Synthesis and Characterization of New Polyamide Derived from Crystal Violet Dye Utilizing as Light Emitting Diode

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Abstract

New polymer Poly Crystal Violet Terephthalate (PCVT) was synthesis by condensation polymerization of Crystal Violet dye with Terphthalic acid in acidic medium .The polymer was characterized by several technique such as FT-IR spectroscopy , ^{1}H NMR spectroscopy , X-Ray diffraction (XRD) and Fluorescence technique . Curing study of new polymer was carried out by Differential Scanning Calorimetry (DSC) under Nitrogen gas, the optimum conditions of curing were obtained like curing temperature ,the curing energy and the activation energy of curing (ΔE).These analysis indicated the correct composition of polymer .From DSC curve indicate that the reaction type Exothermic ,also the Fluorescence spectrum of polymer indicate that there are large change of emission wavelength with high intensity as compare with dye only .So the new polymer can be use in applications of light emitting diodes .

Keywords: Crystal Violet , Fluorescence ,Light Emitting Diode .

Introduction

Polymeric materials introduced in many applications such as photovoltaic devices[Brabec et.al. (2001)] solar cell [G.Tu et.al.(1998)] ,Light Emitting Diodes(LEDs)[Sholin et.al.(2006)] ,Field Effect Transistor(FETs)[Bao(2000)].The important property for polymers can be forming in any shape at any substrates , also can be fabricated many layers with different conductivity .In the same time ,low cost ,easily manufactured with large area and

good mechanical and thermal properties compared with semiconductor make polymers very desired .In technologies .Many materials used as polymers but not all them used successfully as active layers .One of these materials are dyes .Dyes widely used as lasers as active materials when solution with preferred solvent ,but dyes have brittle behaviour especially when using as thin films application so, we change to polymers in order to avoid this brittlness.This processes successful to enhancement the thermal and mechanical properties of dyes after change to polymer were we can prepared thin films with lower cost and applicability for large area displays[A.Q.Abdullah et.al. (2007)].

The aim of this paper is synthesis and characterization of new polymeric materials based on dyes and use as active materials as luminance converter materials.

Experimental

Materials:

Crystal Violet dye ($C_{16}H_{12}ClN_3O$) provided by Spectral Physics without any purification .Terphthalic acid ($C_8H_4O_3$) provided by Aldrich .Dimethyl Sulphoxide ($CH_3.SO.CH_3$) (DMSO) provided by BDH Ltd.Co. .Phosphoric acid (H_3PO_4) provided by Fluka.

Instruments:

The FTIR spectra were obtained with a FT/IR – model 8400S spectrophotometer by SHIMADZU ,under ambient condition .The ^1H N M R spectra were recoded using ^1H N M R spectrophotometer model 300BB"NMR300 " by Mercury Co. The fluorescence spectra were obtained from SHIMADZU 450 spectra fluorescence fitted with macro processor data recorded. The differential scanning calorimetry (DSC) was performed on DSC – 50 by SHIMADZU Co . at the heating rate of 10^oC/min under a nitrogen atmosphere. Melting point measurement by apparatus model Cat . No . (1A6304) by Electrothermal Co. The X - Ray diffraction (XRD) chart obtained with Phillips diffractmeter 1253 CuKα with the wavelength ($\lambda = 1.54A^o$) with Nicle (Ni) filter .

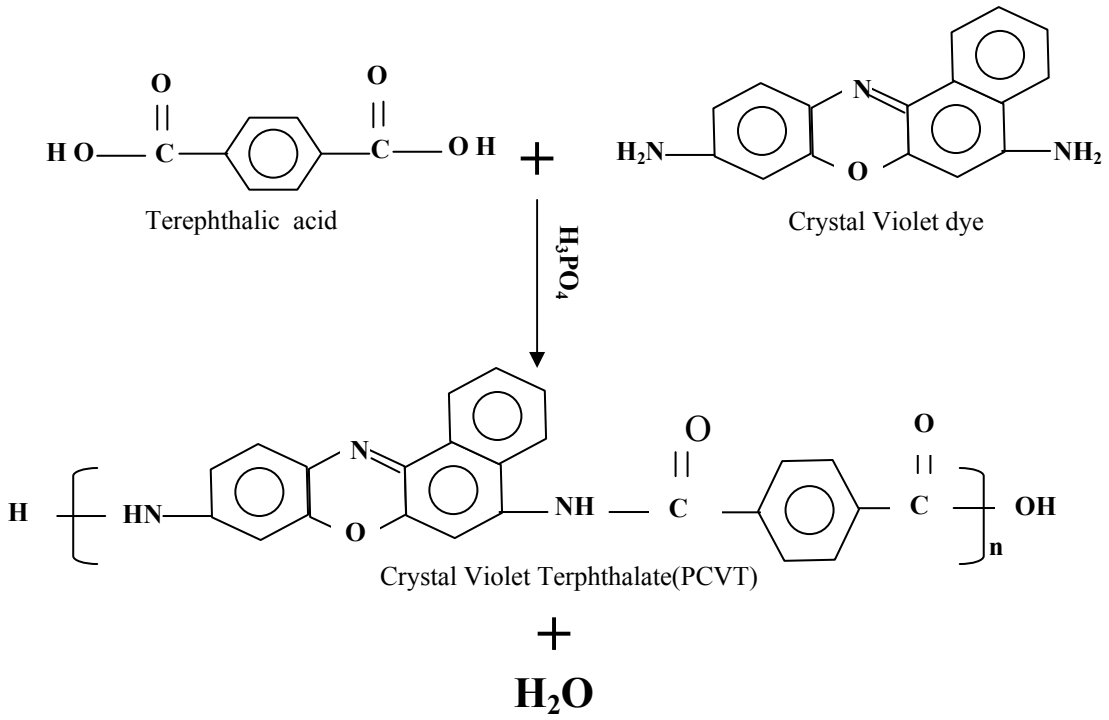
Procedure:

Synthesis of Poly Crystal Violet Terephthalate (PCVT)

A three - necked flask equipped with thermometer , mechanical stirrer and condenser , was charged with (2.376 g ,

8mmol) Crystal Violet dye (1.184g, 8 mmol) Terephthalic acid , 100 ml Dimethyl Sulphoxide (DMSO) as a solvent and three drops of phosphoric acid as catalyst.

The reaction mixture was stirred and heated at 150 ^{o}C for 10 hr's then the reaction was evaporated by rotary evaporator to remove the solvent, then dried under reduced pressure (0.1mmHg) for 24hr's at 25 ^{o}C, to obtain a solid material with melting point(m.p) in the range (190-193^{o}C) and which was characterized by several techniques .the reaction scheme are shown below in Figure (1).



Figure(1):Chemical structure of PCVT

Results and Discussion

Infrared spectra of PCVT

The FT- IR spectra of PCVT is shown in Figure(2).Polymer have a very broad and strong peak in the position 3350cm^{-1} , due to N-H group while in crystal violet dye we see] this group very small and narrow. However, Amide groups I and II clearly at position 1380 cm^{-1} and 1590cm^{-1} respectively. This observation indicates that most of the NH_2 groups reacted with the terephthalic acid to form the corresponding polymer.

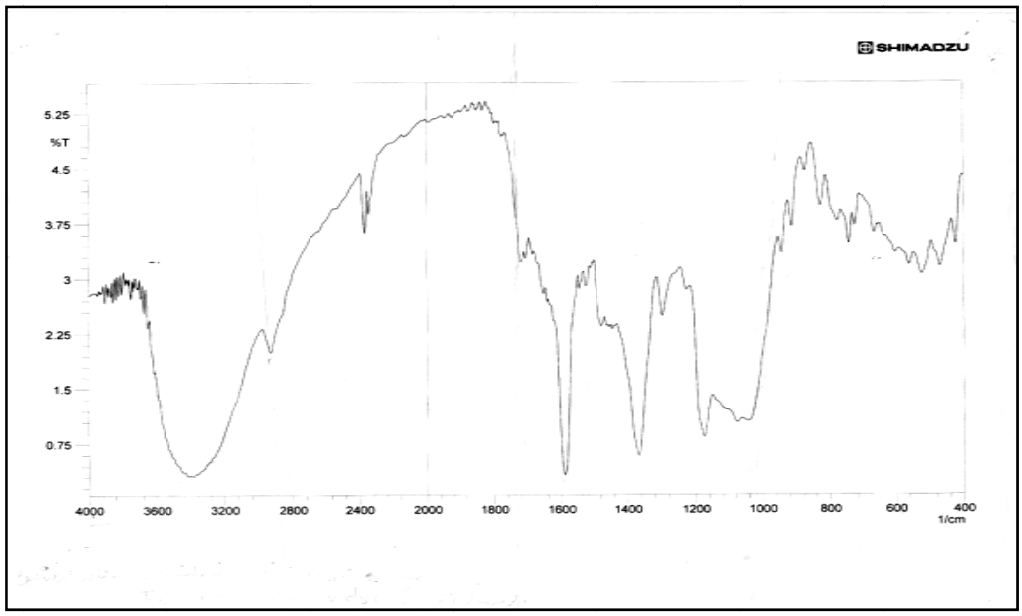
Nuclear Magnetic Resonance Spectroscopy (NMR)

The new polymer was characterized by ^{1}H NMR in d^{6}DMSO solvent as shown in Figure (3)

The quantitative analysis for PCVT was estimated by integrating selective bands and as shown in Table (1).

X-Ray Diffraction for PCVT

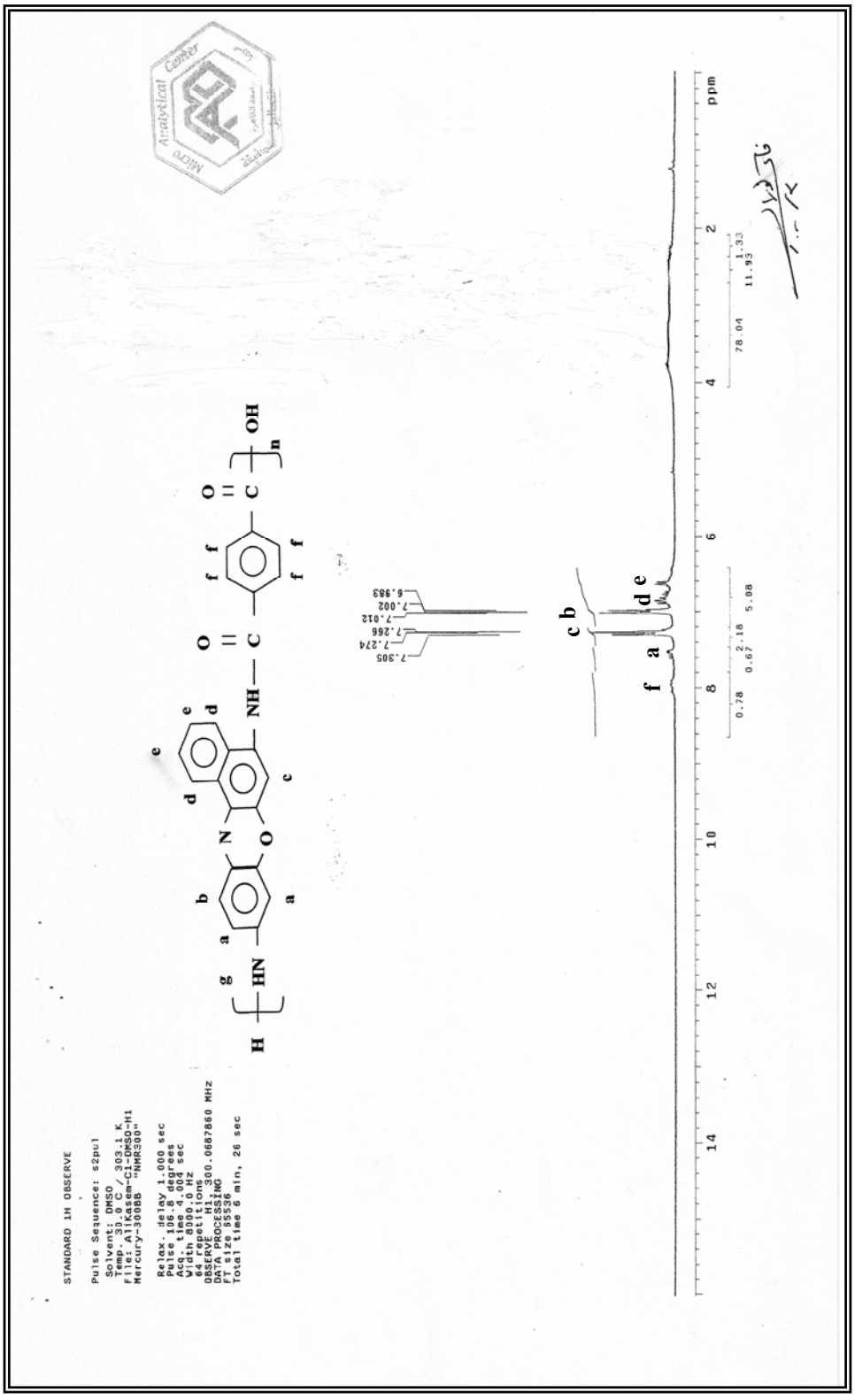
The crystalline in polymer is small and usually organized into larger shallow pyramid like structure called spherulities which may be seen by the naked eye and viewed as malts cross-like structure with polarized light and crossed Nicole prisms in a microscope as shown in Figure(4)..Figure(5) shown XRD for polymer confirmed this result where we are see peaks at angle 5.4^{o} and 16.4^{o} respectively related to polycrystalline structure for polymer ,also this results confirmed the synthesis of polymer



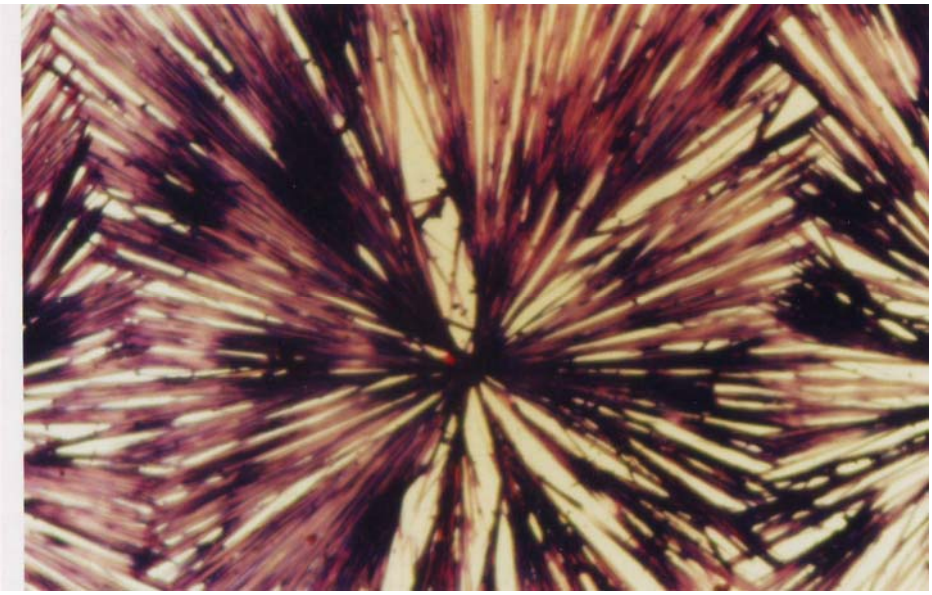
Figure(2):FT-IR for PCVT

Table (1) : Chemical shift of ^{1}H NMR for PCVT

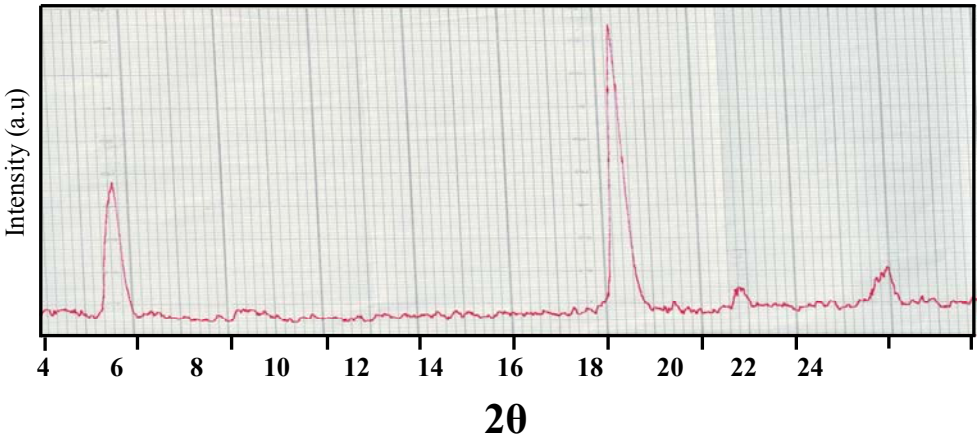
Polymer Protons H	Chemical Shift δ ppm					
	H_a	H_b	H_c	H_d	H_e	H_f
PCVT	7.305	7.012	7.240	6.916	6.821	7.527



Figure(3): ^{1}H NMR spectrum for PCVT



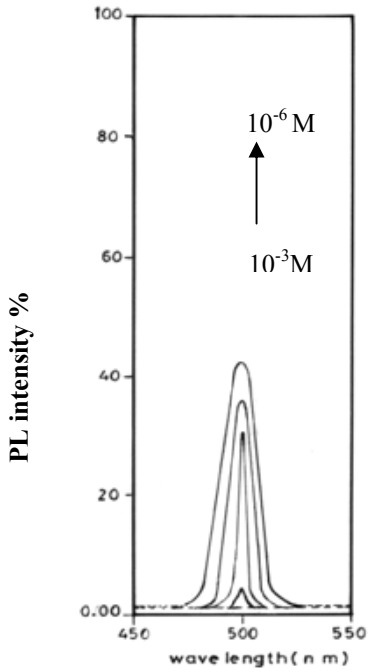
Figure(4):Malts cross-like pattern for Spheralites viewed under polarizing microscope ,the large and small Spherulites are result of crystallization



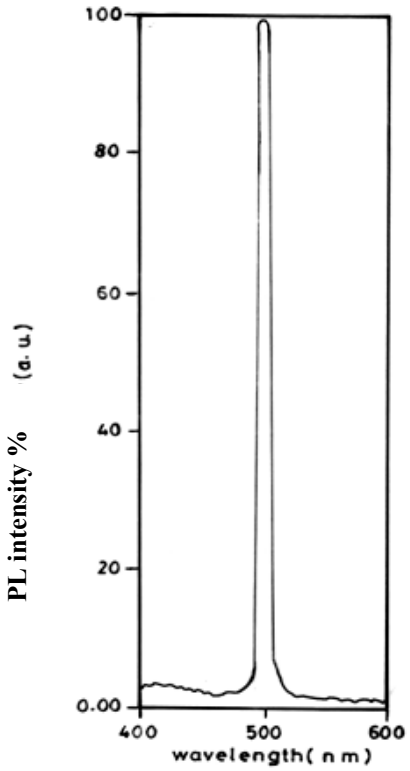
Figure(5):XRD for PCVT thin film at R.T

Fluorescence spectra of PCVT

Fluorescence spectra were recorded under ambient condition .Figure(6)shown the PL spectra for polymer solution at different concentration in DMSO solvent (10^{-3}-10^{-6})M and the results were obtained (wavelength of excitation (λ_{ex}=509nm) ,wavelength of emission (λ_{em}=510nm) while to crystal violet dye λ_{em} equal to about 610nm [Al-Luabia (1991)] .To fabricate light emitting diode from dyes we are must study the PL spectra for polymer thin film ,so Figure(7) shown the PL spectra for PCVT thin film and we are noticed high intensity peaks to be 98% indicated primary that polymer can be using as LEDs devices[Riess (2001)] .



Figure(6):The PL spectrum for PCVT at different concentration in DMSO solvent (10^{-3}-10^{-6} M) at R.T λ_{em}=510nm , λ_{ex}=509nm



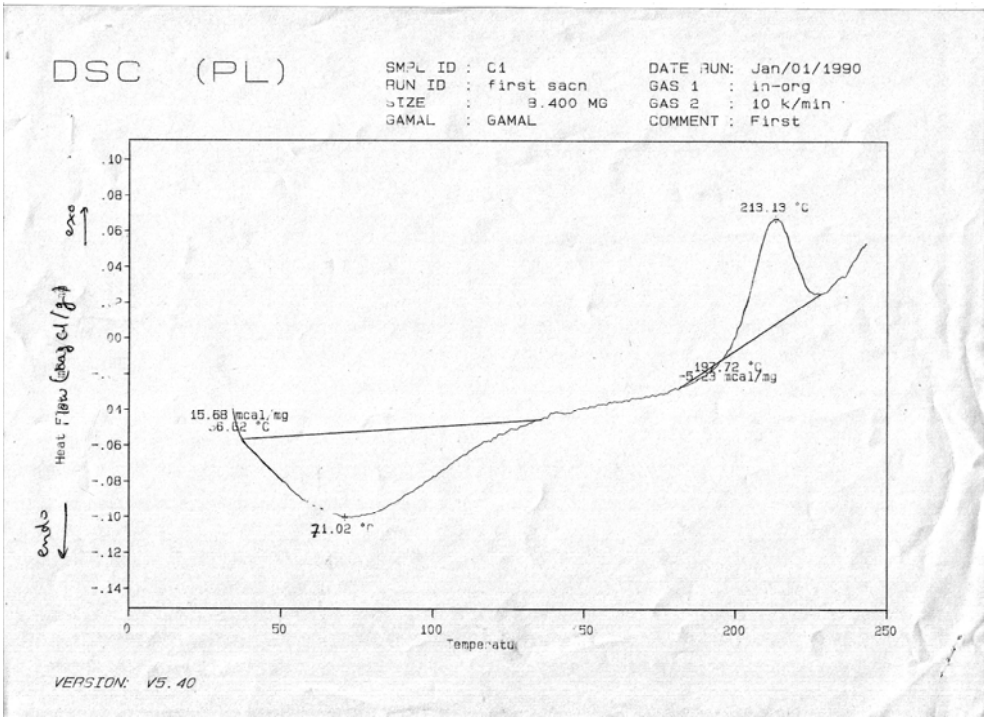
Figure(7):The PL spectrum for PCVT thin film at R.T
λ_{em}=504nm ,λ_{ex}=497nm

DSC analysis for PCVT

Figure(8) show the DSC trace of polymer recorded under nitrogen atmosphere. Exothermic peak was observed due to curing polymer ,several curing parameters such as ,initial curing temperature which was determined from the thermograms as a deflection point of the curve from the tangent to the base line (T_i),optimum curing temperature(T_{op}) which was taken as the temperature when rate of curing reach optimum and final curing temperature (T_f) which was taken as at the temperature at which the curing reaction was completed and the curve return to the base line .The activation energy of curing (ΔE) was calculated from Arrhenius plots between log curing rate and 1/T [Hashim (1995)]. On other hand curing energy (E_{cur}) which was calculated from the area under the curve relatively to standard indium melting peak [Hashim (1995)] .The results were obtained can be tabulated in Table (2) .

Table (2): The differential scanning calorimetry for PCVT

Polymer	Curing Temperature (^oC)			Ecu rmcal/mg	EΔ KJ/mole	Range (^oC)	Curing Temperature (^oC)			Ecur mcal/mg	EΔ KJ/mole	Range (^oC)
	T_i	T_{op}	T_f				T_i	T_{op}	T_f			
PCVT	36.62	71.02	134.10	15.68	21.40	40-52	197.72	213.13	226.40	5.23	109.99	190-200



Figure(8):DCS for PCVT

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الملخص:

تم تحضير نوع جديد من البوليمرات من خلال تكثيف حامض التيرفثالك مع صبغة الكريستال البنفسجية في وسط حامضي وقد تم تشخيص البوليمر الجديد بوساطة تقنيات عدة منها طيف الأشعة تحت الحمراء والرنين النووي المغناطيسي والأشعة السينية وتقنية التفلور.

درست عملية التقسية بوساطة تقنية المسح التفاضلي ألمسعري وتحت جو متحرك من النتروجين وتم تحديد الظروف المثلى لعملية التصلب مثل درجات حرارة التقسية وطاقة التصلب وطاقة التنشيط. أثبتت الدراسة من خلال التشخيص الطيفي صحة التركيب المقترح ومن دراسة منحنى المسح التفاضلي ألمسعري أن التفاعل من النوع الباعث للحرارة وكذلك اثبت طيف التفلور إن هناك تغير كبير في طول موجي الانبعاث وبشدة عالية جدا عما هو عليه في دراسة أطياف التفلور للصبغة وعليه يمكن مبدئيا استخدام البوليمر الجديد في تطبيقات الثنائيات الباعثة للضوء.