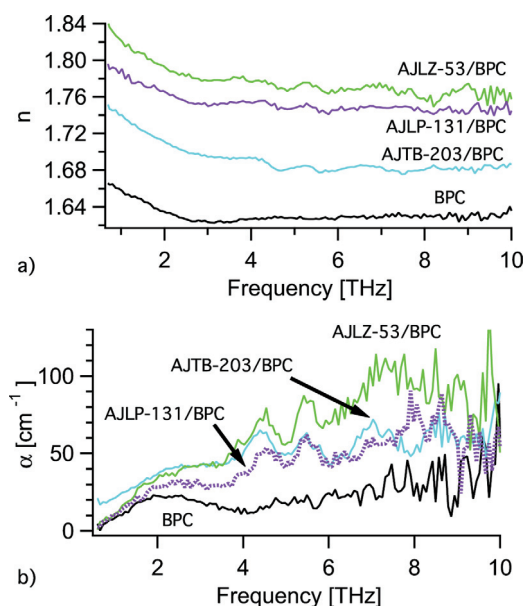


FIG. 7. (Color online) The (a) refractive index and (b) absorption coefficient of AJLZ53/BPC, AJLP131/BPC (dotted), and AJTB203/BPC, compared to pure BPC.

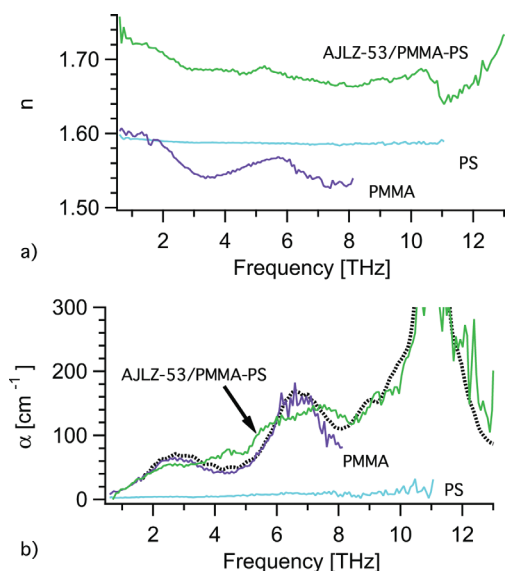


FIG. 8. (Color online) The (a) refractive index and (b) absorption coefficient of AJLZ53/PS-PMMA, with PMMA and PS for reference. FTIR of PMMA (dotted) is also included.

higher glass transition temperature than PS alone, allowing for stability of the poling-induced nonlinearity. THz spectra of a 93 μm AJLZ53/PS-PMMA sample shows a lower refractive index than AJLZ53/BPC but significantly more absorption, Fig. 8. The AJLZ53 absorptions at 4.5, 5.5, and 7.3 THz can still be identified on top of the PMMA absorptions at 2.7 and 6.6 THz. Despite the inclusion of 40 mol% of PS, the AJLZ53/PS-PMMA spectrum resembles the FTIR spectra of PMMA alone. The very strong absorption near 11 THz has previously been assigned to the wagging of the methyl groups on the PMMA repeat units.¹⁸ We see that any guest-host polymer system using PMMA or a PMMA copolymer as a host will exhibit significant THz absorption, leading to significant losses and spectral gaps if used for THz emission or detection.

III. CONCLUSIONS

We examined the dielectric properties of important linear and EO polymers from 0 to 10 THz. By using a broadband, air-plasma/EO polymer THz-TDS system, we have identified absorption features in Teflon, Kapton, and PMMA that make these materials poor choices for broadband THz components such as lenses, beam splitters, optical windows, or substrates. Topas and PS have relatively constant refractive indices and show low loss across the THz regime, making them ideal materials for passive broadband THz optical components, even for THz guided wave applications. However, the nonpolar nature of Topas makes it difficult to heavily dope this polymer with the highly dipolar chromophores potentially precluding its use as a host polymer for guest-host THz generation and sensing. The addition of nonlinear optical chromophores into polymer hosts generally increases

the refractive index and induces weak absorption features due to the specific structure of the chromophores. EO polymers based on APC and BPC, although ideal for broadband FSEOS of THz pulses in thin solid films, may exhibit too much absorption for long THz emitting waveguide structures.

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