



OPTICAL LIMITING ACTION IN POLY (ETHYLACETYLENECARBOXYLATE)

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The optical limiting action of poly(ethylacetylenecarboxylate) dissolved in dichloroethane were investigated under irradiation with 8 ns laser pulses at 532 nm. The optical limiting measurements were performed at a series of concentrations. The threshold limiting fluence was observed for high concentrations at 5 J/cm² with a transmission of about 20 %. No optical limiting action was observed at very low concentration of the prepared polymer in the dichloroethane solvent. The observed data show that poly(ethylacetylenecarboxylate) has the potential for the use as optical limiting material for future applications.

INTRODUCTION

With the development of laser technology, much interest in the development of optical limiting materials has been made among researches working on materials. Devices for human eyes protection and solid-state sensors from intense optical beams are sought.¹⁻³

The use of conjugated polymer as an optical limiting material is growing rapidly. These materials are considered to be promising. They offer many advantages such as large third order nonlinearities, χ^3 due to the presence of the delocalized π -electrons, fast response time, high damage thresholds, ease of processing, structural modifications, and a wide range of application wavelength.⁴

There are several different mechanisms for optical limiting of organic compounds such as Reverse Saturable Absorption (RSA); two-photon absorption, nonlinear refraction, and optically induced scattering. Conjugated polymers exhibit the ability of all these mechanisms.^{5,6}

Among the requirements of a highly optical limiting behavior, an excited state absorption cross section that is higher than the ground state to have a fast intersystem crossing rate with the presence of a metastable state and the duration of the excited

pulse lower than the excited state lifetime; so that there is a cumulative buildup of population in the excited state leading to increased levels of absorbance for pumping beam as the basic requirement for optical limiter.⁷

The optical limiting action of poly(para-methoxy phenylacetylene) was measured with unfocused nanosecond laser pulses at 532 nm in the solution state and the threshold limiting fluence was found at 65mJ/cm².⁷

Nonlinear optical absorption and optical limiting behavior of a novel σ - π alternating polymer, poly(disilanylene-2,2'-bipyridine-5,5'-diyl) ruthenium complex was evaluated at three different concentrations with nanosecond pulses at 532 nm. The experimental results indicated that the investigated material was very efficient and having excellent optical limiting properties.⁸ Gong and his co-worker reported the nonlinear transmittance of a novel hyper-branched conjugated poly(dimethylaminobenzene-hyperbranched phenylene vinylene). DMA-HPV polymer in CHCl₃ solution using a nanosecond optical parametric oscillator. The prepared polymer shows excellent optical limiting performance in the visible region from 490 to 610 nm. The results were explained based on the

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combination of two-photon absorption and reverse saturable absorption mechanisms.⁹

Song and his co-worker reported the synthesis, light-emitting and optical limiting properties of three new donor-acceptor conjugated polymers derived from 3,5-dicyano-2,4,6-tristyrylpyridine, (PY) unit.¹⁰ The optical limiting performance of $-(C_{56}H_{52}N_4)_n-$ polymer had been measured at 532 nm with nanosecond pulse, the limiting threshold was 728 mJ/cm^2 , and the throughput of $-(C_{56}H_{52}N_4)_n-$ was limited to 344 mJ/cm^2 for incident fluence as high as 1.1 J/cm^2 suggesting that the previous polymer may be promising as light-emitting polymer and optical limiting material.¹⁰

Preparation and optical properties of soluble azobenzene-containing substituted poly(1-alkene)s has been reported by Hongyao Xu.¹¹ The optical limiting and nonlinear optical properties were investigated using 8 ns pulse at 532 nm. Their results show that these soluble poly(1-alkene)s possess good optical limiting properties and large nonlinear optical properties.

Finally, Hongyao Xu *et al* have reported recently the synthesis and properties of long conjugated organic optical limiting materials with different π -electron (C=C, C=N and N=N) conjugation bridge structure. The C=C double bond as conjugation bridge shows better optical limiting property than compounds having C=N and N=N conjugation bridges under the same linear transmittance while the compound with N=N double bond as conjugation bridge is superior in nonlinear optical properties in comparison with C=C or C=N double bond as conjugation bridge.¹²

Following our previous optical limiting observation of poly(dimethylacetylenedicarboxylate), in three different organic solvents: 1,2-dichloroethane, chloroform and tetrachlorocarbon with a concentration at 10^{-3} M from the prepared polymer, it was found that the threshold limiting fluence was observed at about 20 J/cm^2 with a transmission of 77% with CCl_4 solvent.¹³

This paper focuses on the optical limiting behavior of conjugated poly(ethylacetylenedicarboxylate) material at 532 nm with laser pulses at five different concentrations of the prepared polymer dissolved in dichloroethane.

EXPERIMENTAL

1. Preparation of Poly(ethylacetylenedicarboxylate)

The preparation of poly(ethylacetylenedicarboxylate) has been carried out as follows: 0.54 mole of

hexacarbonyl molybdenum from Fluka and about 0.06 mole of toluene from Merck with GR purity, were placed in a 50 mL single-necked flame-dried flask containing magnetic stirring, the mixture was refluxed for six hours under nitrogen atmosphere in an oil bath. After cooling, 10.9 moles of ethylacetylenedicarboxylate, $\text{HC} \equiv \text{CCOOC}_2\text{H}_5$ was added and the mixture was refluxed with stirring under nitrogen atmosphere for 24 hours in an oil bath. The reaction mixture cooled down and the polymer was precipitated by pouring into excess of dried ethanol. The product was filtered and washed three times with hot methanol and dried under vacuum. The obtained material was re-precipitated with methylethyl ether and dried under vacuum. The yield was about (0.3 g, 79%) and it was dark brown viscous form and stable at room temperature.

2. Instrumentation and material characterization

The following instruments were used to measure and properties characterization of all prepared materials:

2.1. Nuclear Magnetic Resonance

^1H and ^{13}C NMR was performed on a Bruker Bio spin 400 MHz spectrophotometer.

2.2. FTIR spectra

The infrared spectra were recorded on Nicolet 6700 with a resolution of 4 cm^{-1} as a liquid form for both starting material and the prepared polymer.

2.3. Differential Scanning Calorimetry (DSC)

The glass transition temperatures of the composites were determined by use of a Mettler DSC20 instrument. All samples were tested in aluminium pans at a heating rate of $10^\circ\text{C}/\text{min}$ over a temperature range from room temperature to 200°C . The precision of the used instrument is $\pm 0.2^\circ\text{C}$, and the experimental errors in the measurements were estimated to be about $\pm 0.5^\circ\text{C}$.

2.4. Thermogravimetry (TG)

The dynamic weight loss tests were conducted by using a Mettler instrument. All tests were conducted in a nitrogen purge ($30 \text{ mL}/\text{min}$) using sample weights of 10 -15 mg at a heating rate of $10^\circ\text{C}/\text{min}$. The resolution of the balance is given, as 1 microgram for weights less than 100 milligram, and the temperature precision of the instrument is $\pm 2^\circ\text{C}$. The total experimental errors in the determination of the decomposition temperatures were estimated to be not more than $\pm 3^\circ\text{C}$.

2.5. Molecular weight determination

The number average molecular weight was performed using Osmomate 090 from Gonatec, Germany

3. Optical limiting measurements

The optical limiting behavior of the prepared polymer was measured in solution at five different concentrations of the polymer dissolved in dichloroethane.

The test cell used for this test was 10 mm thick quartz cell. The optical limiting measurements were performed with frequency doubled Nd: YAG laser system. The laser energy can be varied by changing the rate of applied voltage on the flash lamp. Pulses of 8 ns and 1 Hz repetition rate were guided onto the sample cell through a lens with 100 mm focal length. In order to avoid damaging the quartz cell, the sample located out of the focus point, the radius of the laser beam at the sample was approximately $250 \mu m$ in the $1/e^2$ diameter.

The energy of the incident and output pulses were measured using calorimeter sensor, with linear response (Scientich PHF 50 energy detector).

RESULTS AND DISCUSSION

It should be point out first that, the number average molecular weight of the prepared polymer is estimated below 5×10^3 Dalton. Figure 1A shows the FTIR spectrum of ethylacetylenecarboxylate, $HC \equiv CCOOC_2H_5$

The most characterized bands of the monomer were observed and centered at 3267, 1716, 1295 and 2118 cm^{-1} which were assigned to C-H, C=O, C-C-O and C \equiv C stretching modes, respectively. Figure 2 shows the most characterized band of the polymer observed at 1445 cm^{-1} which is assigned to the backbone conjugated double bond mode. This band was not seen in the starting material, ethylacetylenecarboxylate, Figure 1A which confirms the polymerization process. Also, the C \equiv C bond at 2118 cm^{-1} has disappeared in Figure 1 (bottom) suggesting that the triple bond of the monomer has been converted to double bond which has observed at 1612 cm^{-1} in the polymer which confirms the polymerization process. The remaining three bands in Figure 1B were observed at 3267, 1716 and 1295 cm^{-1} which can be assigned to C-H, C=O, and O-C-O stretching modes presented in the papered polymer, respectively.

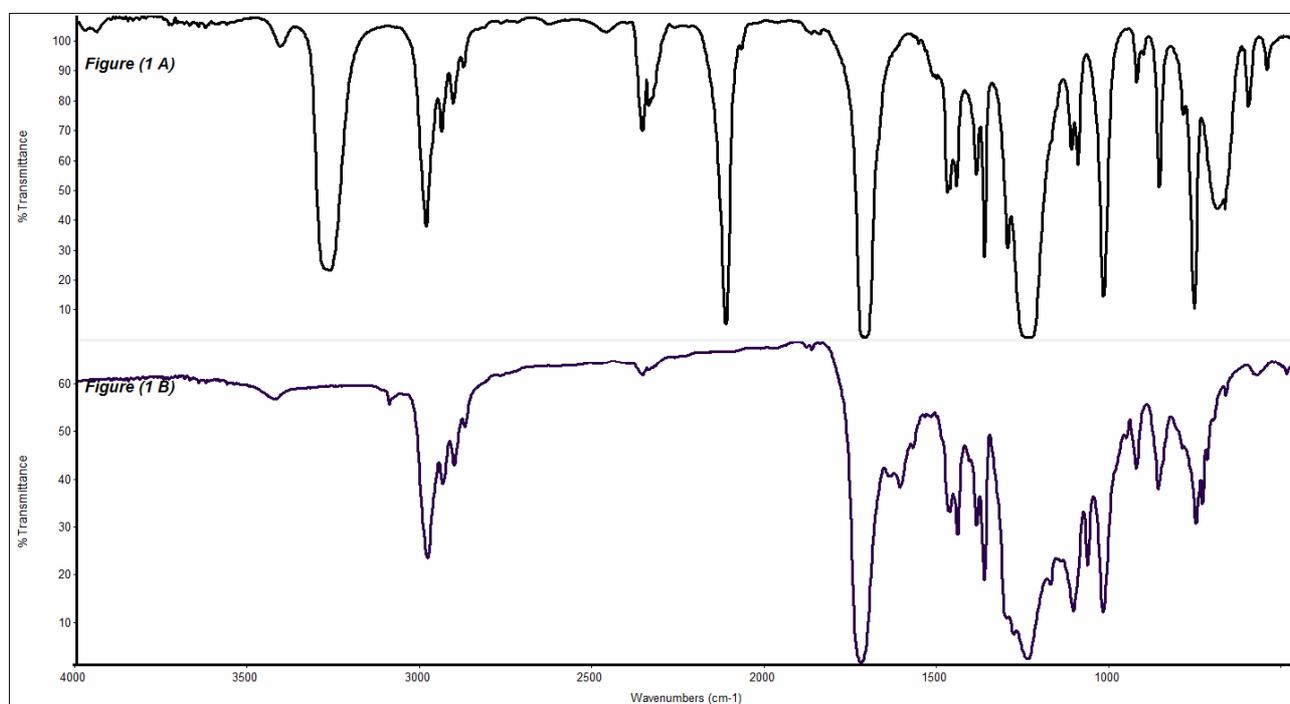


Fig. 1 – A FTIR spectrum of the ethylacetylenecarboxylate, $HC \equiv CCOOC_2H_5$, B: FTIR spectrum of the poly(ethylacetylenecarboxylate).

The ^{13}C and ^1H NMR spectra for both starting and the prepared polymer materials were recorded. The ^1H NMR (400 MHz, CDCl_3 , 25 °C) of ethylacetylenecarboxylate, $\text{HC} \equiv \text{CCOOC}_2\text{H}_5$ shows singlet peak at $\delta\text{H} = 3.1$ ppm due to the isolated hydrogen in the structure of the both starting material and polymer, while the ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) of the starting material shows three peaks at $\delta = 62.50$, 74.72, and 152.67 ppm corresponding to the following C-C, $\text{C} \equiv \text{C}$ and C=O bonds, respectively. After polymerization, the ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) shows three peaks at $\delta = 62.50$, 132.60, and 165.10 ppm corresponding to the following C-C, C=C and C=O bonds, respectively. Note the chemical shift taking place with C=O and C=C bonds in comparison with non-polymerized compound as an evidence of polymerization process.

Differential scanning calorimetry (DSC) was used to locate the glass transition temperature (T_g) and/or the melting temperature of the prepared

polymer. The DSC thermograms were recorded in two ranges from -150 to 100°C and from room temperature to around 500°C . Also the samples were cooled down to -100°C and to room temperature within the available range, and the cooling curves were also recorded. Further heating thermograms were recorded again. A melting temperature for the polymer could not be observed in the recorded DSC thermograms. The DSC thermograms (Figure 2, DSC) show a typical threshold at around -50°C , which can be attributed to glass transition. The obtained polymer has then been investigated using thermogravimetry (Figure 2, TGA) in order to follow the thermal degradation reactions. The TGA experimental measurements of the polymer indicate that the polymer has relatively good thermal stability with the 60% weight loss temperature in the range (25-300) $^\circ\text{C}$

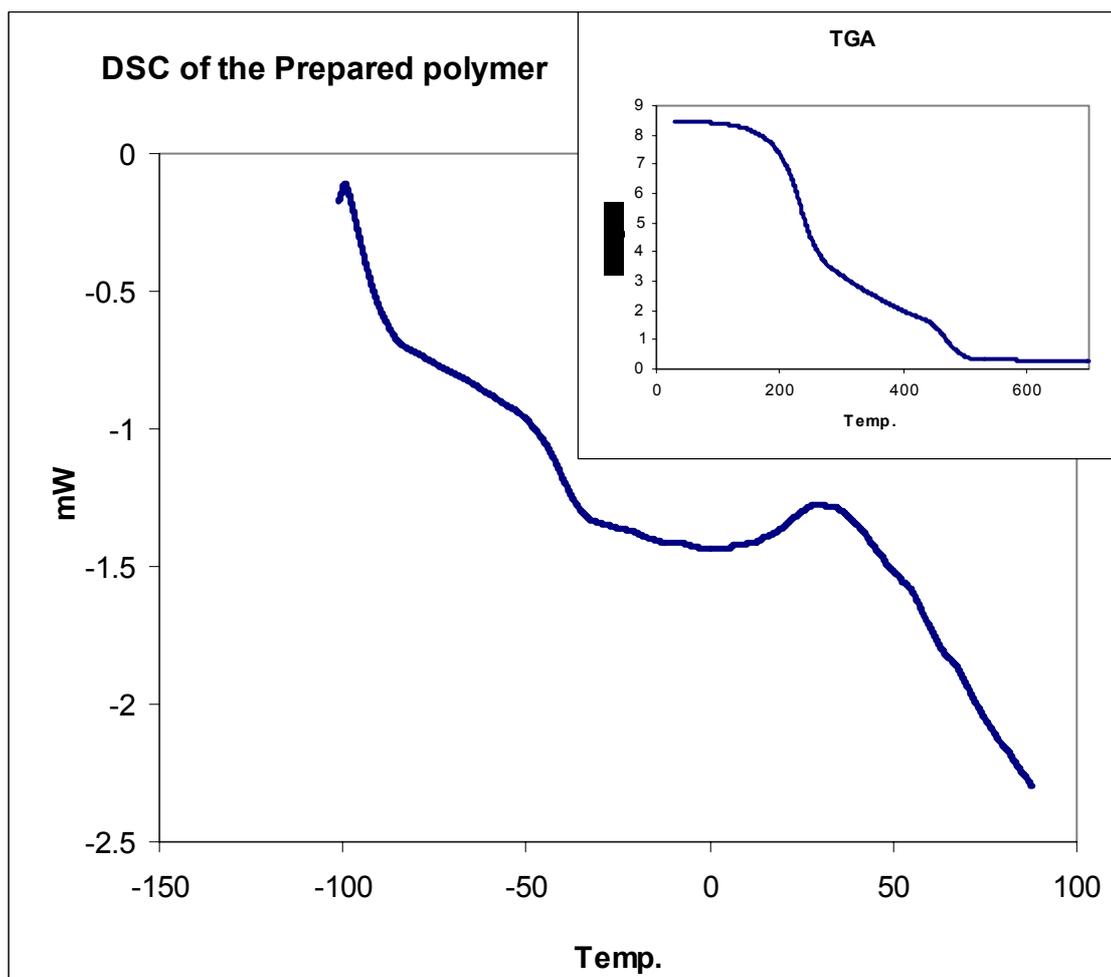


Fig. 2 – Thermal analysis of the poly(ethylacetylenecarboxylate), (DSC) and (TGA) curves.

Having confirmed the existence of the prepared polymer, the next step is focused on the optical limiting action of poly(ethylacetylenecarboxylate). The prepared polymer has been dissolved in dichloroethane at different concentrations. The optical limiting measurements were shown in Figure 3. Each of the data points represents a single shot measurement.

As shown in Figure 3 a linear variation of output fluence with different values of input fluence can be seen at low concentrations at 0.15×10^{-3} , 0.6×10^{-3} , 0.75×10^{-3} , 1.5×10^{-3} M /L with linear transmission of 80%, 77 %, 75 %, 72 % respectively. The transmittance obeyed Beer's law: $I=I_0 e^{-\alpha l}$, where I , I_0 , α and l are the incident energy, the output energy, the absorption coefficient and the sample path length, respectively. In the same figure at high concentration (3×10^{-3} , and 5×10^{-3} M /L) the output fluences are first linear with input fluences and then level off and reach a plateau at high input fluences. The saturated I_{OUT} values at the plateau are 5 and 10 J/cm^2 respectively.

Our results show that the optical limiting responses of poly(ethylacetylenecarboxylate) polymer solution toward nanosecond laser pulses at 532 nm are strongly dependent on solution concen-

trations, with the changes particularly dramatic in the 1.5×10^{-3} to 3×10^{-3} M/L concentration range.

The optical limiting responses of the low-concentration solution are generally much weaker than those of more concentrated solutions. While high concentrated solution exhibits strong optical limiting, reaching a plateau at an I_{IN} of 5 J/cm^2 and 10 J/cm^2 (Figure 3). This result is similar to that observed for the C_{60} and its derivatives.¹⁴

The inclusion of more dilute solutions (0.15×10^{-3} to 5×10^{-3} M /L) in the measurements is particularly important because the optical limiting responses of the poly (ethylacetylenecarboxylate) polymer solution change significantly over the concentration range.

The optical limiting action of the polymer is due to the increase length of conjugated double bond in the solution and to solution concentrations which play a positive and remarkable role for such action.¹⁵ This result may be explained on the assumption that concentrations, the intermolecular electron transfer is more efficient in both ground and excited singlet states and charge transfer and quenching between the polar solvents and the carbonyl group in the polymer are the most likely to reduce the optical limiting action.

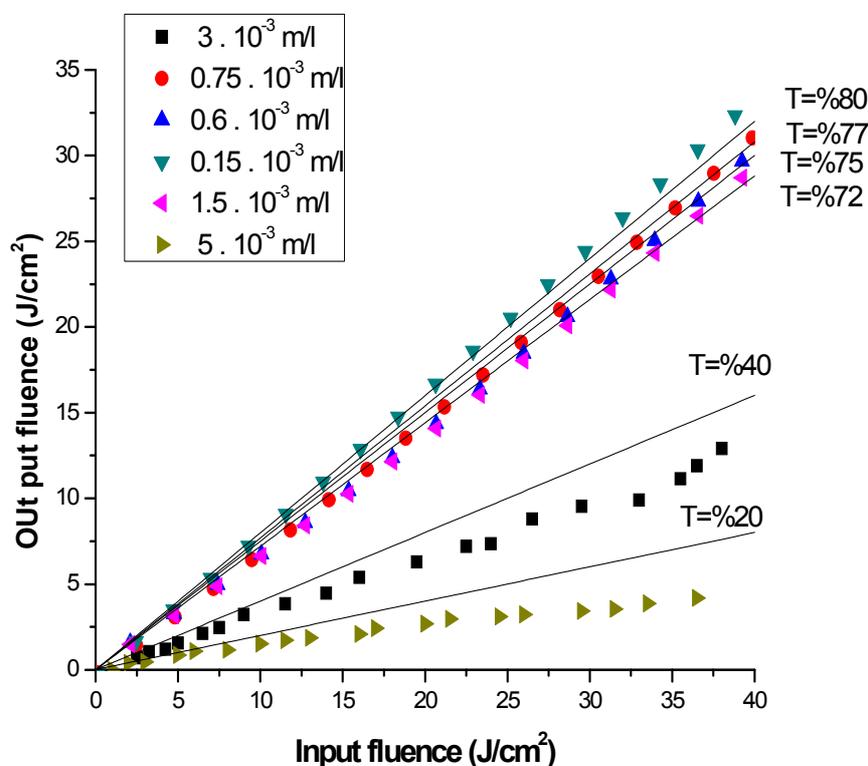


Fig. 3 – Output versus input fluence for three poly(ethylacetylenecarboxylate) solutions with many different concentrations.

The optical limiting mechanism of organic compounds is often based on two-photon absorption (TPA) or reverse saturable absorption (RSA). Generally, TPA-based optical limiting effect can result in principle under the laser irradiation of picosecond or shorter pulses. RSA is taking place on a nanosecond or longer time scale, rather than a shorter a picosecond time, owing to the different excited-state lifetimes involved in a multilevel energy process.¹⁶ For the poly(ethylacetylenecarboxylate) with π -delocalized electron system, the lifetime of a singlet state is very short (1ps). It is much smaller than the pulse width (8ns) of the laser source. The molecule population in these levels may be neglected. The triplet excitation state absorption plays a dominant role. Therefore, it can be said the optical limiting mechanism of the studied polymer is RSA in which the triplet excitation state absorption is dominant.

Finally, absorption spectra of the polymer were acquired before and after the laser irradiation and found that the pattern and its intensity have almost no change, hinting that the prepared polymer processes photostability.

CONCLUSION

It can be concluded that the conjugated poly(ethylacetylenecarboxylate) acts as an optical limiter with laser pulses at 532 nm in dichloroethane solvent. The limiting threshold depends on the solution concentrations at 5 and 10 J/cm² with 3×10^{-3} , and 5×10^{-3} M/L respectively. The observed data show that poly(ethylacetylenecarboxylate) has the potential for the use as optical limiting material for future applications.

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REFERENCES

1. T. J. Bunning, I. V. Natarajan, M. G. Schmitt, B. L. Epling and R. L. Crane, *Appl. Opt.*, **1991**, *30*, 4341 – 4349.
2. L. W. Tutt and A. Kost, *Nature*, **1992**, *356*, 225-226.
3. R. Chari, S. R. Mishra, H. R. Rawat and S. M. Oak, *Appl. Phys. B*, **1996**, *62*, 293 - 297.
4. D. S. Chemla and J. Zyss (Eds.), "Nonlinear optical properties of organic molecules and crystals", Academic Press, New York, **1987**.
5. J. A. Hermann and J. Staromlynska, *Int. J. Opt. Phys.*, **1993**, *2*, 271-275.
6. R. L. Sutherland. "Handbook of Nonlinear Optics", **1996**, Marcel Dekker, Inc. New York,.
7. R. Vijaya. Murti., Y. V. G. S, T. A Vijayaraj. and G. Sundararajan, *Current Science*, **1997**, *72*, 507-508.
8. C. Liu, H. Zeng., Y. Segawa and M. Kira, *Optics Communications*, **1999**, *162*, 53-56.
9. L. Chao, L. Chunling, L. Quanshui and G. Qihuang, *Chem. Phys. Lett*, **2004**, *400*, 569-572.
10. W. Hongli, L. Zhen, H. Bin, J. Zuoquan, L. Yanke, W. Hui, Q. Jingui, Y. Gui, L. Yunqi and S. Yinglin, *Reactive and Functional Polymers*, **2006**, *66*, 993-1002.
11. Y. Shouchun, X. Hongyao, S. Xinyan, W. Lei, S. Yinglin and T. Ben Zhong, *Dyes Pigments*, **2007**, *75*, 675-680.
12. G. Shanyi, Y. Shouchun, X. Hongyao, Z. Weiju, G. Yachen and S. Yilin, *Dyes Pigments*, **2007**, *73*, 285-291.
13. A. Al-Zier, A. Allahham and. A.W Allaf., *Current Science*, **2008**, *95*, 75-78.
14. J. E. Riggs and S. Ya- Ping, *J. Phys. Chem. A.*, **1999**, *103*, 485-495.
15. S. Ya-Ping and J. E. Riggs, *Int. Rev. Phys. Chem.*, **1999**, *18*, 43-90.
16. W. F Sun, M. M. Bader, T. Carvalho, *Optics Communications*, **2003**, *215*, 185-190.