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CONCENTRATION AND SOLVENT SENSITIVE VISIBLE SPECTRA OF POLY(TRICYANOVINYLDIMETHYLANILINE): AGGREGATION AND SOLVATOCHROMISM

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ABSTRACT

This work presents unusual spectral behavior of poly(tricyanovinyl-dimethylaniline) (**1**) in dilute solutions. A new conjugated polymer(**1**) was prepared from p-(tricyanovinyl)N,N-dimethylaniline via the use of a methylglucopyranoside reagent. It is observed that dilute solutions of **1** exhibit spectral features associated with aggregation. The associative interaction is studied by changing the salt concentration of LiBr in DMF solution, by changing the concentration of **1**, and by varying the solvents. The association modifies the visible spectrum of **1** in dilute solution. Spectra of **1** in DMF solution exhibit an intense absorption maximum at 429 nm, which can be assigned to the side group, with tailing past 700 nm. With increasing concentration, a new absorption band arises between 480 nm and 700 nm. LiBr dissociates the aggregate to decrease the additional spectral features. The visible spectrum of **1** varies in different solvents. The spectrum of **1** in chloroform solution exhibits two maxima at 490 nm and 550 nm. The associative interaction presumably arises from a dipole–dipole interaction among pendant side groups. In DMF solution of **1** in the presence of p-chloranil, the spectrum shows a

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maximum at 429 nm with a distinct shoulder near 520 nm which does not originate from **1** and p-chloranil(CA) itself.

Key Words: Aggregation; Solvatochromism; Poly(tricyanovinyl-dimethylaniline); Charge-transfer complexation

INTRODUCTION

Herein we describe concentration and solvent sensitive visible spectra of poly(p-(tricyanovinyl)N,N-dimethylaniline)(**1**) in various organic solvents. We recently^[1] described the use of unprotected sugars to polymerize dicyanoalkenes and –arenes to materials with conjugated backbones. One of the conjugated polymers was prepared from p-(tricyanovinyl)N,N-dimethylaniline via the use of a methylglucopyranoside reagent. It was reported^[2] that p-(tricyanovinyl)N,N-dimethylaniline(TCVDMA, **2**) was reacted with magnesium pentoxide in pentanol to give a cyano-substituted Mg-porphyr-azine. In contrast, by the use of sugar reagents in alkaline methanol, a new conjugated polymer from **2** is obtained instead of a cyclotetramer. This work presents unusual absorption behavior of **1** in dilute solution.

Tricyanovinyl and dicyanovinyl compounds, such as **2** and 4-dimethylaminobenzylidenemaleonitriles (**3**), have been of interest for optical studies. It was known^[3] that **2** formed solid pi-complexes in which it behaves as a donor with some molecules and as an acceptor with another. **2** may thus be termed pi-amphoteric. Comparison of ionization energies, electron affinities, and redox potentials indicated that TCVDMA is more easily oxidized and less readily reduced than 2,4,7-trinitrofluorenone(TNF) and it is less easily oxidized and more easily reduced than N,N-dimethylaniline(DMA). Solid state spectra^[4] of **2** were modified when the films evaporated onto quartz substrates were exposed to benzene vapor or heating. Absorption maxima of these spectra were shifted to lower energies compared to solution spectra. A series of p-N,N-dialkylaminobenzylidenemaleonitriles derivatives has been reported to exhibit a strong intramolecular charge-transfer(ICT) absorption.^[5] Donor-acceptor substituted organic compounds have received considerable attention because they possess large molecular second-order nonlinear optical susceptibilities (β). The use of acceptor groups such as dicyanovinyl or tricyanovinyl and/or donor group such as dithiolyldine-methyl for donor-acceptor molecules have been recognized to increase β substantially.^[6]

Intermolecular charge transfer interaction was utilized to fabricate the layer-by-layer deposited films between methacrylate-based polymers having the electron-donating carbazole group and electron-accepting 3,5-dinitrobenzoyl group in the side chains.^[7–10] The pi-complex of poly(N-vinyl-carbazole) and 2,4,7-trinitrofluorenone, PVK-TNF, has been commercially

used in photoelectronic devices.^[11] Conjugated polymers having electron-donating dithiafulvene units have been described to form soluble charge-transfer complexes with TCNQ and showed an unusual high electrical conductivity due to incorporation of the electron-deficient pyridine unit in the dithiafulvene polymer.^[12]

Yamamoto et al. have demonstrated that the progression of peaks or shoulders in the spectra of regioregular polymers are associated with aggregate formation (π -stacking)^[13] and the spectra of nonaggregated solutions of regioregular poly(3-alkylthiophene)s, and poly(4-alkylthiazole)s consist of a single, relatively narrow, absorption peak. In the solid state, or in colloidal aggregates, there is a large bathochromic shift of λ_{max} with a series of shoulders. Recently, it has been reported^[14] that PPE-type oligomers which incorporate the metal chelating 2,2'-bipyridine-5,5'-diyl unit aggregate in dilute solution at low temperatures and the formation of the aggregate contributes to the unusual photophysical behavior.

EXPERIMENTAL

All chemicals and solvents were used without further purification as received unless otherwise noted. N,N-dimethylformamide(DMF), and chloroform were purchased from Allied Signal. Tetrahydrofuran(THF), dichloromethane, acetone, and acetonitrile were purchased from EM SCIENCE. Lithium Bromide(LiBr) was purchased from Aldrich Chemical Co. **2** was prepared^[15] by condensation of tetracyanoethylene with dimethylaniline. **1** was synthesized by the method previously reported.^[1] The polymer(**1**) was prepared from **2** via the use of a methylglucopyranoside reagent. The weight average molecular weight (M_w) is analyzed by Gel Permeation Chromatography (GPC) using polystyrene standards. M_w of this polymer was estimated to be 9200. The structure proposed for this polymer is shown in Fig. 1. The UV-vis spectra were acquired on a Perkin-Elmer Lambda 9 spectrophotometer. The solutions were thoroughly mixed prior to recording of UV-Vis absorption spectra.

RESULTS AND DISCUSSION

We have observed that **1** forms an aggregate which exhibits a spectrum modified from the spectrum in dilute solution. Electronic absorption spectra in N,N-dimethylformamide (DMF) solution are shown with different concentrations in Fig. 2.

The absorption spectrum of **1** in 0.0001 wt.% DMF solution gives a maximum at 429 nm, with a shoulder at 480 nm with tailing past 700 nm. A maximum at 429 nm, similar to **3**,^[5] can be assigned to side group absorption. Due to the intense absorption of the side group, the π - π^* transition of the

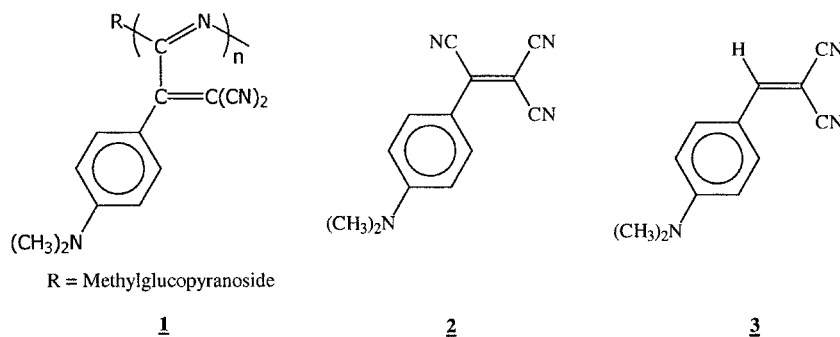


Figure 1. Chemical structures for poly(TCVDMA)(**1**), p-(tricyanovinyl)N,N-dimethylaniline(**2**), and 4-dimethylaminobenzylidenemalonitrile(**3**).

polymer backbone is not clearly observed in the visible spectrum of **1**. With increasing the polymer concentration up to 0.04 wt.% in DMF solution, the new absorption bands arise between 480 nm and 850 nm. Above this concentration, instrumental limitation of the absorbance measurement doesn't allow more information. The absorption intensity of each spectrum was normalized to the absorption maximum at 429 nm. These observations suggest that **1** forms an aggregate that exhibits broad absorption bands in the longer wavelength regions. It has been reported^[16] that the absorption spectrum of a polymer with a terminal electron donor group and an electron acceptor group in solution exhibited a charge-transfer (CT) absorption band. In **1**, the side group contains the electron-accepting dicyano group and

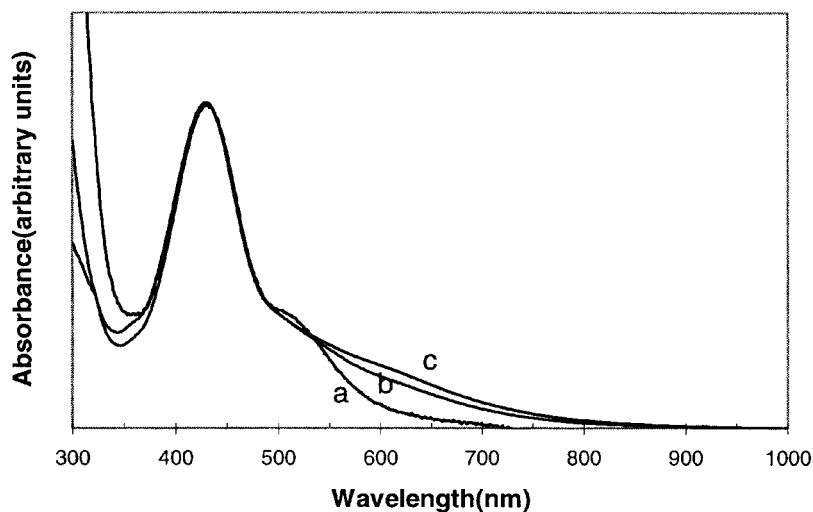


Figure 2. Concentration dependent absorption spectra of **1** in DMF solution: (a) 0.0001 wt%; (b) 0.001 wt%; (c) 0.04 wt%.

electron-donating amine group. The driving force to form the aggregate in dilute solution may be the strong interchain/intrachain interaction through the side groups of the polymers.

Salts, such as LiBr, have been employed to dissociate aggregated polymers, such as polyphenol, in DMF solution.^[17] As a method to confirm the formation of the aggregate, LiBr is added to 0.001 wt/v DMF solution of **1**. Absorption intensities at 429 nm are increased as the amounts of salts increased but intensities of longer wavelength absorption are decreased (Fig. 3). The addition of LiBr dissociates the aggregate to decrease the additional spectral features.

UV-Vis spectra of **1** in various organic solvents are shown in Fig. 4. The concentration of **1** is 0.001 wt/v% in each solution. The absorption maximum in various solvents, such as acetonitrile, acetone, THF, and dichloromethan, is slightly shifted in comparison to that of **3**. It was suggested^[18] that intramolecular donor-acceptor interaction is related to the dipole moment which reflects resonance structures for **3**. In the absorption spectra of **3** in organic solvents, a slight red shift of the absorption maximum was observed within the range of 6 nm in polar solvents but no longer wavelength absorption band was observed. Similarly the absorption at 429 nm in DMF solution of **1** is slightly shifted on the solvents but the absorption at lower energy is distinct. It may be inferred that a broad new longer wavelength band originates from interchain/intrachain interaction of the polymers. We attribute this new band to aggregation because this band also arises with increasing concentration in DMF solution. In acetonitrile solution, the intensity of long wavelength absorption bands increased

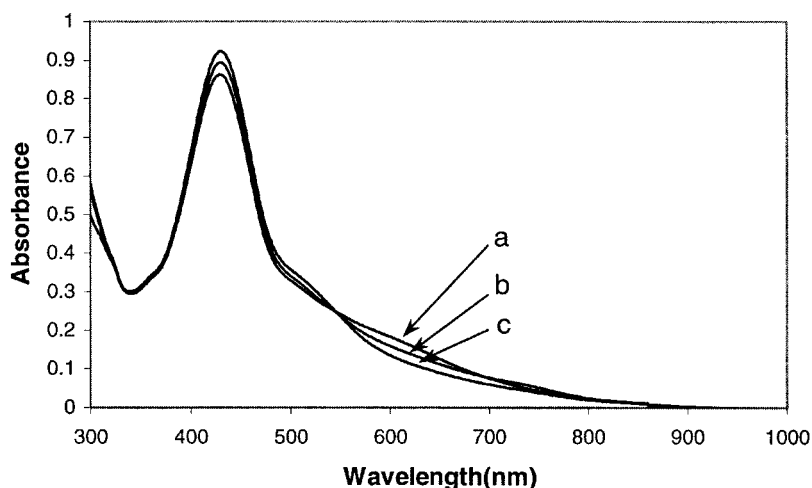


Figure 3. Absorption spectra of **1** (0.001 wt% DMF solution) with different amounts of LiBr: (a) 0%; (b) 0.5%; (c) 1.0%.

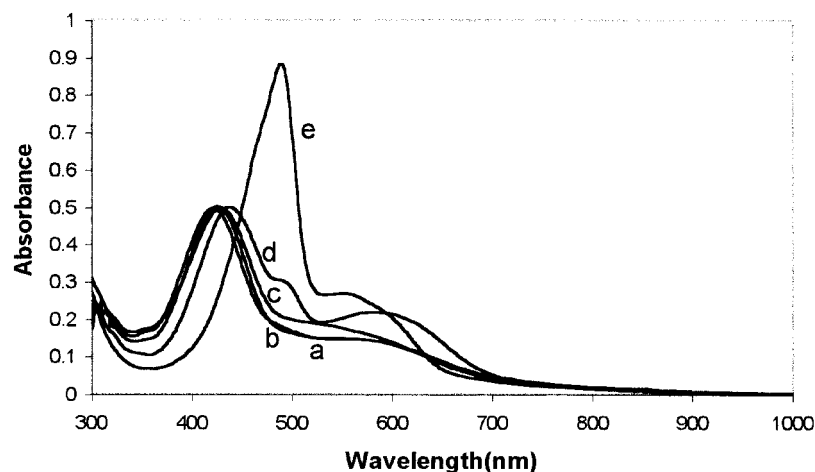


Figure 4. Absorption spectra of **1** in various solvents: (a) THF; (b) Acetone; (c) Acetonitrile; (d) Dichloromethane; (e) Chloroform.

noticeably. Significant changes of the absorption behavior are shown in chlorinated solvents. The spectral features of **1** vary remarkably in chlorinated solvents. The spectrum of **1** in dichloromethane shows λ_{\max} at 437 nm, 582 nm with a distinct shoulder at 488 nm which does not appear in non-chlorinated organic solvents. In sharp contrast to absorption spectra in other solutions, the absorption maximum in chloroform solution shifts to longer wavelengths. The electronic absorption spectrum of **1** in chloroform solution exhibits two maxima at 490 nm, 550 nm. λ_{\max} at 490 nm in chloroform solution and shoulder at 488 nm in dichloromethane may be related. Chloroform is more electron deficient than dichloromethane.

To investigate the interaction with **1** and chloroform, mixtures of DMF and chloroform are employed (Fig. 5). The concentration of **1** is 0.001 wt/v % in each solution. In 1/99(V/V) chloroform/DMF solution, visible spectrum is very similar to that from DMF solution with λ_{\max} at 429 nm. By contrast, two absorption maxima are observed at 435 nm and 490 nm in 5/95(V/V) chloroform/DMF solution. At 10% chloroform content, there is one absorption maximum at 490 nm. In chloroform solution, the absorption spectrum exhibits two absorption maxima with a sharper intense absorption band at 490 nm and a broad absorption band at 550 nm. The absorption intensity at 490 nm in chloroform solution is stronger than that in 10/90 chloroform/DMF solution. Although it is not clear yet, significant shift of λ_{\max} from 429 to 490 nm is not due to the difference of solvent polarity and/or refractive index of the solvent. It can be assumed that solute(polymer) to solvent interaction may occur. We attribute λ_{\max} at 550 nm to aggregation because chloroform is a poorer solvent than DMF. The aggregation of **1** changes the absorption behavior in dilute solution which has been of considerable interest in conjugated polymers. To

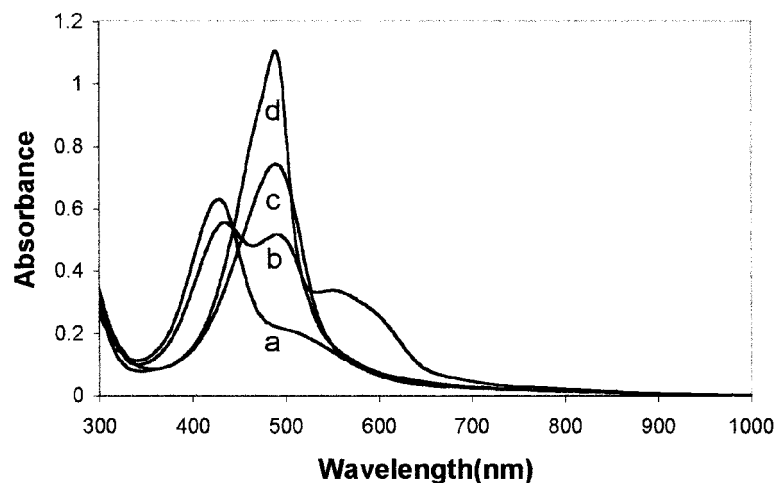


Figure 5. Absorption spectra of **1** in various ratio of CHCl_3/DMF solvent mixtures: (a) 1/99; (b) 5/95; (c) 10/90; (d) 100/0.

our knowledge, this work is the first demonstration of concentration and solvent sensitive absorption behavior of **1** involving dipole–dipole interaction among the pendant side groups.

An attempt was made to investigate the possibility of electron donor–acceptor interaction between **1** and electron acceptors (Note that **2** complexes with p-chloranil^[4]). 0.004 wt% p-chloranil(CA) is dissolved in a 0.001 wt%

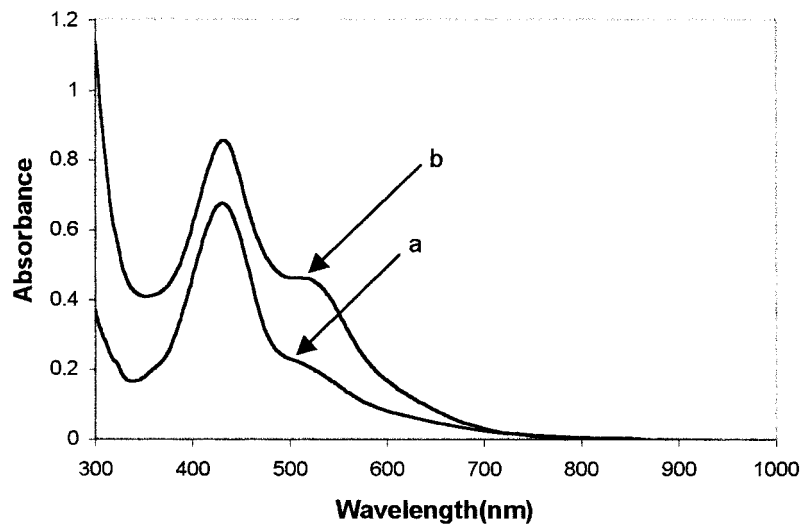


Figure 6. Absorption spectra of (a) **1**(0.001 wt.%) and (b) a mixture of **1**(0.001 wt.%) and p-chloranil(0.004 wt.%) in DMF solution.

DMF solution of **1**. The absorption spectrum shows a maximum at 429 nm with a distinct shoulder near 520 nm which does not originate from **1** and CA itself. It has been established^[19] that CA can quench C₆₀ triplets and lead to formation of CA⁻ free radicals with C₆₀ by electron transfer in benzonitrile solution. Our results imply that **1** interacts with CA in dilute solution and gives new spectral features which indicate charge-transfer complexation.

CONCLUSION

We have described concentration and solvent sensitive visible spectra of **1**. The visible spectra of **1** vary in different concentrations and in various organic solvents. With increasing concentration of **1** in DMF solution, new absorption in long wavelength regions arises. The addition of LiBr in DMF solution decreases the additional spectral features. Our observations suggest that the **1** forms the aggregate presumably driven by a dipole–dipole interaction among pendant groups. The associative interaction apparently modifies the electronic absorption spectra of **1** in dilute solution. The low energy transitions are considered to be the consequence of the aggregation through intermolecular interactions of the polymer. The spectral features of **1** vary remarkably in chlorinated solvents which may interact with **1**. These results indicate that the pendant groups of a polymer can greatly modify the absorption spectrum in various solvents. Electron accepting molecules, such as CA, can interact with **1** in dilute solution, suggesting the electron donating capability of the side group of **1**.

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REFERENCES

1. Kim, I.-B.; Rixman, M.A.; Tsai, Z.-H.; Wu, D.; Njus, J.M.; Stark, J.C.; Hankins, J.; Sandman, D.J. Use of Unmodified Carbohydrate Reagents for the Polymerization of Dicyanoalkenes and Dicyanoarenes. *Macromolecules* **2001**, *34* (22), 7576–7578.
2. Kopranenkov, V.N.; Gorcharova, L.S. Cyano-substituted Porphyrazines. *Zh. Obshch. Khim.* **1979**, *49* (6), 1408–1412.
3. Sandman, D.J.; Richter, A.F. The Intermolecular π -Amphoteric Character of p-Tricyanovinyl-dimethylaniline. *J. Am. Chem. Soc.* **1979**, *101*, 7079–7080.
4. Sandman, D.J.; Richter, A.F.; Warner, D.E.; Fekete, G.T. Solid Complexes of the π -Amphoteric Molecule p-Tricyanovinyl-N,N-Dimethylaniline. *Mol. Cryst. Liq. Cryst.* **1980**, *60*, 21–36.

5. Loutfy, R.O.; Law, K.Y. Electrochemistry and Spectroscopy of Intramolecular Charge-Transfer Complexes. p-N,N-Dialkylaminobenzylidenemalonitriles. *J. Phys. Chem.* **1980**, *84*, 2803–2808.
6. Katz, H.E.; Singer, K.D.; Sohn, J.E.; Dirk, C.W.; King, L.A.; Gordon, H.M. Greatly Enhanced Second-order Nonlinear Optical Susceptibilities in Donor-acceptor Organic Molecules. *J. Am. Chem. Soc.* **1987**, *109*, 6561–6563.
7. Shimazaki, Y.; Tsutsumi, N.; Ito, S. Adsorption-induced Second Harmonic Generation from the Layer-by-Layer Deposited Ultrathin Film Based on the Charge-transfer Interaction. *Langmuir* **2000**, *16*, 9478–9482.
8. Shimazaki, Y.; Mitsuishi, M.; Ito, S.; Yamamoto, M. Alternate Adsorption of Polymers on a Gold Surface through the Charge-transfer Interaction. *Macromolecules* **1999**, *32* (24), 8220–8223.
9. Shimazaki, Y.; Mitsuishi, M.; Ito, S.; Yamamoto, M. Preparation and Characterization of the Layer-by-Layer Deposited Ultrathin Film Based on the Charge-transfer Interaction in Organic Solvents. *Langmuir* **1998**, *14* (10) 2768–2773.
10. Shimazaki, Y.; Mitsuishi, M.; Ito, S.; Yamamoto, M. Preparation of the Layer-by-Layer Deposited Ultrathin Film Based on the Charge-transfer Interaction. *Langmuir* **1997**, *13* (6), 1385–1387.
11. Weigl, J.W. *Electrophotography* *Angew. Chem. Internat. Edit.* **1977**, *16*, 374.
12. Naka, K.; Uemura, T.; Chujo, Y. Synthesis and Properties of π -Conjugated Poly(dithiafulvene)s by Cycloaddition Polymerization of Heteroaromatic Bisthioketenes. *Macromolecules* **2000**, *33* (13), 4733–4737.
13. Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B. L.; Sugauma, H.; Asakawa, N.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; Matsuda, H. *J. Am. Chem. Soc.* **1998**, *120*, 2047–2058.
14. Walters, K.A.; Ley, K.D.; Schanze, K.S. Photophysical Consequences of Conformation and Aggregation in Dilute Solutions of π -Conjugated Oligomers. *Langmuir* **1999**, *15*, 5676–5680.
15. McCusick, B.C.; Melby, L.R. *Organic Syntheses*; John Wiley & Sons: 1963; Coll. Vol. 4, 953–954.
16. Sisido, M.; Shimizu, T.; Imanishi, Y.; Higashimura, T. Intra- and Intermolecular Charge-transfer Interactions between Terminal Electron Donor and Acceptor Attached to Poly(γ -benzyl-L-glutamate) in Solution. *Biopolymers* **1980**, *19* (3), 701–711.
17. Ayyagari, M.S.; Marx, K.A.; Tripathy, S.K.; Akkara, J.A.; Kaplan, D.L. Controlled Free-Radical Polymerization of Phenol Derivatives by Enzyme-Catalyzed Reactions in Organic Solvents. *Macromolecules* **1995**, *28*, 5192–5197.
18. Kuder, J.E.; Limburg, W.W.; Pochan, J.M.; Wychick, D. Structural Effects on the Electrochemistry and Charge Distribution of Mono-, Di-, and Tri-cyanovinyl Aromatic Compounds. *J. Chem. Soc., Perkin Trans. II* **1977**, *13*, 1643–1651.
19. Steren, C.A.; Willigen, H.V.; Biczók, L.; Gupta, N.; Linschitz, H. C₆₀ as a Photocatalyst of Electron-transfer Processes: Reactions of Triplet C₆₀ with Chloranil, Perylene, and Tritolylamine Studied by Flash Photolysis and FT-EPR. *J. Phys. Chem.* **1996**, *100* (21), 8920–8926.