New Unsaturated Copolyesters: Synthesis and Characterizations

Momen S.A. Abdelaty
Polymer Lap, Chemistry Department, Faculty of Science (Assiut),
Al-Azhar University, Assiut, Egypt

Abstract — New series of unsaturated copolyesters based on diarylidene cyclohexanone, were synthesized by the interfacial polycondensation polymerization technique. Aldol condensation reaction in acid media was used for preparation of three kinds of monomers and investigated by FT IR and 1H NMR. The copolymers have been synthetized by the polymerization of 2,6-bis(4-hydroxybenzylidene) cyclohexanone I, 2,6-bis(3-hydroxybezylidene) cyclohexanone II, or 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone III with isophthaloyl, terphthaloyl, adipoyl, sebacoyl and azobenzene 4,4-dicarboxyldichloride. The resulting copolyesters were characterized by FT-IR, 1HNMR. The intrinsic viscosity of these copolyesters was used for the determination of the molecular weight. The thermal stabilities of the prepared copolyesters were evaluated thermogravimetric analysis (TGA). Differential thermal analysis (DTA) was used for determination of glass temperatures. X–ray analysis showed that polymers have low degree of crystallinity. The morphological properties of some selected copolyesters were detected by SEM. The dielectric and electrical resistance, capacitance, inductance, demonstrating the insulator behavior of copolymers.

Keywords — Copolyester; Unsaturated; Synthesis; Characterization; Diarylidene cyclohexanone; Dielectric.

I. INTRODUCTION

Unsaturated polyesters are among the most common polymers used in conjunction with glass fiber reinforcing [1, 2] and widely used as thermosetting resins in various industrial areas [3-5]. They are prepared by polycondensation of diacids and diols using titanium or tin alkoxides as catalysis [6]. The reaction temperature is usually up to 150 °C [6, 7]. For this condition many monomers are not suitable for the formation of linear polyesters, due to uncontrollable side reactions and formation of gel [8-10]. Typically linear unsaturated polyesters processed to a relatively low molecular weight then it is dissolved in a monomer such as styrene to form a viscous solution. Crosslinking occurred usually initiated with free radical initiator, as vinyl copolymerization between the polyester and the solvent as vinyl acetate or methyl methacrylate. Halogenated monomers can use for improving flame-resistance, such as ortho- and para-bromostyrene [11, 12]. The unsaturation has been commercially synthetized by introducing low cost material like maleic anhydride and fumaric acid in the polymer main chain [13]. If only unsaturated acid and glycol are used, the final product is too highly cross-linked and brittle to be useful. For this reason, copolyesters are normally prepared containing both unsaturated acid and a non-cross-linkable acid [13]. Due to the highly extensive uses of unsaturated polyesters, recycling process has been suggested to solve the problems of waste materials. One recent method involves the alcoholises of waste resin with propylene glycol, followed by re-esterification with additional maleic anhydride [14, 15]. More
styrene is then added to the reconstituted polymer for cross-linking. Many studies for fabricated polyesters using biocatalysts and green monomers from renewable resources were introduced, attributed to the eco-friendly products. Furthermore, polymers are biodegradable [16,17]. Nowadays, many studies were focused on the formation of unsaturated polyester composites and their mechanical properties [18-19]. Others studied the unsaturated polyesters as layered silicate nanocomposites [20]. The ratio of the capacitance of a condenser containing the material to the capacitance under vacuum referred to the dielectric constant of material ($\varepsilon$). The capacitance of a condenser measures the extent of charges was stored. One approach has focused on studying polymer thin films and their electrical properties with special interest to dielectric behavior for their important applications as insulation, isolation and microelectronics [21, 22]. Addition of some conducting fillers to improve the magnitude of electrical conductivity of insulating polymers materials have been published in recent articles [23, 24]. The dielectric constant was measured for a variety of materials like cellulose, [25] protein, and synthetic fibers [26].

The work presented here outlines the synthesis and characterization of new copolyesters of diarylidene cyclohexanone. A major target for this work was to study the effect of alkyl-cycloalkanone moiety on the thermal stability properties of copolyesters. The crystallinity, solubility, morphologic properties of this new class of copolyesters were also examined. Moreover, the electrical properties have been measured for the solid polymers.

II. EXPERIMENTAL

2.1 Materials

p-Hydroxybenzaldehyde and m-Hydroxybenzaldehyde were purchased from Aldrich (Germany). 4-Hydroxy-3-methoxybenzaldehyde (vanillin) from El-Nassr Chemical Company (Egypt). p-Nitrobenzoic acid from Merck (Germany). Adipoyl, sebacoyl, isophthaloyl and terephthaloyl chlorides were purchased from Merck (Germany), Cyclohexanone Fluka (Germany). Other chemicals were purchased from Aldrich, Merck, Fluka or BDH companies and purified by standard methods.

2.2 Instrumentations

The infrared spectra for all solid samples were recorded on IR–470 infrared spectrophotometer, Shimadzu; and Pye Unicam SP3-100 spectrophotometer (Japan) using KBr pellet technique. Nuclear Magnetic Resonance spectra for monomers and models were recorded on a Varian EM-390 (90MHz) spectrometer and GNM-LA (400MHz) (USA) spectrophotometer at room temperature in DMSO or CDCl3 using TMS as the internal reference. Nuclear Magnetic Resonance spectra for polymers were recorded on a Bruker AVANCE 500 (USA) spectrometer (500 MHz) at room temperature in CF3COOD. The ultra-violet visible spectra were scanned on U.V.-Visible spectrophotometer, Labomed, (USA), Spectro Double Beam 8 Auto cell, U.V D 3200, 190-1100nm in conc. H2SO4 as solvent. The solubility of the polymer were examined using 0.02 g of polymer In (3-5 ml) of solvent at room temperature. The inherent viscosities of the polymer solution (0.5%w/v) in conc. H2SO4 were determined at 30 °C using an Ubbelohde suspended level viscometer VWR (Germany). X-ray diffract graphs of the polymer were obtained with Philips X-ray Pw 1710 (Japan) diffractometer, using Ni-filtered CuKα radiation. Thermogravimetric analysis (TGA), differential thermal analysis they are carried out in air with Shimadzu TGA-50 and DTA-50 (Japan), thermal analyzer at heating rate of 10 °C/min. The morphology of the polymer were examined by Scanning Electron Microscopy (SEM) using a JSM-5400 LV instrument; images were recorded with a Pentax Z-50P Camera with Ilford film at an accelerating voltage of 15KV (USA). Dielectric constant, capacitance, inductance, resistance of polymers were analyzed by HIOKI 3532-50LCR Hi TESTER apparatus 4(Japan) in the form of disks with 10 mm diameters and different thickness.

2.3 Synthesis of monomers I, II, III and their models Ia, IIa, IIIa.

The monomers I and III and their models were synthesized as described in our previous work [27, 28]. A new monomer II and its model were prepared by the same procedure by condensation of m-hydroxy benzaldehyde with cyclohexanone for 3 hrs. as brown needles from ethanol, yield 91%, m.p 215°C.
Model IIa was obtained by the reaction of 2,6-bis(3-hydroxybenzylidene) cyclohexanone and benzoyl chloride as yellow plates from benzene yield, 93%, m.p 216 °C.

$^1$H NMR (90 MHz, DMSO-d$_6$, δ): = 9.75 ppm ( s , 2H, 2OH group ), at 7.65 ppm ( s , 2H of 2CH=C ) ; at 6.8 - 7.35 ppm ( m , 8H of Ar -H ) , at 2.85 ppm ( m , 4H of 2CH2 ) and at 1.85 ( pented , 2H of CH¬2 of cyclohexanone ).

IR (KBr)(II monomer): $\nu =$ IR spectra recorded from KBr pellets showed characteristic bands for C=O cyclohexanone at 1690-1700 cm$^{-1}$; C=C stretching at 1590-1600 cm$^{-1}$; phenylene rings at 1590-1510 cm$^{-1}$.

$^1$H NMR (90 MHz, CDCl$_3$, δ): 8.25- 8.60 ppm (m , 4H 30,34,35,39 Ar-H), 7.50 – 8.10 ppm  (m , 12H 14-19 ,31-33, 36-38 Ar-H), 7.15 –7.25 ppm  (s , 2H ,8,9- CH=C), 2.60- 2.90 ppm ( t ,4H,2,4- 2CH2 ), 1.25 – 1.85 ppm (pent . , 2H 3- CH2 ) of cyclohexanone.

IR (KBr) (IIa model): $\nu =$ 1735 (s) (C=O of ester group), 1670 (s) (C=O of cyclohexanone ) , 1600 (s) ( C=C ).

### 2.4 Synthesis of 4,4-azodibenzoyldichloride

This has been done in two steps the first is the formation of azobenzene 4,4-dicarboxylic acid followed by conversion to acid chloride azobenzene 4,4-dicarboxylchloride as described previously [29,30].

### 2.5 Synthesis of Copolymers

In a three necked, round – bottomed flask (500 cm$^3$ volume) equipped with a mechanical stirrer (2000 rpm/min ), dry nitrogen inlet and out let, and dropper, a mixture of two different monomers (mol/mol ) of diarylidenecyclohexanone, and a suitable quantity of sodium hydroxide; that is stoichiometric quantity (0.02mol ) of 100% excess (0.04 mol ) dissolved in 100 ml of water was introduced. After mixing (0.02 mol.) of acid chloride dissolved in 40 ml methylene chloride was added over a period 2-3 min. at 25 °C and vigorously stirring. After complete addition of acid chloride, the stirring was continued for 60 min., during which yellow solid product separated out. The solid polymer was filtered off, washed by water, hot ethanol, hot acetone, and dried under reduced pressure (1 mmHg) at 100 °C for two days. Three copolysters series were separated and casted from methylene chloride.

Copolysters of series IV were prepared by copolymerization of monomers 2,6-bis(4-hydroxybenzylidene) cyclohexanone I, 2,6-bis(3-hydroxybenzylidene) cyclohexanone II, series V monomers 2,6-bis(4-hydroxybenzylidene )cyclohexanone I, 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone III, and series VI 2,6-bis(3-hydroxybenzylidene) cyclohexanone II 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone III, with acid chlorides IVa (isphthaloyl chloride), IVb (terphthaloyl chloride), IVc (adipoyl chloride), IVd (sebacoyl chloride) and IVe (azobenzene 4,4-dicarboxylchloride) as shown in Table 1.

### Table 1: Mole Ratios Of Monomers, Acid Chlorides, Physical States, Yield%, Viscosity Average Molecular Weight And Glass Temperature Of Synthetic Copolyesters Series IV, V And VI.

<table>
<thead>
<tr>
<th>Code</th>
<th>Acid chloride (0.04mol) in 100ml dry CH$_2$Cl$_2$</th>
<th>Yield [%]</th>
<th>Mv $10^3$ g/mol</th>
<th>T$_g$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Series IV</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Va</td>
<td>4.02g</td>
<td>93</td>
<td>9.00</td>
<td>70</td>
</tr>
<tr>
<td>Vb</td>
<td>4.02g</td>
<td>91</td>
<td>8.78</td>
<td>78</td>
</tr>
<tr>
<td>Vc</td>
<td>3.66g</td>
<td>87</td>
<td>8.45</td>
<td>55</td>
</tr>
<tr>
<td>Vd</td>
<td>4.76g</td>
<td>82</td>
<td>10.75</td>
<td>67</td>
</tr>
<tr>
<td>Ve</td>
<td>6.14g</td>
<td>83</td>
<td>7.43</td>
<td>95</td>
</tr>
<tr>
<td><strong>Series V</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Va</td>
<td>4.02g</td>
<td>88</td>
<td>6.89</td>
<td>65</td>
</tr>
<tr>
<td>Vb</td>
<td>4.02g</td>
<td>91</td>
<td>8.93</td>
<td>82</td>
</tr>
<tr>
<td>Vc</td>
<td>3.66g</td>
<td>85</td>
<td>9.38</td>
<td>77</td>
</tr>
<tr>
<td>Vd</td>
<td>4.76g</td>
<td>94</td>
<td>9.77</td>
<td>80</td>
</tr>
<tr>
<td>Ve</td>
<td>6.14g</td>
<td>83</td>
<td>6.55</td>
<td>105</td>
</tr>
<tr>
<td><strong>Series VI</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vla</td>
<td>4.02g</td>
<td>94</td>
<td>9.73</td>
<td>88</td>
</tr>
<tr>
<td>Vlb</td>
<td>4.02g</td>
<td>90</td>
<td>7.45</td>
<td>93</td>
</tr>
<tr>
<td>Vlc</td>
<td>3.66g</td>
<td>92</td>
<td>7.75</td>
<td>85</td>
</tr>
<tr>
<td>Vld</td>
<td>4.76g</td>
<td>89</td>
<td>8.32</td>
<td>86</td>
</tr>
<tr>
<td>Vle</td>
<td>6.14g</td>
<td>87</td>
<td>6.23</td>
<td>115</td>
</tr>
</tbody>
</table>

**III. RESULTS AND DISCUSSION**

Here, in this study we used new monomers based on 3-
hydroxybenzaldehyde for the formation of 2,6-bis(3-hydroxybenzylidene) cyclohexanone II by the reaction condition as described in Scheme 1. Further, the model compound was also synthesized and both were characterized by IR and $^1$HNMR.

The new copolyester series containing diarylidenecyclohexanone moiety in the main chain were synthesized by interfacial condensation polymerization technique for one mole of both monomers and two moles of acid chloride as described in scheme 1. The same technique was used to synthesize a series of polyesters and copolyesters of diarylidenecyclopentanone [31].

Scheme 1: Synthesis of 2,6-bis(3-hydroxybenzylidene cyclohexanone) II, its model compound and copolyesters of series IV, V and VI.

3.1 Polymer characterizations

**IR spectra:** IR spectra recorded from KBr pellets was mixed with respective polymer showed characteristic bands for C=O ester at 1730-1745 cm$^{-1}$; C=O cyclohexanone at 1690-1700 cm$^{-1}$; C=C stretching at 1590-1600 cm$^{-1}$; phenylene rings at 1590-1510 cm$^{-1}$; and C=O-C bonds (ether linkage) at 1250-1260 cm$^{-1}$.
3.1.1 ³H NMR spectra

³H-NMR spectra were recorded using a BRUKER DRX-500 spectrometer. ³H-NMR spectra were measured at 25 °C in CF₃COOD as an internal reference. The chemical shifts (in ppm) are referenced to tetramethylsilane Figure 1, shows the ³H-NMR for selective copolymers (Va, Vd, Ve, Vla, Vlb, Vle) all spectra recorded the presence of: 0.90-1.05, 1.30-1.65, 3.00-3.50 ppm (m-CH₂-cyclohexanone), 4.00-4.30 ppm (m-OCH₃), and 7.00-8.90 (m-Ar-H). Moreover, polymer Vd with sebacate main chain showed at 2.5-2.90 ppm (m-CH₂).

3.1.3 The Viscosity average molecular weight (Mᵥ)

Polymers under measurement and standards were dissolved in trifluoroacetic acid as solvent. The viscosity average molecular weights of polymers were determined according to Mark-Houwink equation [32-33] as shown in Table 1.

3.1.4 Thermal analysis

The thermal stabilities of selected examples of copolyesters were evaluated by thermogravimetric analysis (TGA), Differential thermal analysis (DTA) in air at a heating rate of 10 °C min⁻¹.

3.1.5 Thermogravimetric analysis (TGA)

TGA curves of all polymers showed similar patterns of decomposition. The temperature for 10% weight loss is

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series IV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IVa</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>IVb</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>IVc</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>IVd</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>IVe</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Series V</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Va</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Vb</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Vc</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Vd</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Ve</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Series VI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vla</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Vlb</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Vlc</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Vld</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Vle</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Figure 1: ³H NMR (CF₃COOD) of copolyester.

Table 2: Solubility Characteristics of Copolyesters Series IV, V and VI.
considered to the polymer decomposition (PDT), temperature ranges between 280 –370 °C. It should be noted from Figure 2A that copolyester that contain aliphatic group in the main chain are thermally less stable than the other with aromatic groups in the main chain. It should be noted that the presence of methoxy groups in the main chain increase the thermal stabilities.

It is clear that copolyesters with azo group as shown in Figure 2B underwent decomposition in two stages. The first stage in the thermal decomposition of these polymers may be the elimination of azo group, probably as molecular nitrogen. Back and Black [34], reported that the first step in the thermal decomposition of certain aromatic polymers prepared by oxidative coupling of primary amines occurs in loss of nitrogen.

![Figure 2A, B: TGA of copolyesters.](image)

3.1.6 Differential Thermal Analysis (DTA):

The selected examples of copolyesters were examined by DTA measurements as shown in Figure 3. The values of $T_g$ were summarized in Table 1. From the DTA curves it is easy to determine the glass transition temperature $T_g$ of these copolyesters. It should be noted that polymers with rigid chains would be expected to have $T_g$ higher than those with flexible molecules. This is because, on melting, polymers with stiff backbones have lower conformational entropy changes than those with flexible backbones. The chain flexibility is enhanced by the presence of -COO- and by increasing the length of -(CH$_2$)$_n$- units in the main. The chain rigidity is enhanced by the presence of aromatic groups in the main chains [34].

It should be noted that $T_g$s for copolyesters with azo groups have higher values than copolyesters others. The interpretation, attributed to the presence of azo groups in the copolyester main chain, causes high hindrances to internal rotation about primary valence bonds, and hence raises $T_g$[35]. The higher $T_g$s values of copolyesters Ve and VIe than IVe, attributed to the presence of methoxy groups as aside groups, which increase the intermolecular bonding in copolyester chain, will significantly increase $T_g$ [35].

3.1.7 X-ray analysis:

X-ray diffractograms of selected examples of copolyesters showed an amorphous patterns in the region 2θ = 5-30°, after this region showed a few reflections of sharpness peaks with an amorphous back ground in the region 2θ = 30-60°, this indicate some degree of polycrystallinity of the polymer. It was noted from the Figure 4 that the presence of cyclohexyl ring in the polymer chain beside the presence of methylene groups, four or eight, increase the polymer chain flexibility, that urge the approach and mutual attraction of the adjacent chains might be induced some extent of crystallinity. Moreover, it should be noted that the presence of methoxy groups as substituent in the phenyl ring caused some hindering between the repeating units and enforced its to the unsymmetrical orientation in the polymer chains and reduced the close packed structure and hence these copolyesters exhibit only a low degree of crystallinity [30]. Moreover, in copolyesters (IVe, Ve, Vie) the presence of –N=N- as a polar group in addition to –C=C- bonds induces some order between two adjacent chains in the polymer towards some extent of crystallinity [36-37] as shown in Figure 4.
3.1.8 Morphological features:

The morphology of the synthesized copolyesters was examined by scanning electron microscopy (SEM). The SEM samples were prepared by putting a smooth part of polymer on a copper holder and subsequently coating it with gold palladium alloy. SEM images were taken on a penta Z Z50 P Camera with Ilford film at an accelerating voltage of 15 kV using a low-dose technique [30, 37]. The study of selected examples of copolyesters showed that the surface of copolyester IVa in Figure 5, magnification of X=750 likes scapolite shape which appear as fibrous aggregates. In Figure 6, magnification of X=5000, showed granoblastic, mosaic-type, which likes quartzite rock. In Figure 7, magnification of X=1500 likes coral shape. In Figure 8, high magnification of X=750.

Figure 9 magnification of X=350 showed fibrous aggregates, like scapolite group. In Figure 10 magnification of X=150; appear as granular and compact waxy-looking masses which likes gypstum.

Figures 5: SEM images of copolyesters IVa surface at 750nm magnifications.
IV. CONCLUSION

Here we synthetized new aliphatic and aromatic copolyesters by interfacial condensation polymerization technique. The solubility of polymers was very poor in organic and inorganic solvent except in very strong acids such as sulphuric and trifluoroacetic acids. XRD results showed amorphous case with respect to some semi-crystalline with aromatic and azo copolyesters. Thermogravimetric analyses indicate one and two steps of decompositions. The glass temperature was determined by DTA showed increasing with aromatic and azo copolyesters. The heterogeneous surface with the formation of layers has shown by SEM images.

Figures 6. SEM images of copolyesters, IVd, surface at 5000nm magnifications.

Figures 7. SEM images of copolyesters VIc, surface at 1500nm magnifications.

Figures 8. SEM images of copolyesters, Va, surface at 750nm magnifications.

Figures 9. SEM images of copolyesters Vd, surface at 350nm magnifications.

Figures 10. SEM images of copolyesters IVe surface at 150nm magnifications.
REFERENCES


[34] VS. Prasad, KS. Pillai Synthesis and thermal behavior of thermotropic terpolymers based on 8-(3-hydroxyphenyl)octanoic acid, 2,6-naphthalenedicarboxylic acid, and substituted hydroquinones. J of applied polymer science (82), pp. 1021-1029, 2001.
