

Synthesis and Application of Fluorophore-Enriched Epoxy-Graft-PVA Copolymers

¹Nader Zabbarjad Shiraz, ¹Elaheh Sadat Sharifzadeh, ²Mohammad Bayat and ¹Shiva Masoudi

¹Department of Chemistry, Islamic Azad University, Central Tehran Branch, Tehran, Iran

²Department of Chemistry, Imam Khomeini International University, Qazvin, Iran

Abstract: In this study some new fluorophore-enriched polymers were synthesized using the reactions of bisphenol-A resin and fluorescein in the presence of PVA or polyetherdiamine as hardener. The structures of polymers were elucidated by IR, UV and fluorimetry spectrometry. Polymers applied as coating on water diffusible surface. The results of fluorimetry on penetrated water containing fluorescent polymer, was a suitable procedure to monitor the leakage of oil pipelines.

Key words: Fluorescein · PVA · Epoxy Resin · Oil Leakage

INTRODUCTION

During the past decades, research on fluorophore-enriched polymers has become an interesting area because of their versatile applications as luminescent probes in various fields [1]. The assembling of many fluorophores onto one polymer chain affords the polymer high brightness under conventional microscope. In general, there are two ways to synthesize such fluorophore-enriched polymers. One of them is the polymerization of a polymerizable fluorescent monomer with some common monomers; the other is the chemical modification of polymers by fluorescent molecules or fluorescent oligomers [2-4].

The aim of present work was to synthesize a water-soluble fluorescent polymer for the coming use as a detector of water leakage in oil pipelines. On the other hand, the purpose was to facilitate exploration of the polymer in different media using the fluorescein which was linked to polymer. So, epoxy and fluorescein moieties were grafted to PVA in order to modify the tendency of PVA to water, as well improve its physical and mechanical resistance.

MATERIALS AND METHODS

Bisphenol A resin and D2000 were purchased from Huntsman. UV, FT-IR, Fluorimetry, DSC and TGA spectra were recorded using JASCO (V-530), Shimadzu (410), Perkin Elmer (LS 55) DSC Pyris 6 Perkin Elmer and TGA Pyris Diamond Perkin Elmer respectively.

Procedure for the Synthesis of (3): A mixture of epoxy resin **2** (5 gr) and fluorescein (**1**) (1 gr) [5-7] was mixed at 80°C for an hour and a redish paste separated and dried at r.t. IR (KBr, cm⁻¹): 3442 (OH), 1733 (C=O), 1660 (C=C), 1453 and 1246 (epoxy).

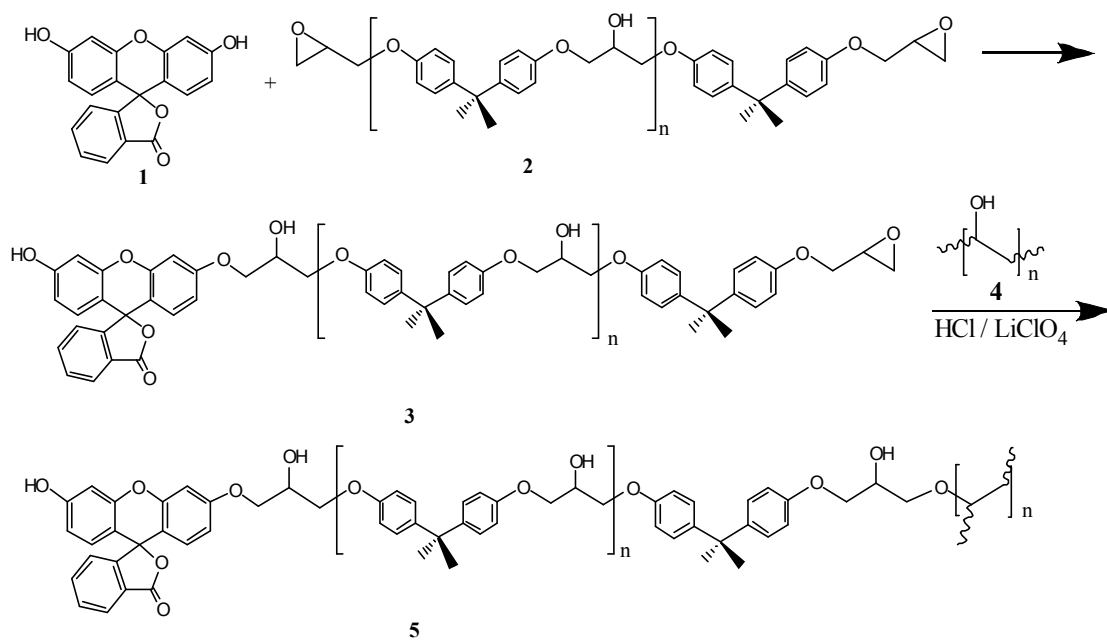
Synthesis of Epoxy-Graft-PVA (5): To epoxy resin **3** (5 gr) was added a solution of PVA (5 gr in 25 ml water) in the presence of catalytic LiClO₄ (0.1 gr). Mixture was stirred at 100°C for an hour and water evaporated in vacuum and reddish-brown paste (**5**) separated. IR (KBr, cm⁻¹): 3370-2500 (CO₂H), 1738 (C=O), 1600 (C=C).

Synthesis of Copolymer (7): A mixture of epoxy resin **3** (5 gr) and polyetheramine D2000 (**6**) [8] (2 gr) were mixed at 100°C for an hour and copolymer **7** obtained as viscose orange liquid. IR (KBr, cm⁻¹): 3443 (OH), 3350 (NH), 1761 (C=O), 1607 (C=C).

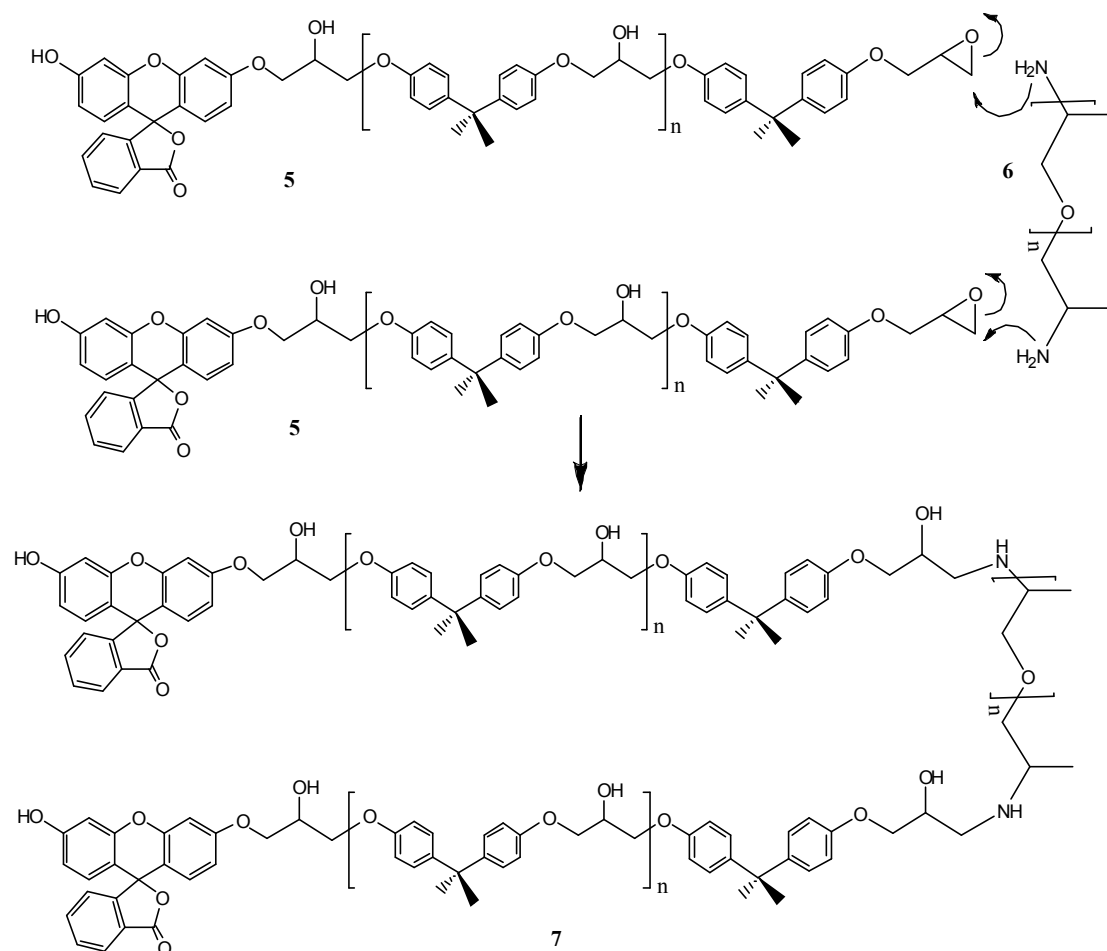
RESULTS AND DISCUSSIONS

The reaction of fluorescein (**1**) with epoxy resin (**2**) led to the formation of fluorescein linked epoxy resin (**3**) in good yield (Scheme 1). To improve the water solubility of polymer, the epoxy resin **3** reacted with polyvinyl alcohol (PVA) (**4**) solution in the presence of catalytic HCl/LiClO₄ and epoxy resin-graft-PVA copolymer **5** separated as redish-brown precipitate (Scheme 1).

Polyamines are well known hardener for epoxy resins. In this study poly etherdiamine (D 2000) **6** was used as hardener and its reaction carried out with epoxy resin **5** to produce cross-linked polymer (**7**) (Scheme 2).



Scheme 1:



Scheme 2:

Table 1: Fluorimetry parameters of polymers (10^{-5} molar in H_2O)

Comp.	λ_{max} (Absorption)		λ_{max} (Emission)	
	200-400	400-600	450-500	500-600
1	233	481	441	511
5	229	487	480	513
7	226	457	476	513
Sample	231	477	-	514

The structures of polymers were elucidated by IR, UV, TGA, DSC and fluorimetry methods. In IR spectrum vibrational stretching of C=O and epoxy groups appeared at 1753 and 1244 cm^{-1} respectively. In IR spectrum of **5**, the stretching of epoxy groups vanished while

strong vibration of O-H of PVA appeared at about 3000-3500 cm^{-1} . N-H stretching of **7** was appeared at 3448 cm^{-1} .

UV spectrum of polymers clearly showed UV absorbtion at 200-400 nm.

Fluorimetry studies indicated that fluorescein labled polymers had emissions in 513-519 nm region (Table 1).

In order to use the polymer, it was applied as a coating inside the concrete petroleum tank and its efficiency was considered in determining the water leak into oil tank. Studies indicated that during the penetration of water through coating into the oil, dissolved polymer cooperated to recognition of leakage via measuring and exploring of fluorescent property.

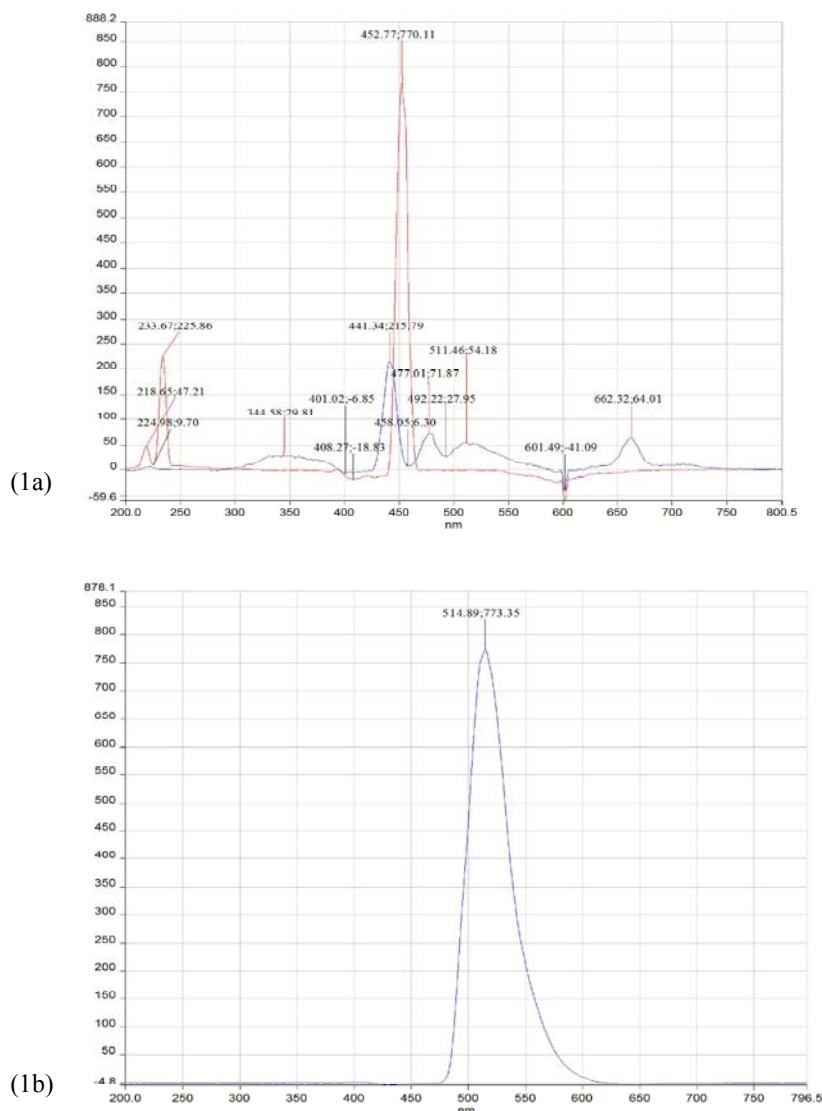


Fig. 1: Fluorimetry spectrum of **5**

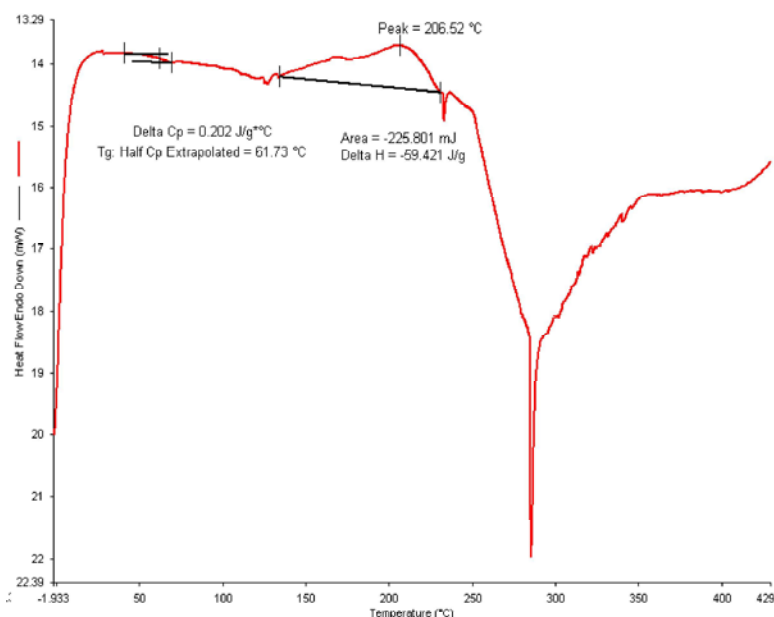


Fig. 2: DSC thermograph of **5**

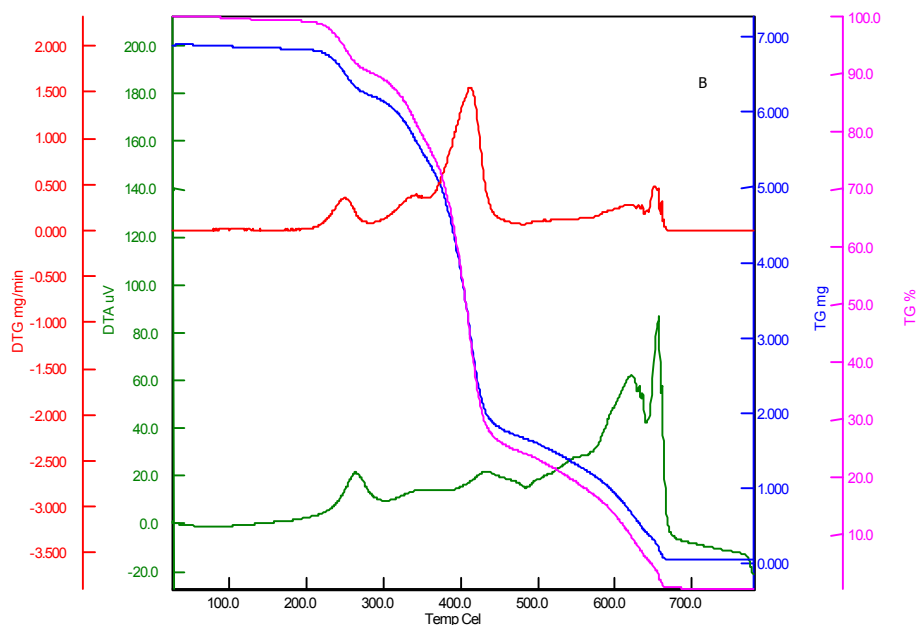


Fig. 3: TGA thermograph of **5**

Fluorimetry studies showed similar patterns for all synthesized compounds. They had two distinct peaks at 450-480 nm (Sharp peak) and 510-520 nm (Broad peak) (Figure 1a).

In fluorimetry spectra of water extracted from oil-phase, one peak vanished from 450-480 nm (Figure 1b). Instead, a sharp signal appeared at 514 nm, which was a proper indicator for leakage monitoring of water into oil tanks or pipelines.

DSC thermograph of **5** showed identical signals for T_g and T_m of polymer at 62 and 206°C respectively. An endothermic process took place at 273°C which would be due to phase-transfer and/or degradation processes (Figure 2).

TGA thermograph of **5** indicated that polymer was stable up to 220°C, after that 85% of polymer degraded at 220-430°C. At the end, 430-700°C, the remain of polymer disappeared gradually (Figure 3).

CONCLUSION

In conclusion, represented procedure was a facile method to synthesize the fluorophore-enriched copolymers with diverse functionalities. These polymers have good fluorescent property and could be applied as probe for monitoring in chemical analysis. As well fluorimetry of fluorescein-labeled polymers at 515 nm could be successful method in monitoring of oil pipeline leakage in water media like marine transportations.

REFERENCES

1. Duan, Y., M. Liu, W. Sun, zM. Wang, Sh. Liu and Q. X. Li, 2009. Recent Progress on Synthesis of Fluorescein Probes. *Mini Reviews in Organic Chemistry*, 6: 35-43.
2. Wang, K., W. Huang, P. Xia, Ch. Gao and D. Yan, 2002. Fluorescent Polymer Made from Chemical Modification Poly(styrene -co-maleic anhydride). *Reactive and Functional Poly (styrene-co-maleic anhydride)*. *Reactive and Functional Polymers*, 52 (3): 143-148.
3. Tanaka, K., N. Kitamura and Y. Chujo, 2010. Biodegradable Main-Chain Phosphate-Caged Fluorescein Polymers for the Evaluation of Enzymatic Activity. *Macromolecules*, 43(14): 6180-6184.
4. Suhara, Y., Sh, Abe, A. Murakami, Y. Shimomura, K. Nakagawa, M. Kamao, N. Tsugawa and T. Okano, 2008. Synthesis and Development of Biologically Active Fluorescent-Labeled Vitamin K Analogues and Monitoring of Their Sub Cellular Distribution. *Tetrahedron*, 64(37): 8789-8796.
5. Song, A., T. Wu, S. Chen, M. Zhang and T. Shen, 1998. Synthesis and Photophysical Properties of Amphiphilic Dyads of Fluorescein and Carbazol Linked with Flexible or Semi-rigid Bridge. *Dyes and Pigments*, 39(4): 371-382.
6. Lakowiz, J.R., 1999. *Principles of Fluorescence Spectroscopy*. New York.
7. Gao, H., Ch. Wang, W. Yang and Sh. Fu, 2004. Preparation of a Water- Soluble Fluorescent Polymer. *Journal of Macromolecular Science Part-A- Pure and Applied Chemistry*, A41(4): 357-371.
8. www.basf.com/usa/intermediates.