Synthesis, characterization, and dielectric properties of polymers functionalized with coumarone and diethanolamine

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ABSTRACT: A series polymers of the poly(4-{[bis(2-hydroxyethyl)amino]methyl}-2-oxo-2*H*-chromen-7-yl-2-methylpropanoate), P(CIMMAOC)-DEA, were synthesized by modification of poly(4-(chloromethyl)-2-oxo-2*H*-chromen-7-yl-2-ethylpropanoate), P(CIM-MAOC), with diethanolamine (DEA). All polymers were structurally characterized by FTIR, ^{1}H NMR, UV–vis, and Fluorescence spectra. The electronic features of the polymer, such as lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energies and electrostatic potential (ESP), and the vibrational frequencies were computed by the Becke3–Lee–Yang–Parr (B3LYP) functional using 3–21G* basis set. Dielectric measurements for P(CIMMAOC) and P(CIMMAOC)-DEA were performed by means of an impedance analyzer as a function of frequency and temperature. It was found that the dielectric constant values decreased in the applied frequency range. The values of dielectric constant increased with a rise in concentrations of DEA in polymer for all temperatures. Dielectric constants of P(CIMMAOC) and P(CIMMAOC)-DEA (60%) were calculated as 3.93 and 12.29 at 1 kHz, respectively. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42164.

INTRODUCTION

Photopolymers are worked in the features of the photosensitive unity and for their macromolecular features. These polymers usually include vinyl aromatic polymers with pendent chromophores which have effective light collection and long termed energy transfer. Therefore, these polymers are known as antenna or light harvesting polymers. Photoresponsive polymers as a dielectric material can have a role in an active area of polymer chemistry research due to its uses in the areas of photolithography, liquid crystal, non-linear optical materials, laser dyes, fluorescence materials, and forward microelectronics. The significance of the coumarone and derivatives as fluorescent materials arise from their sensible stability, effective light emission features, and comparatively easy synthesis. The fluorescent coumarones both absorb in the UV region and emit blue light or longer wavelengths.[1] To photopolymers make, 7-hydroxycoumarone is a extensively used in the polymer.[2,3] Coumarone and derivatives have been employed as photoreactive agents for practices such as photoresists and photorecording[4–6] and as photolabile conservation unities for biological practices.[7] Modification of inorganic and organic polymers have been investigated as an effective way to add to a single material.

The different features added to the polymers may be leading to improvements in many areas. This has attracted both industrial and academic interest.[8,9] Modification of polymers can usually be substituted chlorine atoms by nucleophilic substitution reactions as a suitable way of constructive features.[10] The chemical modification of polymers carried out with nucleophiles, such as phthalimide anion and I–, SCN–, OH–, N_3–,[11] pyrazole, 2-mercaptobenzimidazole, and 3,5-dimethylpyrazole,[12] ethylenediamine,[13] potassium ethyl xanthogenate,[14] 1,4-phenylenediamine,[15] and amino thiophenol.[16] The chemical modification of polymers including coumarone allows us to vary emission wavelength continuously throughout the visible spectrum.[17] Dielectric materials are fundamentally used as capacitors because they store electrical energy. Amongst these, polymeric materials have the advantages of high durableness, lightness, processability, and flexibility. With these properties, the polymeric materials use as an embedded capacitor for electronics.[18–27] Diethanolamine (DEA) is a multi-functional material that are capable of hydrogen bonding by not only donating, but also accepting hydrogen bonds.[28] On this subject, rely on these properties, we investigated spectroscopic and dielectric properties of homopolymer and polymers derived from its modified with DEA. The structural and spectroscopic investigations of coumarone and its
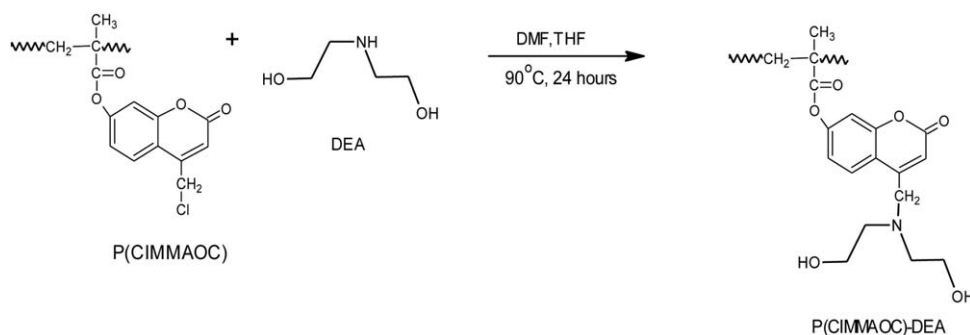
Scheme 1. The synthesis of P(CIMMAOC)-DEA.

derivatives attract experimental and theoretical due to its extraordinary importance of technological applications. The vibrational spectra have been used as an effective means in the functional group analysis of active compounds. Infrared spectroscopy is an effective way to research geometric and electronic structure of molecules, and has been greatly used in working the structural results.[29] Therefore, the vibrational appointments of the infrared spectrum of drug molecules,[30] biological compounds,[31] and natural products[32] have been greatly worked in structural research in these days. During the recent years, density functional theory (DFT) functionals have occurred best way in the determination of molecular structures and vibrational spectra, especially Becke3–Lee–Yang–Parr (B3LYP) functional[33–35] has been greatly used.

This article details UV–vis absorption, emission spectra, and dielectric behavior of photosensitive polymers. In this research, we state that the synthesis of poly(4-(chloromethyl)-2-oxo-2H-chromen-7-yl-2-methylpropanoate, P(CIMMAOC), and polymers derived from modification with DEA. All of polymers were structurally characterized by FTIR, ^{1}H NMR, Fluorescence, and UV–vis spectra. Dielectric measurements for homopolymer and its modified with DEA were performed by means of an impedance analyzer as a function of frequency and temperature. Besides, the structural optimization and the characteristic vibrational frequencies of polymers (for two units) were determined with the experimental and theoretical methods. This electronic and vibrational study, both serves for the appropriate appointments of the computed and observed frequencies and offers both industrial and academic interest about the electronic features and molecular dynamics of polymer molecule.[36]

EXPERIMENTAL

Materials and Methods

Methacryloyl chloride, triethylamine (TEA), CuBr, 2,2′-bipyridyne (bpy), dichloromethane, tetrahydrofuran (THF), DEA, sodium bicarbonate (NaHCO$_3$), and N,N-dimethylformamide (DMF) were obtained from Sigma-Aldrich. Ethyl alcohol was obtained from Fluka. 4-Chloromethyl-7-hydroxycoumarone was obtained from our previous study.[37,38]

The Synthesis of 4-(Chloromethyl)-2-oxo-2H-chromen-7-yl-2-methyl propanoate, (CIMMAOC)

The synthesis of 4-chloromethyl-7-methacryloyloxy coumarone (ClMMAOC) monomer is carried out in accordance with the

standard method and our previous study.[37,38] The monomer was synthesized by the reaction of 4-chloromethyl-7-hydroxycoumarone and methacryloyl chloride at 0–5°C by using TEA. The product was recrystallized within ethanol. The resulting product, ClMMAOC, was then dried in a vacuum oven at 40°C for 24 hours.

The Synthesis of Poly[4-(chloromethyl)-2-oxo-2H-chromen-7-yl-2-ethylpropanoate], P(CIMMAOC)

The monomer, ClMMAOC, was recrystallized within ethyl alcohol. The monomer was polymerized in the presence of 2,2′-azobisisobutyronitrile (AIBN) as an initiator at 60°C in 1,4-dioxane. The homopolymer, P(ClMMAOC), was precipitated into pure ethyl alcohol. This precipitation was repeated two times. The resulting product, P(ClMMAOC), was then dried in a vacuum oven at 40°C for 24 hours.

Modification of Poly (4-(chloromethyl)-2-oxo-2H-chromen-7-yl-2-ethylpropanoate) with Diethanolamine, P(CIMMAOC)-DEA

Modification with DEA of P(ClMMAOC) was performed accordingly the method concerted from the literature.[39] About 12 g (—CH$_2$—Cl unity) of the P(ClMMAOC) was dissolved in 10 mL of THF and 30 mL of DMF. Different rates of DEA and NaHCO$_3$ were appended into the polymer solution. The admixture was blended and warmed for 24 hours in a vacuum oven at 90°C underneath argon gas. The reaction admixture was chilled to at room temperature and filtered off. The resulting product, P(CIMMAOC)-DEA, was precipitated into pure ethyl alcohol and cleansed from the THF solution by reprecipitating in ethyl alcohol and water. The reaction details are indicated in Scheme 1.

Instrumentation

The infrared spectra of polymers were registered on a Perkin–Elmer Spectrum One Fourier transform infrared spectroscopy (FTIR; Waltham, Massachusetts, USA) spectrometer at 0.5 to 64 cm^{-1} resolution. The spectra were collected using scans over the range from 4000 to 450 cm^{-1} and a film deposited on a salt plate from a dichloromethane solution. Proton nuclear magnetic resonance (^{1}H NMR) spectra was acquired on a 400 MHz Bruker AVIII 400 machines (Billerica, Massachusetts, USA), using tetramethylsilane as an interior standard and deuterated chloroform, DMSO, and acetone as the solvent. Ultraviolet–visible (UV–vis) spectra were registered using a Shimadzu

spectrophotometer (Japan). The emission spectra were registered on a Perkin–Elmer LS 55 Fluorescence spectrometer (USA). Calorimetric measurements were performed on a Shimadzu DSC–50 thermal analyzer (Japan) underneath N_2 flow with a heating rate of 20°C min^{-1}.

Computational Methods

The molecular structure of polymer was determined by the DFT/B3LYP method using 3–21G* basis set with the Gaussian 5.0.9 program. The optimized structure and the vibrational frequencies of the molecule were determined by the DFT/B3LYP (the hybrid functional) method using 3–21G* basis set. The assignments of the calculated wavenumbers are determined by the animation option of Gaussian 05 view software for Gaussian programs, which gives a visual presentation of the shape of the vibrational modes along with available related molecules.[40] The molecular geometry, LUMO energies and HOMO, Frontier orbital energy gap, electrostatic potential, and vibrational frequencies were determined by the DFT/B3LYP (the hybrid functional) method using 3–21G* basis set.

Dielectric Properties Measurements

First of all, the polymers were crushed with a mortar and pound and then fine powders were compressed at four tons of pressure into disc shapely polymers with a diameter of 12 mm and a thickness ranging from 0.94 mm to 2.22 mm. Because the silver paste behaves as a good contact for dielectric measurement, all of the surfaces of the discs were painted with it. The dielectric measurements of polymers were obtained at room temperature and at different temperatures with a QuadTech 7600 precision LRC meter impedance analyzer over the frequency range 0.05 kHz–2 MHz. The dielectric properties against the frequency and temperature of polymers were investigated.

RESULTS AND DISCUSSION

Synthesis and Characterization of P(ClMMAOC)

Figure 1(a) indicates the FTIR spectra of PCIMMAOC: 3090–3005 and 2990–2855 (—CH stretching of the aromatic and aliphatic), 2986 (—CH3), 1737 (C=O stretching vibration), 1614 (C=C stretching of the aromatic ring), 1230 (asymmetric C—O—C), and 1142 (symmetric C—O—C). In this work, so as to performed modification on homopolymer, the chlorine atom on coumarone ring was altered using diethanolamine, resulting in P(CIMMAOC)-DEA (Scheme 1).

Consequently, it was determined that the amine group in the homopolymer was to be in rates of 2, 12, 16, 18, 54, and 60% (by mole). Figure 1(b–g) indicates a typical FTIR spectrum of PCIMMAOC-DEA has a characteristic absorbance at 3422 cm^{-1} (O—H stretching vibration), which is not there in P(CIMMAOC).

Figure 2 indicates a typical ^{1}H NMR spectrum of P(CIMMAOC) [Figure 2(a)] and P(CIMMAOC)-DEA [Figure 2(b)]. It clearly indicates that besides the typical signals of coumarone unity, which shows characteristic signals at 6.36–8 ppm (protons of aromatic ring), 4.99 ppm (Cl—CH2— protons), and 2.54–1.39 ppm (aliphatic protons in the polymeric chain). The other assignments are indicated in detail in Figure 2. When Figure 2(a) is compared *via* Figure 2(b), it is seen that on the cou-
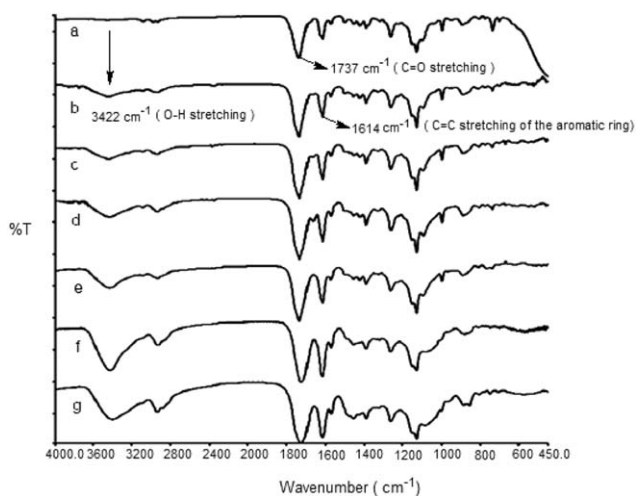

Figure 1. The FTIR spectra of (a) PCIMMAOC, (b) P(CIMMAOC)-DEA (2%), (c) P(CIMMAOC)-DEA (12%), (d) P(CIMMAOC)-DEA (16%), (e) P(CIMMAOC)-DEA (18%), (f) P(CIMMAOC)-DEA (54%), and (g) P(CIMMAOC)-DEA (60%).

marone ring CI—CH2— methylene signals of the homopolymer P(CIMMAOC) at 4.99 ppm. The signal of CI—CH2— protons at 4.99 ppm decreased after the replaced with the amine group of chlorine atoms in the reaction of P(CIMMAOC) in the presence of diethanolamine, and the novel signals at 3.6 ppm and 2.7 ppm seemed [Figure 2(b)]. The previous result can be ascribed to —CH2 protons between the four protons of the
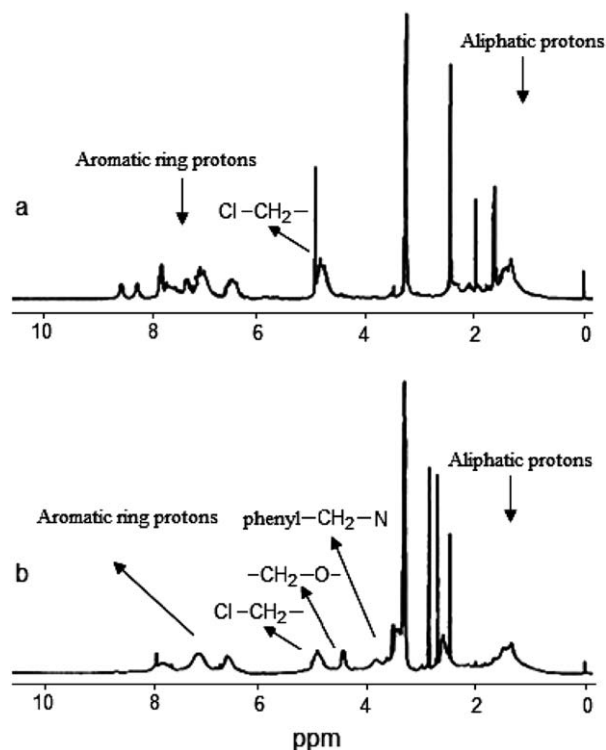
Figure 2. The ^{1}H-NMR spectra of (a) P(CIMMAOC) and (b) P(CIMMAOC)-DEA.
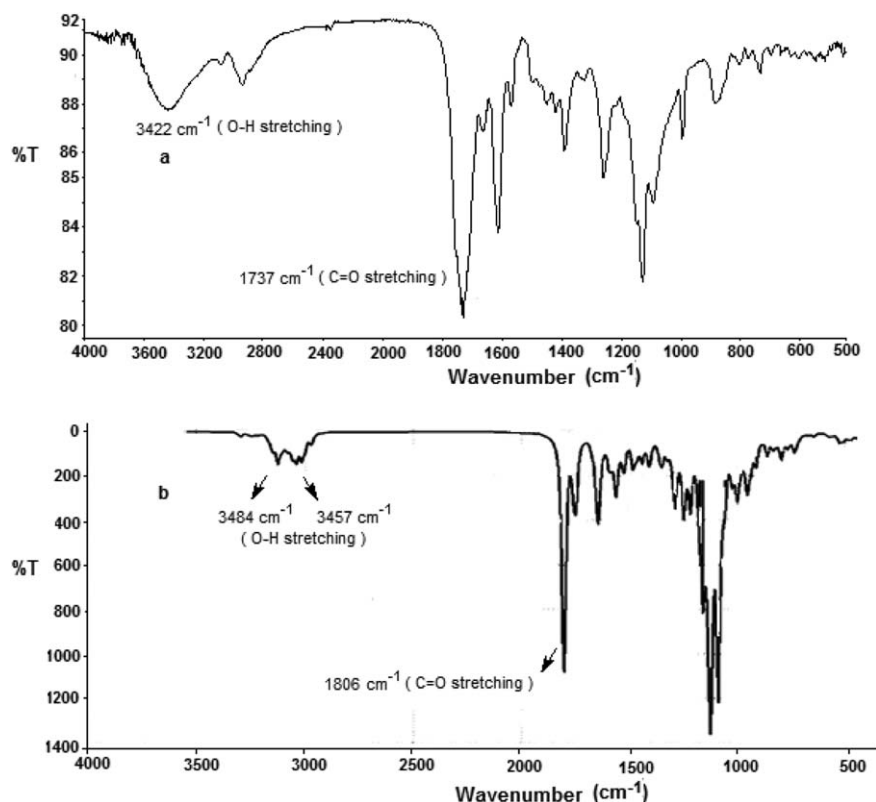
Figure 3. The comparison of (a) experimental and (b) theoretical FTIR for P(CIMMAOC)-DEA (two units).

methylene unity contiguous to the oxygen of the DEA structure and nitrogen. The subsequent signal is a result of the four protons on the methylene corded to nitrogen. The ^{1}H NMR spectrum [Figure 2(b)] of the modified homopolymer, P(CIMMAOC)-DEA, indicates the expected signals at 7.98–6.45 ppm (protons of aromatic ring), 4.99 ppm (CI—CH$_2$— protons), 3.52 ppm (phenyl–CH$_2$–N protons), 2.6 ppm (—N—CH$_2$— protons), and 2.5–1.7 ppm (—CH$_3$ and —CH$_2$ protons in the polymer chain), and other details are indicated in Figure 2.

Computed Vibrational Frequency Analysis

Figure 3(a) indicates the experimental FTIR spectra of P(CIMMAOC)-DEA has a characteristic absorbance at 3422 cm^{-1} (O—H stretching vibration), 3090–3005 and 2990–2855 (—CH stretching of the aromatic and aliphatic), 2986 (—CH3), 1737 (C=O stretching vibration), 1614 (C=C stretching of the aromatic ring), 1230 (asymmetric C—O—C), and 1142 (symmetric C—O—C).

Figure 3(b) indicates the theoretical FTIR spectra of P(CIMMAOC)-DEA has two characteristic absorbance at 3457 and 3484 cm^{-1} O—H stretching vibration. The aromatic C—H stretching vibrations in coumarone ring are hoped to see in the 3302–3213 cm^{-1} frequency ranges as multiple weak signals. In the presence of the substituent, these signals can not be very affected.[41,42] The aliphatic C—H stretching vibrations of polymer are hoped to see in the 3169–3120 cm^{-1} frequency ranges as multiple weak signals. Two diverse kinds C=O stretching

vibrations are observed at coumarone compounds. The first one is C=O stretching vibrations and these are observed in the region 1757–1746 cm^{-1}. The second one is C=O ring stretching vibrations. The C=O ring stretching vibrations is observed in the region 1780–1700 cm^{-1}.[43,44] In this work, the signals were observed at 1806 cm^{-1} belong to C=O group. The theoretical wavenumber is at 1801 cm^{-1} for two conformers of coumarone. The reported values of stretching vibrations of C—O—C in the coumarone ring was 1216 and 919 cm^{-1} for 3– (bromoacetyl) coumarone[43] 1297 and 909 cm^{-1} for 3-cyano-4-methylcoumarone.[45] In this work, these vibrations were observed at 1254 and 838 cm^{-1} in FTIR spectrum. The C—N and C—Cl stretching vibrations are observed in the region 1190–1091 and 772–738 cm^{-1}, respectively. The theoretical and experimental vibrations of polymer in this work indicates an agreement with the literature data.

Molecular Orbitals (MOs) can directly give us insights into the nature of electronically excited state of polymer. The LUMOs and HOMOs are named as frontier molecular orbitals (FMOs). In this work, the FMOs of the polymer were calculated and indicated in Figure 4. According to the results obtained using DFT/B3LYP method, polymer conforms to the orbital passing from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. From HOMO to LUMO, the obvious electron density distribution is surveyed for polymer. FMOs play a part in not only the electronic and optical features, but also in UV–vis spectra and quantum chemistry. The HOMO reflects the capability to give an electron whereas LUMO as
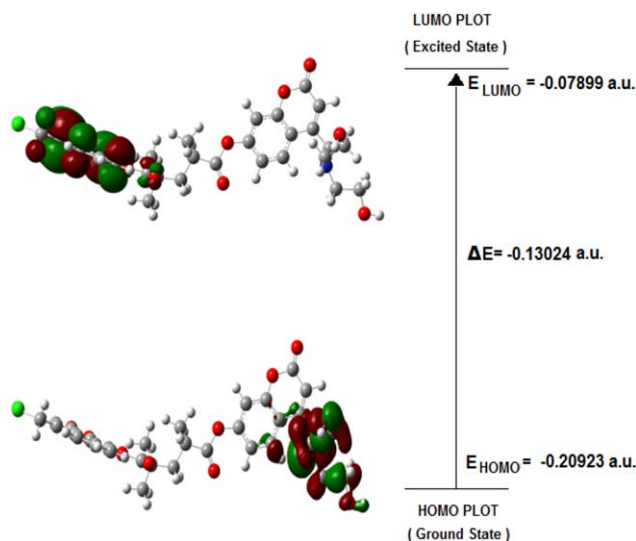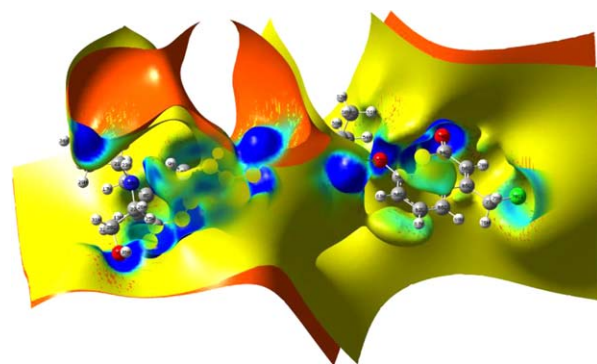
Figure 4. The Frontier Molecular Orbitals (FMOs) for P(CIMMAOC)-DEA (two units). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]


Figure 5. The electrostatic potential (ESP) map for P(CIMMAOC)-DEA (two units). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electron acceptors reflect the capability to receive the electron. The energy gap between the LUMO and HOMO reflects not only the hardness and softness of the molecule, but also molecular chemical stability and chemical reactivity.[46]

The energy gap between ($\Delta E = \text{HOMO–LUMO}$) transition from HOMO to LUMO of the molecule were computed by the Becke3–Lee–Yang–Parr (B3LYP) functional using 3–21G* basis set and the calculation was about -0.13024 a.u. The Frontier orbitals, which the lowest and highest occupied molecular orbitals, are most significant because they help to comprehension the bonding properties of the molecule. The lowest and highest unoccupied molecular orbitals, which LUMO and HOMO, indicated in Figure 4. The highest occupied molecular orbital is placed mostly on the amino group, whereas the lowest unoccupied molecular orbital is placed mostly on the chloro group.

Electrostatic potentials (ESP) have been used to explicating and estimating the reactive behavior of a great variety of chemical

systems in not only electrophilic but also nucleophilic reactions.[47] On the surface of polymer, ESP measurements identify two complementary regions within molecule.

That is, we can say that the negative ESP is located more over the oxygen, chlorine and nitrogen atoms and is reflected as a rufescent or yellowy spot, the positive ESP is localized on the rest of the molecules.[47,48] The ESP map of P(CIMMAOC)-DEA is indicated in Figure 5.

UV–vis Absorption of Polymers

The UV–vis spectra of polymers are indicated in Figure 6. The strong UV–vis absorption peak are shown at about 320 nm. Even so, the weaker UV–vis absorption intensities of the polymer from 280 nm to 325 nm wavelength could be ascribed to the evanescence of inter- or intra-molecular exciton between the electron lacking acrylic carbon–carbon couple bonds and the electron giver chromophore.[49] Moreover, the UV–vis spectra of different rates of P(CIMMAOC)-DEA were gauged and are indicated in Figure 6. The results in Figure 6 indicate that the different rate of DEA had a significant effect on the UV–vis spectra. This status was along with the constant concentration of coumarone chromophore ($<1.10^{-4}$ mol L^{-1}). The UV–vis spectrum of P(CIMMAOC) before and after the modification was indicated in Figure 6. The increase of the absorption band at 325 nm with
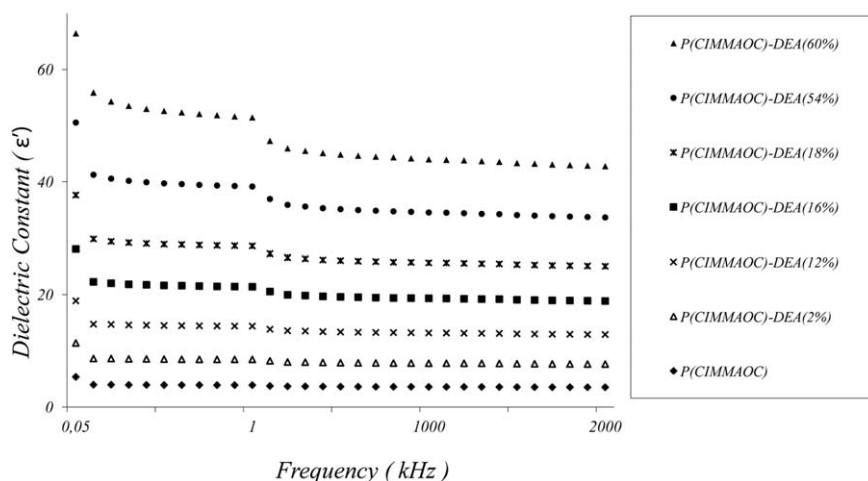
Figure 6. The UV-vis absorption spectral change of P(CIMMAOC) with modification.
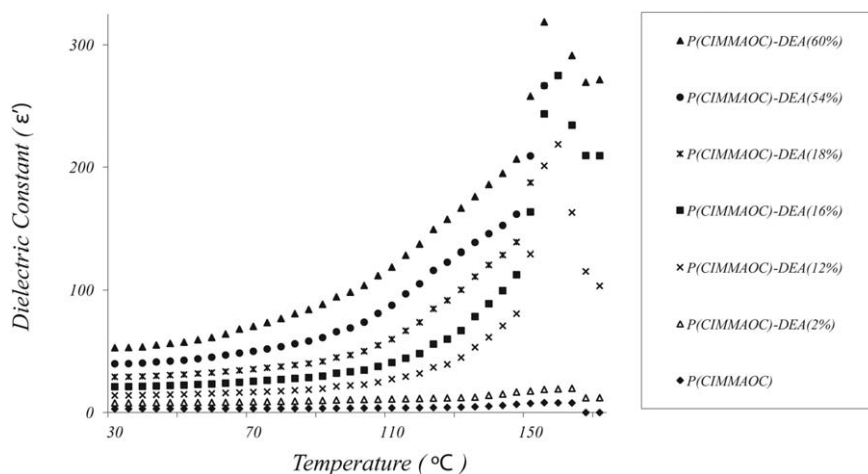
Figure 7. The emission spectral change of P(CIMMAOC) with modification.

modification is ascribed to the inter- and intra-molecular interplays. These interplays may include the spin or align of the dipoles available in the polymer with the increase of rate modification.

Fluorescence Intensity of Polymers

The fluorescence spectra of polymers are indicated in Figure 7, and indicated a strong fluorescence peak at about 406 nm. This peak wavelength was the characteristic fluorescence peak of the coumarone chromophore.[50] The fluorescence intensity of polymers increased with the raising concentration of polymers with the constant concentrations of coumarone chromophore. This status explained that the increase in fluorescence intensity of the polymer could be ascribed to the structural self-quenching effect with the interaction between the electron lacking chromophore and the electron giver carbon–carbon couple bond present in the polymer.[51–54] With increasing the hydrogen bonding, it was observed that the absorbance of coumarone red-shifted and its emission widened.[55] In addition to this, the hydrogen bonding also shifts both the absorption and emission peaks. A dual fluorescence detected for P(CIMMAOC)-DEA with emission peaks centered at 385 and 455 nm respectively. The emission peak at shorter wavelength (385 nm) is assigned to coumarone and that at the longer wavelength (455 nm) is assigned to DEA. This result indicates that in aprotic solvent, the P(CIMMAOC)-DEA exists as two different emission peaks due to hydrogen bonding.

Dielectric Constant Values

A measure of the effect of a certain dielectric on the capacitance of a capacitor is the dielectric constant. The value of dielectric constant shows how much bigger or smaller the place keeps. When a dielectric is placed between two electric loads, it decreases the motion force between them, just as if they had been moved apart from each other. Therefore, the dielectric constant of a material affects how electromagnetic signals pass through the material. The frequency- and temperature- dependent measurements of dissipation factor, Df, and parallel capacitance, Cp, were obtained with impedance analyzer for various frequencies in the range 0.05 kHz–2 MHz and from room temperature to 180°C. The dielectric constant (ε') and dielectric

loss factor (ε'') were determined as per the following expressions: where $\varepsilon°$ is permittivity in free space $(\varepsilon° = 8.854.10^{-12}$ F/m),[28] Cp is parallel capacitance, A is surface area of the polymer specimen, and d is thickness of the specimen. If an electric field is loaded on the P(CIMMAOC), the polymer occurs polarized. And the quantity of the accumulated charge is related to the polarity of the polymer. As the polarization of the polymer having new additional functional groups makes an additional contribution to the accumulated charge, the quantity of accumulated charge in case of modified P(CIMMAOC) will rise. The plot of dielectric constant, ε' versus frequency for P(CIMMAOC) and P(CIMMAOC)-DEA (2, 12, 16, 18, 54, and 60%) at various frequencies for constant temperatures is indicated in Figure 8, respectively. The dielectric constant of homopolymer was determined in the range 3.01–7.84 at 1 kHz. This tendency in dielectric constant is in concordance with the reported data for analogic poly(methacrylate) systems.[56–58] Figure 8 indicates the dependence of the dielectric constant on frequencies (0.05 kHz–2 MHz) for P(CIMMAOC) and P(CIMMAOC)-DEA (2, 12, 16, 18, 54, and 60%). According to that of its modified, the dielectric constant of P(CIMMAOC) has a value very lower. The dielectric constant (ε') occurs larger at lower frequencies and at higher temperatures, which is ordinary in oxide glasses and isn't a sign of self-produced polarization.[59] This may be due to the fact that as the frequency rises, the polarizability contribution from ionic and adoption sources declines and eventually vanish because of the immotility of the ions. Also, this may be because of the tendency of induced dipoles in the polymer to adapt themselves in the direction of the applied field.[60]

The decline in bond energies is generally associated with the rise of ε' with temperature.[61] In other words, when the temperature rises two impacts on the dipolar polarization may become. First one, it gets weaker the intermolecular forces and so raises the positional vibration. Second one, it raises the thermal tension and so violently discomforts the positional vibrations. In Figure 9, it can also be seen that ε' value rises with increasing temperature and at high temperatures it rises more quickly. This behavior is alike to the dielectric of polar group in which
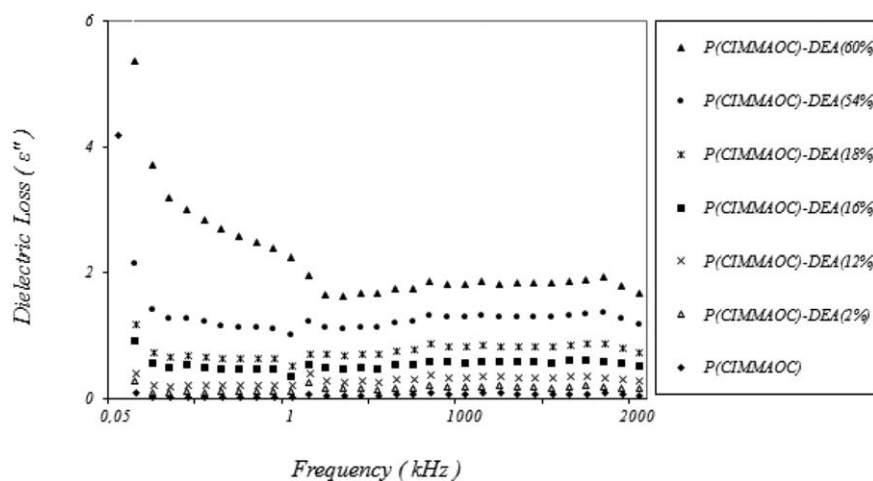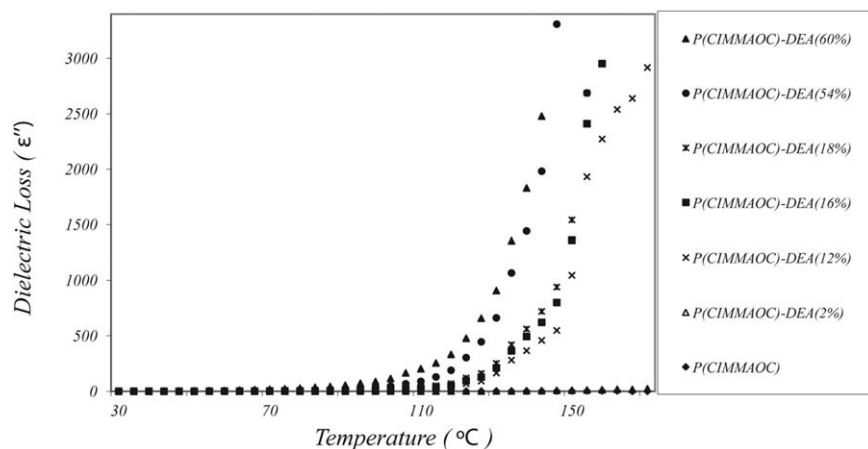
Figure 8. Variation of the dielectric constants of polymers with frequency.

the adoption of dipoles occurs with increasing temperature and thence the dielectric constant is increased. The contribution of ionic and electronic components to the total polarizability will be little at low temperatures. When the temperature is increased, the ionic and electronic polarizability sources begin to rise or the dipoles relatively occurred free and they reply to the applied electric field.[62] The glass transition temperatures (Tg) of polymers are closed to these temperatures. Figure 9 indicates the variation of dielectric constant with temperature at 1 kHz for seven different specimens. Though the values of ε' rise with the temperature at a fixed frequency for all the specimens, this rise is very slow for P(CIMMAOC). The rise in ε' with temperature is due to more freedom of motion of the dipole molecular group in the polymer chain at high temperature. At lower temperature, the field cannot change the condition of dipoles. As the temperature rises, the dipoles relatively occur free and they react to the applied electric field. This condition causes an increase in polarization and dielectric constant with temperature.[60,63] These temperatures are values closed to glass transition temperatures of corresponding polymers (from 145 to 163°C). The rise of ε' values with temperature up to Tg is performed fundamentally by the change in the intra- and

inter-molecular interplays. These interplays may include the spin or align of the dipoles available in the polymer with the rise of temperature. Above Tg, the dielectric constant begins to fall due to the rise in the irregular thermal vibration of the molecules and the reduction degree of the order of the conformance of the dipoles.[64] In all the polymers the ε' were observed not only decreased with frequency but also increased with temperature.

Figure 10 indicates the variation of dielectric loss factor ε'' with rising frequency at constant temperatures of all the polymers. Because of dispersion occurs, the dielectric constant decreases with frequency. Figure 11 indicates the variation of dielectric loss factor ε'' with rising temperature at 1 kHz frequency for all the polymers. The values of ε'' increased with temperature, especially in the vicinity of the glass transition temperature of the polymers. That is to say the dielectric loss factor due to chain motion of P(CIMMAOC) and P(CIMMAOC)-DEA are more efficient in the vicinity of the glass transition temperature. Due to motion of polymers, dielectric loss factor is more influential in the vicinity of the Tg. Consequently, the variation of dielectric loss factor is akin to that of dielectric constant.

Figure 9. Variation of the dielectric constants of polymers with temperature.
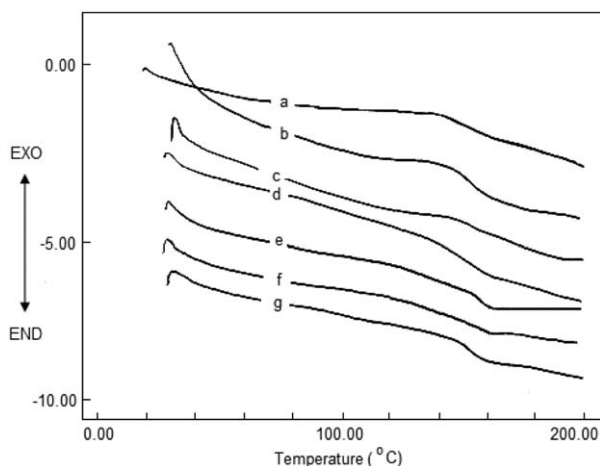
Figure 10. Variation of dielectric loss factor of polymers with frequency.

Figure 12. DSC traces of polymers.

P(CIMMAOC)-DEA (60%) has the highest dielectric constant. The strong effect of the hydroxyl group on molecular polarity can cause this condition. The dielectric constant (ε') and dielectric loss factor (ε'') values are attained in the frequency range from 0.05 kHz to 2 MHz for both P(CIMMAOC) and P(CIMMAOC)-DEA (2, 12, 16, 18, 54, and 60%). The results are indicated in Figures 8–11. It is noticed that the dielectric constant reduces rapidly up to about 100 Hz after which it declines very gradually for all the specimens just as the dielectric loss factor reduces and the Tg of polymers are closed to these temperatures.

The Tg of P(CIMMAOC) and other polymers were determined from the inflection points on the differential scanning calorimetry (DSC) curves. The glass transition temperatures of polymers are indicated in Figure 12 and Table I. All the polymers showed a single transition. P(CIMMAOC) had a Tg value lower than those of all the P(CIMMAOC)-DEA. This is due to more hydrogen bonding due to ─OH group in P(CIMMAOC)-DEA. The similar behavior is also stated in the literature.[65,66] This
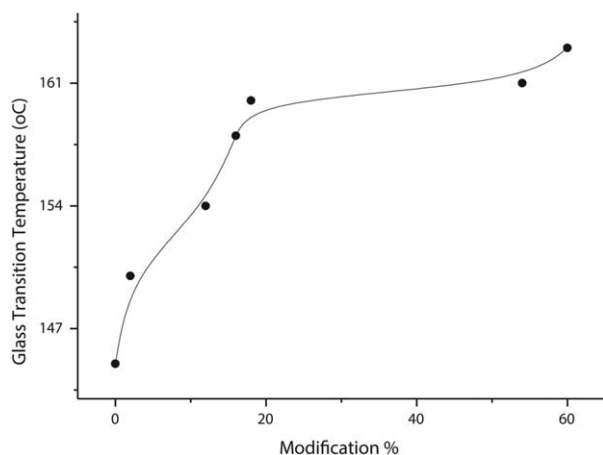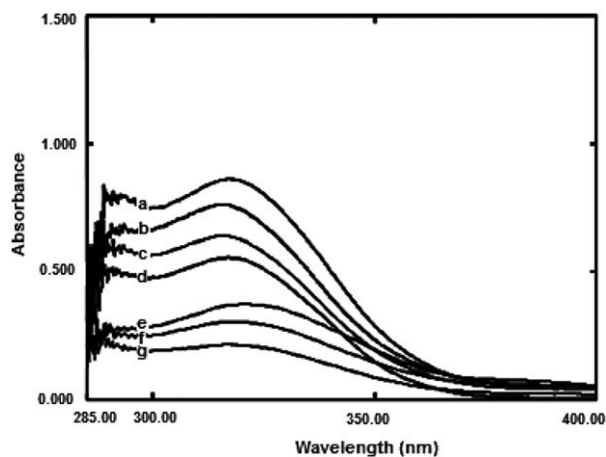
may be because of the disposition of induced dipoles in the polymer to adapt themselves in the course of the applied field.[50]

To detect the variation of glass transition temperature with modification, we used Tg of polymers determined by DSC curves and concentration of DEA in polymer. This variation is indicated in Figure 13.

CONCLUSIONS

Poly(4-{[bis(2-hydroxyethyl)amino]methyl}-2-oxo-2H-chromen-7-yl-2-methyl propanoate) polymers were synthesized by modification of poly(4-(chloromethyl)-2-oxo-2H-chromen-7-yl-2-methylpropanoate) with diethanolamine. The FTIR and ¹H NMR results affirmed the structures of all the polymers. The dielectric properties of the synthesized polymers measured as a function of frequency and temperature. The dielectric constant and loss factor of polymers increased with temperature and decreased in the applied frequency range. As the modification of P(CIMMAOC) increased the dielectric constant increased. That is, the dielectric constant increased with rise of polar side groups in the polymer chain. The reason could be attributed to raising the strength of the bonds with the interaction between –OH groups of polymer. The values of dielectric constant increased with a rise in concentration of DEA in polymer. This study, P(CIMMAOC)-DEA (60%) has the highest dielectric

Figure 11. Variation of dielectric loss factor of polymers with temperature (1 kHz).

Table I. Dielectric Constant and Glass Transition Temperature for Polymers

Polymers	Dielectric constant (ε') at 1 kHz	Tg (°C)
P(CIMMAOC)	3.93	145
P(CIMMAOC)-DEA (2%)	4.57	150
P(CIMMAOC)-DEA (12%)	5.93	154
P(CIMMAOC)-DEA (16%)	7.00	158
P(CIMMAOC)-DEA (18%)	7.19	160
P(CIMMAOC)-DEA (54%)	10.57	161
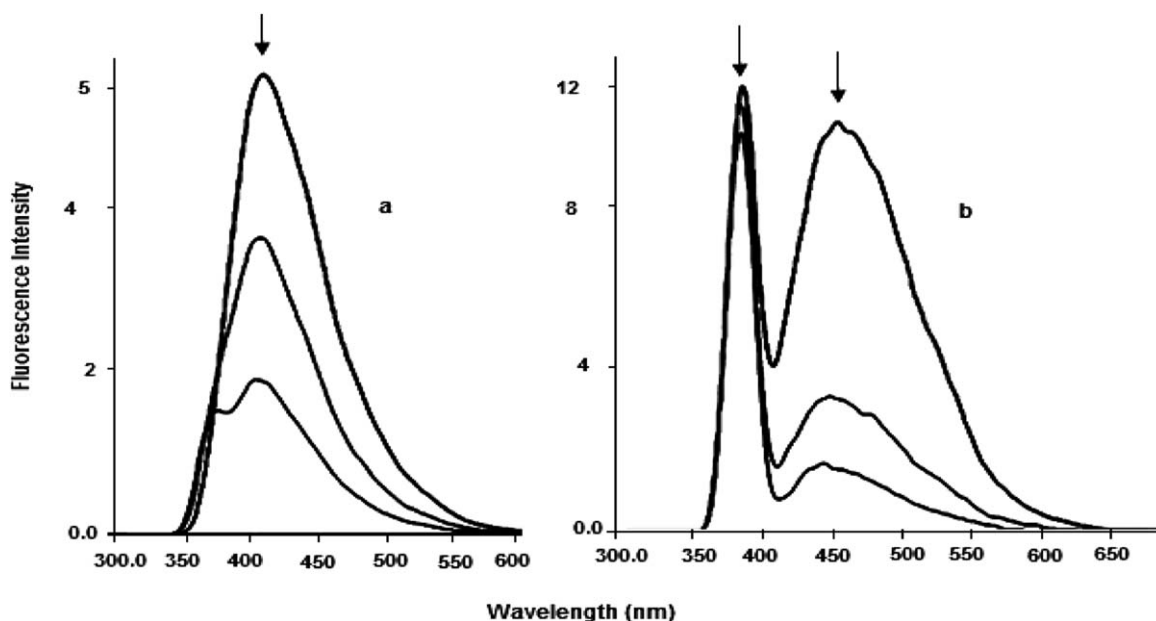
Figure 13. Variation of glass transition temperature of P(CIMMAOC) with modification.

constant. Result likely from the strong effect of the hydroxyl group on molecular polarity. The dielectric constant and loss factor of P(CIMMAOC)-DEA as found to be much higher to that of P(CIMMAOC). The reason could be attributed to raising the strength of the bonds with the interaction between –OH groups due to polar side groups in the polymer chain. This is due to more hydrogen bonding due to ─OH group in P (CIM-MAOC)-DEA. The values of dielectric in the polymer depend on rise in concentration of diethanolamine. The rise in dielectric constant with temperature up to Tg because of a solid/solid phase transition. This well-known feature is a characteristic of the inactivation of the dipolar motion without long range correlation.[64] The fluorescence intensity of P(CIMMAOC) and of P(CIMMAOC)-DEA increased with increasing concentration. The fluorescence intensity of P(CIMMAOC)-DEA was differed from that of the P(CIMMAOC) due to hydrogen bonding. The theoretical FTIR was calculated and the scaled values were compared with experimental FTIR spectra. The differences between the observed and scaled wavenumber values are very small.

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