

SYNTHESIS AND CHARACTERIZATION OF AN ACRYLATE POLYMER CONTAINING CHLORINE-1,3-DIOXALANE GROUPS IN SIDE CHAINS

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Abstract Poly[2-(4-chlorophenyl)-1,3-dioxolan-4-yl]methyl acrylate, poly(CPhDMA), was synthesized with radical polymerization process using 2,2'-azobisisobutyronitrile as radical initiator in 1,4-dioxane at 60°C. The structure of poly(CPhDMA) was confirmed by means of UV-Vis, FT-IR, ¹H-NMR, and ¹³C-NMR spectral techniques. The molecular weight distribution values of the polymer were determined with gel permeation chromatography (GPC). The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of poly(CPhDMA) were determined to be 10300, 21600 and 2.097, respectively. The thermal degradation kinetics of the polymer was investigated by using TG/DTG-DTA and DSC analyses at different heating rates in dynamic nitrogen atmosphere. The apparent activation energy values obtained by Flynn-Wall-Ozawa and Friedman methods were found to be 91.68 and 85.23 kJ mol⁻¹, respectively, for thermal decomposition of poly(CPhDMA). Also, the thermal degradation activation energy value of poly(CPhDMA) was calculated by using the Kissinger method based on the DTG, DTA and DSC data. Then the mechanism function of it was determined by master plots method. Finally, electrical and optical properties of poly(CPhDMA) were determined by four-point probe and UV-Vis techniques, respectively.

Keywords: Synthesis of acrylate polymer; Thermal degradation; Kinetic parameters.

INTRODUCTION

Polymerization technique is an important and useful way for development of new materials. The synthesis of polymers containing active functional groups is of special interest^[1–8]. Many studies have been carried out on synthesis, thermal stability and solid state decomposition kinetics of methacrylate polymers containing various ester moieties as well as on preparing porous polymer structures by using corresponding monomers (acrylates or methacrylates)^[9–13].

Under proper experimental conditions, information about the solid state decomposition kinetics of a selected polymer can also be obtained from thermogravimetric (TG) analyses. Doğan *et al.* have investigated the thermal behavior, kinetic parameters and mechanism of methacrylate polymer with the isobornyl moiety in the side chain in a nitrogen atmosphere with TG/DTG and DTA^[14]. On the other hand, electrically conductive polymers are a research area for both chemists and solid state physics in the recent years due to their electronic and optical properties. In this paper, we synthesized poly[2-(4-chlorophenyl)-1,3-dioxolan-4-yl]methyl acrylate poly(CPhDMA) by free radicalization process in an organic solution using 2,2'-azobisisobutyronitrile (AIBN) as initiator at 60°C, and then poly(CPhDMA) was characterized by ¹H-NMR, ¹³C-NMR, FT-IR, DSC and SEC analysis techniques. Also, we determined the kinetic parameters (E , A , and mechanisms function) related to the

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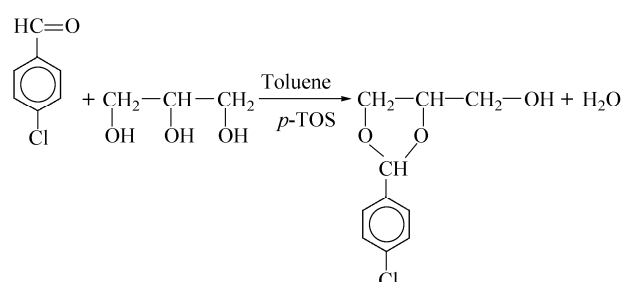
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solid state decomposition kinetics of the poly(CPhDMA) with TG analysis. The electrical and optical properties of poly(CPhDMA) were investigated.

EXPERIMENTAL

Synthesis of [2-(4-Chlorophenyl)-1,3-dioxolan-4-yl]methanol (CPhDM)

Glycerin (6.5 g, 0.07 mol), *p*-chlorobenzaldehyde (10 g, 0.07 mol), toluene (30 mL) and *p*-toluenesulfonic acid (0.6 g, as catalyst) were placed in a 100 mL three-necked flask fitted with a condenser, a thermometer, a stirrer and a dean stark tube (Scheme 1). The mixture was refluxed at 110°C for 1 h with vigorous stirring. The mixture was extracted several times with diethyl ether and then 5% NaOH, toluene and diethyl ether, respectively. The solvents were removed with rotary evaporator. The crude product was washed with water (30 mL $\times$ 2) and dried over anhydrous MgSO₄. The product was characterized by elemental analysis, FT-IR, ¹H-NMR and ¹³C-NMR techniques.

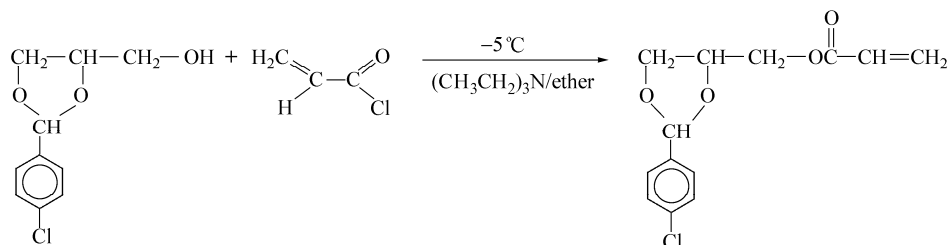


Scheme 1 Synthesis of CPhDM

Calcd. for CPhDM: C, 56.07; H, 5.14. Found: C, 56.47; H, 5.64. FT-IR (KBr, cm⁻¹): 3110–3500, ν (O–H); 2946–2816, ν (C–H aryl and aliphatic); 1550, (aromatic ring, CH=CH); 1180, ν (C–O–C). ¹H-NMR (CDCl₃, δ): 7.46–7.68 (d, 4H, aromatic ring-CH); 5.74 (s, H, aryl-CH); 3.70–4.00 (t, H, –O–CH); 4.11–4.17 (m, 2H, O–CH₂); 3.16 (s, H, –OH); 3.16 (t, 2H, aliphatic-CH₂). ¹³C-NMR (CDCl₃, δ): 63.13 (1C, CH₂); 68.80 (1C, O–CH₂); 77.27 (1C, O–CH); 104.68 (aryl-CH); 126.28–128.00 (4C, aromatic ring-CH); 134.35–137.35 (2C, Aromatic C, ipso carbon).

Synthesis of [2-(4-Chlorophenyl)-1,3-dioxolan-4-yl]methyl Acrylate (CPhDMA)

CPhDM (15 g, 0.07 mol), diethyl ether (30 mL) and triethyl amine (16 mL, as catalyst) were placed in a 500 mL four-necked flask fitted with a condenser, a thermometer, a stirrer and an addition funnel containing 10 mL acryloyl chloride. The acryloyl chloride was added drop wise over the solution, and temperature of the mixture was hold by a cryostat at –5°C for 12 h (Scheme 2). The reaction mixture was extracted several times with 5% NaOH and then dried over anhydrous MgSO₄. Diethyl ether was removed with vacuum evaporator. The obtained monomer was characterized by spectroscopic analyses such as FT-IR, ¹H-NMR and ¹³C-NMR techniques.

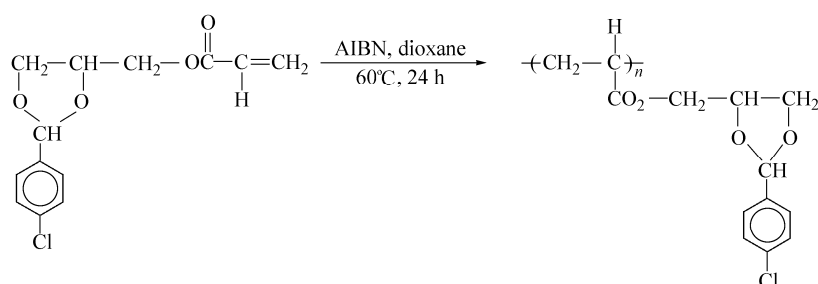


Scheme 2 Synthesis of CPhDMA

Calcd. for CPhDMA: C, 56.69; H, 4.72, Found: C, 57.17; H, 5.14. FT-IR (KBr, cm^{-1}): 3005–2910, $\nu(\text{C}-\text{H}$ aryl and aliphatic); 1727, $\nu(\text{C}=\text{O})$; 1625, $\nu(\text{C}=\text{C})$; 1570, (aromatic ring, $\text{CH}=\text{CH}$); 1195, $\nu(\text{C}-\text{O}-\text{C})$. $^1\text{H-NMR}$ (CDCl_3 , δ): 7.3–7.8 (d, 4H, aromatic ring- CH); 6.35 (s, H, $\text{O}-\text{CH}$); 6.14 (d, H, vinyl= CH); 6.04 (d, 2H, vinyl= CH_2); 5.81 (s, H, aryl- CH); 4.21–3.81 (t, 2H, $\text{O}-\text{CH}_2$). $^{13}\text{C-NMR}$ (CDCl_3 , δ): 72.13 (1C, $\text{O}-\text{CH}_2$); 95.20 (1C, $\text{O}-\text{CH}$); 103.2 (1C, aryl- CH); 125.32–126.05 (4C, aromatic ring- CH); 129.28 (C, $\text{CH}=\text{CH}_2$); 130.02 (C, $\text{CH}=\text{CH}_2$); 135.05–139.41 (2C, aromatic C, ipso carbon); 166.2 (1C, $\text{C}=\text{O}$).

Synthesis of Poly(CPhDMA)

Free radical polymerization reaction of CPhDMA was performed in an all glass Schlenk flask using 2,2'-azobisisobutyronitrile (AIBN) (2%, based on the total weight of the monomer) as initiator in 5 mL of 1,4-dioxane at 60°C for 4 h with 85% conversion (Scheme 3). The obtained polymer was precipitated in ethanol. The resulting homopolymer was dried under vacuum at 40°C for 24 h and characterized by spectroscopic techniques.



Scheme 3 Synthesis of poly(CPhDMA)

Calcd for poly(CPhDMA): C, 57.37; H, 3.58. Found: C, 58.17; H, 3.27. FT-IR (KBr, cm^{-1}): 3018–2932, $\nu(\text{C}-\text{H}$ aryl and aliphatic); 1735, $\nu(\text{C}=\text{O})$; 1565, (aromatic ring, $\text{CH}=\text{CH}$); 1205, $\nu(\text{C}-\text{O}-\text{C})$. $^1\text{H-NMR}$ (CDCl_3 , δ): 7.30–7.70 (s, 4H, aromatic ring- CH); 5.65 (d, H, aryl- CH); 5.85 (s, H, $\text{O}-\text{CH}$); 4.10–3.80 (t, 2H, $\text{O}-\text{CH}_2$); 1.8–2.4 (d, 2H, vinyl- CH). $^{13}\text{C-NMR}$ (CDCl_3 , δ): 36.60–44.20 (2C, vinyl- CH); 70.63 (1C, $\text{O}-\text{CH}_2$); 102.01 (1C, $\text{O}-\text{CH}$); 104.56 (1C, aryl- CH); 126.45–127.67 (4C, aromatic- CH); 138.23–140.96 (2C, aromatic C, ipso carbon); 178.52 (1C, $\text{C}=\text{O}$).

Characterization Techniques

The spectral analyses of CPhDM, CPhDMA and poly(CPhDMA) were recorded by using a Mattson FT-IR-1000 spectrometer with KBr discs ($4000\text{--}400\text{ cm}^{-1}$) and a Varian XL200 (200 MHz) equipment at 25°C using CDCl_3 as solvent. TMS was used as internal standard. Elemental analysis was carried out with a Carlo Erba 1106. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) of the poly(CPhDMA) were determined by using a Hawlet Packard GPC-SEC system calibrated with polystyrene standards at 30°C using THF as eluent at a flow rate of 1.0 mL/min. The TG/DTA and DSC curves were obtained using a Shimadzu TGA-50 thermobalance and a Shimadzu differential scanning calorimeter (DSC) DSC-50 model, respectively. The TG measurements were performed by using a dynamic nitrogen furnace atmosphere at a flow rate of 60 mL min^{-1} up to 273 K. The heating rates were 5, 10, 15 and 20 K/min and sample sizes ranged in mass from 8 mg to 10 mg. Platinum was used as sample container. DSC experiments were performed by aluminum pans with *ca.* 5 mg samples in the temperature range of 20–450°C at different heating rates: 5, 10, 15 and 20 K/min. All experiments were performed twice for repeatability, and the results showed good reproducibility with small variations in the kinetic parameters. $\alpha\text{-Al}_2\text{O}_3$ was used as a reference material. Conductivity was measured on a Keithley 2400 Electrometer. The pellet was prepared in the form of tablets with a thickness of approximately 0.1 cm at a hydraulic press of 1687.2 kg/cm^2 . UV-Vis absorption spectra were measured by using an Analytikjena Speedcord S-600 diod spectrophotometer in the wavelength range 190–1100 nm. The surface morphology of poly(CPhDMA) was evaluated by scanning electron microscopy (SEM), using a Philips XL 30S FEG apparatus.

RESULTS AND DISCUSSION

Characterization Studies

The monomer, [2-(4-chlorophenyl)-1,3-dioxolan-4-yl]methyl acrylate, (CPhDMA) was synthesized by the reaction of [2-(4-chlorophenyl)-1,3-dioxolan-4-yl]methanol (CPhDM) with acryloyl chloride in the presence of diethyl ether at -5°C . Then the radical-initiated homopolymerization of CPhDMA was performed with 2,2'-azobisisobutyronitrile (AIBN) as an initiator in a 1,4-dioxane solution at 60°C . CPhDM, CPhDMA and poly(CPhDMA) samples were characterized using FT-IR, ^1H - and ^{13}C -NMR spectral techniques. Some physical and thermal properties of poly(CPhDMA) were performed by UV-Vis, GPC, TG/DTG-DTA and DSC analyses. As compared the FT-IR spectra of CPhDMA and its homopolymer, it is understood that they have similar bands. In the FT-IR spectrum of the monomer, the most important characteristic absorptions were at 1625 cm^{-1} ($\text{C}=\text{C}$, vinyl structure) and 1727 cm^{-1} ($\text{C}=\text{O}$, carbonyl). In the spectrum of the polymer, the $\text{C}=\text{O}$ vibration was shifted to 1735 cm^{-1} and the band at 1625 cm^{-1} of the monomer disappeared. The signals at $\delta = 1.8\text{--}2.4$ in the ^1H -NMR spectrum are attributed to vinyl protons. These vinyl carbons were observed at $\delta = 36.60\text{--}44.20$ in the ^{13}C -NMR of poly(CPhDMA). Also, the signals at $\delta = 7.30\text{--}7.70$ are due to protons of the aromatic ring. The spectral analyses results showed that CPhDMA was polymerized by the free radical reaction. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) values of poly(CPhDMA) were found to be 10300, 21600 and 2.097, respectively.

Thermal Properties

Figures 1 and 2 show TG/DTG, DTA and DSC curves of the poly(CPhDMA), respectively.

DSC curves of the homopolymer exhibited two endothermic processes. These peaks are relevant to glass transition temperatures and thermal decomposition reaction of the homopolymer, respectively. The glass temperature values (T_g) varies, depending on the heating rates ranging from 5 K/min to 20 K/min, (Table 1). The maxima of these peaks are found to be 145°C , 148°C , 155°C , and 159°C , and 395°C , 404°C , 410°C , and 415°C for each heating rates, respectively. The heat capacity variations ΔC_p related to glass transition temperatures of the homopolymer were calculated from DSC results and were found to be 0.135, 0.147, 0.066 and 0.116 J/(g K). The homopolymer was also studied by DTA from ambient temperature to 1000°C in nitrogen atmosphere with different heating rates. From the DTA profile one endothermic peak for poly(CPhDMA) is noted. On the other

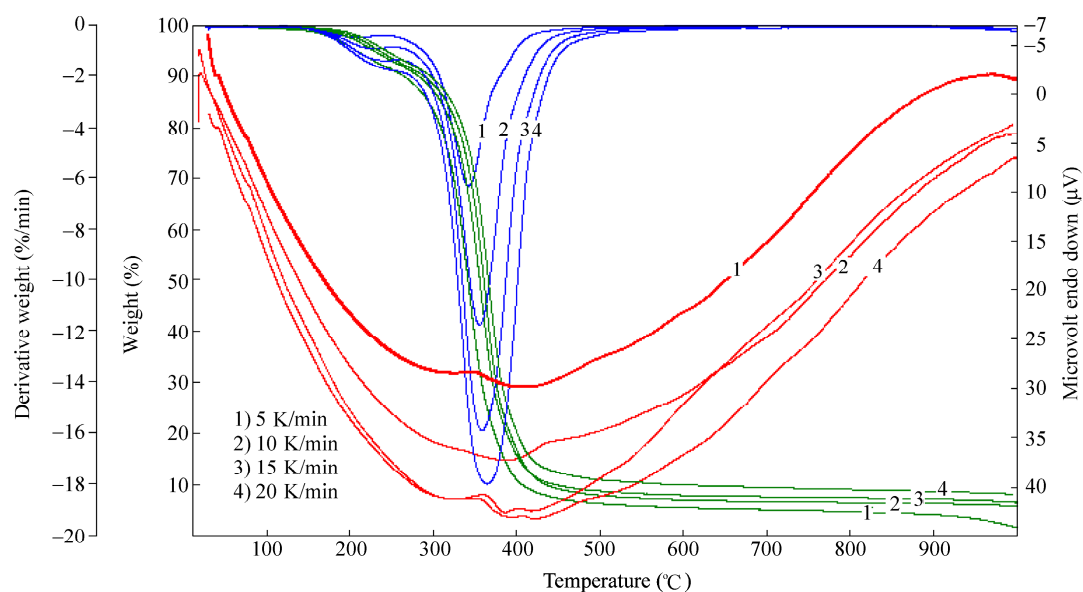


Fig. 1 TG/DTG and DTA curves of poly(CPhDMA)

hand, the typical dynamic TG/DTG-DTA curves of poly(CPhDMA) showed that the thermal decomposition took place mainly in one stage and the curves shifted to the right-hand side with increasing the heating rate. The polymer was thermally stable up to approximately 336°C while the heating rate was 5 K/min. The initial decomposition temperature of poly(CPhDMA) is relatively higher than that of the other methacrylate polymers reported^[15, 16]. The temperature ranges and percentage mass losses for each heating rates are given in Table 1 together with the temperatures of the greatest rate of decomposition (DTG_{max}). Finally the thermal decomposition kinetics of the poly(CPhDMA) was studied by using some mathematic functions based on TG, DSC (see Fig. 4) and DTA techniques under various heating rates in detail. These functions are related to methods of Kissinger^[17], Friedman^[18] and Flynn-Wall-Ozawa^[19, 20] based on multiple heating rates.

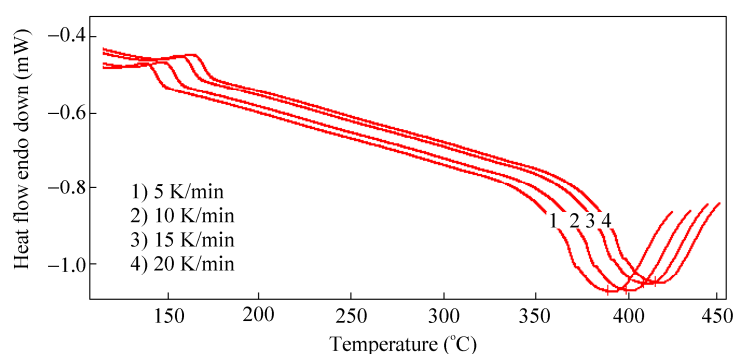


Fig. 2 DSC curves of poly(CPhDMA) at different heating rates ranging 5–20 K/min under N₂ flow

Table 1. TG/DTG, DTA and DSC data of poly(CPhDMA)

Heating rate (K/min)	Step	DTA _{max} (°C)	DTG _{max} (°C)	Temperature range (°C)	DSC _{max} (°C)	T _g (°C)/ ΔC _p (J/(g K))	Mass loss (%)
5	I residue	389/endo > 423.1	393	126.3–423.1	395/endo	145/0.135	98.00
10	I residue	402/endo > 445.9	400	137.9–445.9	404/endo	148/0.147	99.00
15	I residue	392/endo > 454.1	406	146.7–454.1	410/endo	155/0.066	96.00
20	I residue	391/endo > 464.2	413	155.1–464.2	415/endo	159/0.116	93.21

First, the Kissinger method was used to analyze the DTG, DTA and DSC data of poly(CPhDMA), because it is independent of any thermal degradation mechanisms and is one of the differential methods. The Kissinger method assumes that the degradation product $n(1 - \alpha_{\max})^{n-1}$ is independent of heating rate β . The activation energy E related to solid state decomposition are calculated from the following logarithmic differential expression by using the maximum decomposition temperatures ($T_{\max}$).

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \left\{ \ln \frac{AR}{E} + \ln[n(1 - \alpha_{\max})^{n-1}] \right\} - \frac{E}{RT_{\max}} \quad (1)$$

The E value can be calculated from the slope of a plot of $\ln(\beta/T_{\max}^2)$ versus $1000/T_{\max}$ fitting to a straight line. Kissinger's plots obtained by using DTG, DTA and DSC curves of the poly(CPhDMA) are presented in Fig. 3. The activation energy calculated from DTG, DTA and DSC curves of the poly(CPhDMA) compound is 86.91, 90.07 and 88.29 kJ/mol, respectively.

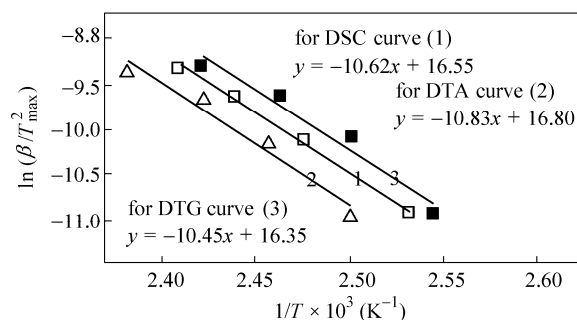


Fig. 3 Kissinger's plots of $\ln(\beta/T_{\max}^2)$ versus $1/T_{\max}$ for DTG, DTA and DSC curves of poly(CPhDMA)

Other methods used to calculate the activation energy in this work were those of Friedman and FWO. The FWO method is an integral method also being independent of the decomposition mechanism.

$$\lg \beta = \lg(AE/R) - \lg g(\alpha) - 2.315 - 0.4567 E/RT \quad (2)$$

The dependence of $\lg \beta$ on $1/T$, calculated by using Eq. (2) for the same α values at the different heating rates β can be used to calculate the activation energy. On the other hand Friedman method provides the following expression for thermal decomposition kinetic studies based on the basic Arrhenius equation:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n \ln(1-\alpha) - \frac{E}{RT} \quad (3)$$

Activation energy E can be calculated from the slope of the linear plot of $\ln(d\alpha/dt)$ versus $1/T$. In the equations above, $g(\alpha)$, α , T , E , R , A and n are the integral function of conversion, the conversion at time t , the absolute temperature (K), activation energy (kJ/mol), gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), pre-exponential factor (min^{-1}) and reaction order, respectively. Equations (2) and (3) were utilized to determine the values of activation energy over a wide range of conversion. The kinetic parameters were calculated from the linear plots of the left-hand side of kinetic equations (Eqs. (1) and (2)) against $1/T$. Figure 4 illustrates the plots of $\lg \beta$ versus $1000/T$ at varying degrees of conversion. The values E were obtained from the slope of the straight lines. In this case $\alpha = 0.05$ – 0.95 for each two methods were chosen to evaluate E values of poly(CPhDMA). The determined activation energies are listed in Table 2 and the average values for FWO and Friedman methods are 91.68 and 85.23 kJ/mol over the given range of α . These results agree well with the activation energies calculated from Kissinger method by using DTG, DTA and DSC techniques.

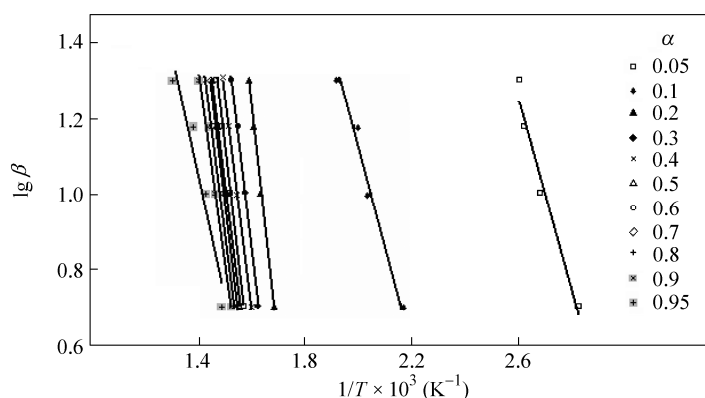


Fig. 4 FWO plots of poly(CPhDMA) at varying conversion in N_2

Table 2. Activation energies and correlation coefficient of poly(CPhDMA) obtained by FWO and Friedman methods

Conversion	FWO method		Friedman method	
	Activation energy, E (kJ/mol)	Correlation coefficient, r	Activation energy, E (kJ/mol)	Correlation coefficient, r
0.05	46.75	0.98671	55.03	0.98788
0.1	47.69	0.98908	51.29	0.98323
0.2	114.5	0.99231	70.91	0.99121
0.3	109.2	0.99621	104.7	0.99223
0.4	101.9	0.99101	93.44	0.99341
0.5	106.8	0.99532	99.51	0.99652
0.6	110.5	0.99061	95.11	0.99786
0.7	107.4	0.99678	96.52	0.99103
0.8	107.4	0.99231	101.1	0.99122
0.9	79.18	0.99125	82.32	0.99166
0.95	77.00	0.98711	88.10	0.97988
Mean	91.68		85.23	

Determination of the Kinetic Model by Master Plots Method

The kinetic model of the decomposition process was determined by the master plots method. Using Arrhenius's integral equation and a reference at point $\alpha = 0.5$, Eq. (4) now can be obtained as

$$\frac{g(\alpha)}{g(0.5)} = \frac{p(u)}{p(u_{0.5})} \quad (4)$$

where $g(0.5) = \left(\frac{AE}{\beta R} \right) p(u_{0.5})$, and $u_{0.5} = E/RT$. (5)

Equation (4) indicates that, for a given α , the experimental value of $p(u)/p(u_{0.5})$ and theoretically calculated values of $g(\alpha)/g(0.5)$ are equivalent when an appropriate kinetic model is used. Plots of $g(\alpha)/g(0.5)$ against α correspond to the theoretical master plots of integral functions $g(\alpha)$ given in the papers^[21–23]. Also the experimental master plots of $p(u)/p(u_{0.5})$ versus α from experimental data are obtained by using an approximate formula^[24] of $p(u)$, ($p(u) = \exp(-u)/[u(1.00198882u + 1.87391198)]$) under different heating rates. The

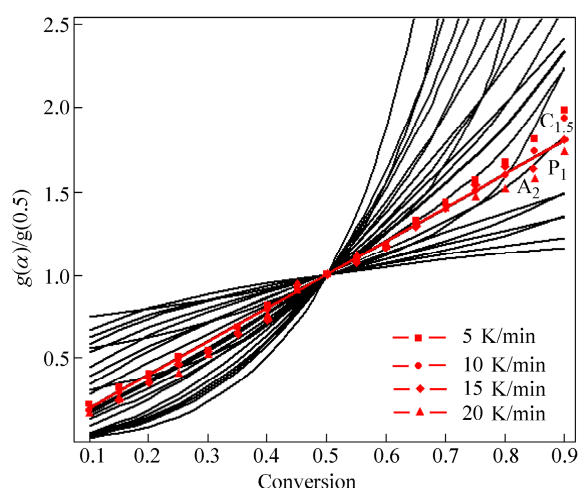


Fig. 5 Master plots of theoretical $g(\alpha)/g(0.5)$ against α for various reaction models (solid curves represent 20 kinds of reaction models given in references^[19–21]) and experimental data ($\square$, $\circ$, $\diamond$ and $\blacktriangle$) of poly(CPhDMA) at the heating rates of 5, 10, 15 and 20 K/min

experimental master plots of $p(u)/p(u_{0.5})$ obtained under different heating rates and the theoretical ones of various kinetic functions against α are shown in Fig. 5. The comparison of the experimental master plots with theoretical ones shows that kinetic model of the solid state decomposition is most probably described by a P_n acceleration type ($n = 1$).

Morphological Properties

Figures 6(a), 6(b), and 6(c) present SEM images of poly(CPhDMA) obtained by free radical polymerization process. These images are different from those of the characteristic methacrylate type polymers. As seen in Fig. 6(a), the particles are condensed, inhomogeneous and not so well-ordered in structure and shape. Looking more closely to the SEM image Fig. 6(c), one may find that the poly(CPhDMA) has a porous structure. The optical, thermal and electrical properties of poly(CPhDMA) are deeply affected by its porous-morphological structure.

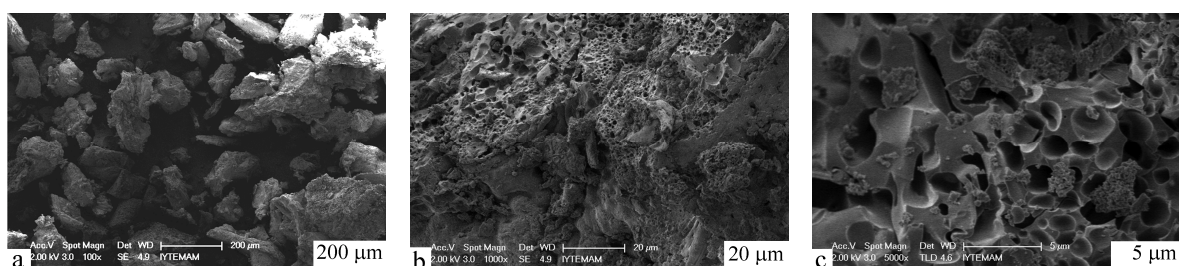


Fig. 6 SEM micrographs of poly(CPhDMA) with different magnifications: (a) 200 μm , (b) 20 μm and (c) 5 μm

The porous morphological structure of a polymer and its formation mechanism (diffusion controlled) can be greatly investigated by phase separation phenomena. Regarding to the phase separation, there is a general consensus among researchers that the liquid-liquid demixing processes are largely responsible for the polymer morphology. The preparation of a porous structure *via* phase-separation consists of two steps. First, the homogeneous polymer solution has to undergo liquid-liquid demixing to obtain a polymer-rich continuous matrix and a dispersed polymer-lean phase of almost pure solvent. The second step is a fixation step for giving the structure mechanical stability^[25]. In the light of the above description, polymer/solvent/nonsolvent system (acrylate derivate polymer/dioxane/ethanol) leads to the formation of porous structure in the resulting polymer.

DC Electrical Conductivity Measurements

The conductivity properties of poly(CPhDMA) films were determined by using the four-point probe technique. Electrical conductivity was measured as a function of temperature by using a Keithley 2400 Keithley 2400 electrometer. The variation in the $\ln\alpha$ as a function of reciprocal absolute temperature of poly(CPhDMA) is shown in Fig. 7. Electrical conductivity studies were also preformed taking into account the thermal decomposition temperature of poly(CPhDMA). The plot of electrical conductivity indicates two regions, I and II, which refer to two different energy levels of the poly(CPhDMA) sample. This suggests that the polymer has different current mechanisms. Regions I and II have a positive temperature coefficient of electrical conductivity and hence it was shown that the electrical conductivity values increase with increasing temperature due to the change in carrier concentration with increasing temperature. Consequently, poly(CPhDMA) has semiconducting property due to an increase in its conductivity with increasing temperature. The room temperature electrical conductivity of the poly(CPhDMA) was found to be 2.17×10^{-10} S/cm. The electrical activation energy of poly(CPhDMA) was calculated from the plot of the electrical conductivity by using the Arrhenius's well-known relation.

$$\sigma = \sigma_0 \exp(-\Delta E/kT) \quad (6)$$

where σ , σ_0 , k and ΔE are the electrical conductivity, pre-exponential rate corresponding to $1/T = 0$,

Boltzmann's constant and electrical activation energy for electron transfer, respectively. Using the Arrhenius theory it was found that the activation energies in the intrinsic region ΔE_1 and impurity scattering region ΔE_2 were 3.90 and 0.36 eV, respectively. The obtained electronic parameters suggest that the poly(CPhDMA) will behave as a typical semiconductor material.

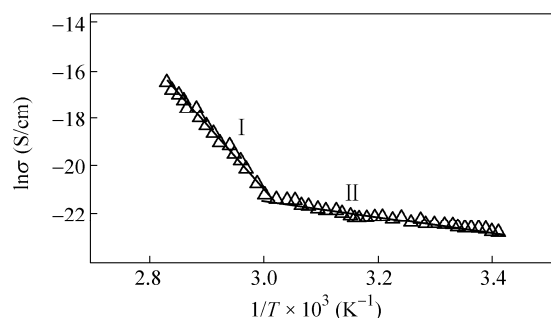


Fig. 7 Temperature dependence of electrical conductivity of the poly(CPhDMA) sample

Optical Properties

The absorption coefficient of organic semiconductors can be determined by the following relation.

$$\alpha h\nu = A(h\nu - E_g)^n \quad (7)$$

where α , A , ν , h , and E_g are linear absorption coefficient, energy-independent constant, frequency, Planck constant, and energy band gap between the valence band and the conduction band, respectively. n is a constant which depends on the type of optical transitions and especially for direct allowed transition $n = 1/2$, for direct forbidden transition $n = 3/2$, for indirect allowed transition $n = 2$ and for indirect forbidden transition $n = 3$. The linear dependence of $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ using the obtained E_g value is presented in Fig. 8 according to Eq. (7), and n value was found to be about 2 from the slope of the curve, revealing an indirect transition for poly(CPhDMA). The extrapolation of the linear portion of the curve to $(\alpha h\nu)^2 = 0$ gave the optical band gap of 2.48 eV. It was shown that the activation energy values obtained from conductivity and optical band gap were different as expected.

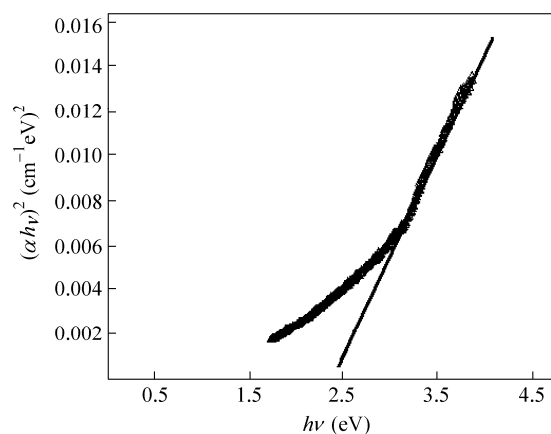


Fig. 8 The optical absorption spectra for poly(CPhDMA)

CONCLUSIONS

The poly[2-(4-chlorophenyl)-1,3-dioxolan-4-yl]methyl acrylate abbreviated as poly (CPhDMA) was synthesized and characterized by spectroscopic means. The kinetics of the thermal decomposition of poly(CPhDMA) was investigated by means of simultaneous TG/DTG-DTA and DSC techniques. The activation energy values calculated from Kissinger method by using DTG, DTA and DSC curves of the poly(CPhDMA) are 86.91, 90.07 and 88.29 kJ/mol, respectively. From TG curves, the activation energy of thermal degradation for poly(CPhDMA) was determined by the Flynn-Wall-Ozawa and Friedman methods and was found to be 91.68 and 85.23 kJ/mol, respectively. It was also determined that most likely the degradation process was a deceleration type in terms of master plots results. On the other hand, the electrical measurements indicated that poly(CPhDMA) had the semiconducting nature. The optical absorption measurements showed that poly(CPhDMA) had an indirect optical-band gap.

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