



Synthesis and Properties of Fluorescent Polymers

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Fluorescent monomer α -N-methacrylamide- β -naphthol (NMAMN) was synthesized by Friedel-Crafts reaction and incorporated into its polymers. The structure of α -N-methacrylamide- β -naphthol was optimized through the programme Gauss03 package implementing the 6-31G basis set. The spectroscopic properties were assessed for their effectiveness and the fluorescence intensity of autopolymer was enhanced significantly. Moreover, the fluorescent compounds showed good thermodynamic stability.

Key Words: Fluorescent polymers, Spectroscopic properties, Thermodynamic stability.

INTRODUCTION

In recent years, many researchers had been interested in synthesis and characterization of fluorescent polymers¹⁻⁴. The approaches to preparation of fluorescent polymers were divided into two parts *i.e.*, the polymerization of a monomer containing a fluorescent chromophore⁵⁻⁷ and the naphthols chemical modification of commercially available polymers containing reactive groups by using fluorescent dyes or organic molecules⁸⁻¹⁰. The first method had already got increasingly extensive application. Several fluorescent chromophores such as naphthalene, anthracene, phenanthrene, fluoranthene, acridine, carbazole, pyrene, chrysene, triphenylene, perylene and their substituted aromatic derivatives, *etc.*, had been developed and employed in diverse fields. Marie¹¹ prepared fluorescent coating which was applied to many aspects especially outdoor coating due to its high ultraviolet durability. The synthetic approaches of fluorescent monomers¹²⁻¹⁴ were complex and needed too much time and the yield was low. Zhu and Zhang¹⁵ synthesized fluorescent monomer from 4-bromo-1,8-naphthalic anhydride and ethanol-amine *via* amidation, amination and quaterization. Some of the problems are poor adhesion to the polymer and difficult synthetic approaches. In this work we had developed Friedel-Crafts reaction to provide stable propenyl containing naphthalene unsaturated fluorescent monomer which could be incorporated directly into the polymer backbone of condensation polymers. The operation was easy, final treatment was simple and yield could reach to 86 %. The polymers may be useful in urban beautification, electro-luminescence devices and antifouling coating in the future. These difunctional compounds would

also serve as base compounds for other fluorescent brightening agents.

EXPERIMENTAL

α -N-methacrylamide- β -naphthol, N-methylolacrylamide (HAM), sodium hydroxide, 2,2-azobisisobutyronitrile, acetone, concentrated sulfuric acid, dehydrated alcohol, methyl benzene, ethyl acetate, glycerine, MA, MMA, BA, BMA, SA, SMA are of quality agents. All solvents used for synthesis were at least reagent grade quality and were used without further purification.

Optimized of molecular structure: Optimization of the molecular structure performed density functional theory¹⁶ (DFT)-B3LYP method. The molecular initial configuration received from Chem3D package. Pre-optimization of the molecular structure adopt the method MOPAC followed by the PC version of the programme Gaussian03 package implementing the 6-31G basis set to obtain fully optimized geometry structure.

General procedure

Synthesis of α -N-methacrylamide- β -naphthol: 0.02 mol β -naphthol and 0.02 mol N-methylolacrylamide dissolved in 100 mL of anhydrous alcohol were put into a 250 mL three-necked round-bottom flask equipped with a heating oil bath and stirrer. Then concentrated sulfuric acid (10 mL) was dropped stepwise as the Friedel-Crafts condensation catalyst. The reactant mixture was heated to 50 °C for 5 h. After completion of the reaction, as monitored with TLC, the resulting mixture was washed with NaOH(aq) to terminate the reaction.

The organic phase was separated and recrystallized to remove the excess β -naphthol. (Yield: 86 %) m.p. 147 °C a pink needle like crystal. IR (KBr, ν_{\max} , cm^{-1}): 3326 (O-H), 3205 (N-H), 1644 (C=O), 1543 δ (N-H), 3063 ν (C-H), 1591, 1464 1435 ν (C=C, naphthalene), 3063 ν (C-H, naphthalene), 2784 ν (CH₂), 1252 ν (C-O, phenol), 948, 973 γ (C-H). ¹H NMR (acetone, TMS): 10.42 (s, OH, 1H), 8.69 (s, NH, 1H), 8.05 (d, naphthalene, 1H), 7.81 (d, naphthalene, 1H), 7.78 (d, naphthalene, 1H), 7.49 (t, naphthalene, 1H), 7.33 (t, naphthalene, 1H), 7.17 (d, naphthalene, 1H), 6.33 (q, =CH₂, 2H), 5.68 (q, CH=, 1H), 5.00 (d, -CH₂-, 2H). Anal. calcd. (%) for C₁₄H₁₃NO₂: C, 73.99; H, 5.7; N, 6.1. Found (%): C, 73.3; H, 5.6; N, 6.1.

Synthesis of autopolymer: According to the optimal reactive condition, a stirred mixture of part of α -N-methacrylamide- β -naphthol (5 g) and AIBN (0.25 g) in acetone (12.25 g) were added into a 100 mL glass reactor. The reactor was put into a thermostatic oil-bath on the oscillator and the reactive mixture was oscillated until the reagents dissolved in acetone and kept oscillating at 80 °C for 0.5 h. The rest of the mixture dropped stepwise in 0.5 h. The temperature controlled 80 °C and went on oscillating for another 5 h. After it was cooled to room temperature, the reaction mixture was poured slowly into anhydrous alcohol, giving rise to a fiber-like precipitate. The precipitated polymer was washed with anhydrous alcohol repeatedly until the solution is clear. The solid polymer was collected by filtration, dried under vacuum at 37 °C to constant weight and ground to a powder. (C₁₄H₁₃NO₂)_n, IR (KBr, ν_{\max} , cm^{-1}): 3294 ν (O-H), 3193 ν (N-H), 1632 ν (C=O), 1518 δ (N-H), 1632, 1518, 1435 ν (C=C), 3066 ν (C-H), 1230 ν (C-O).

Synthesis of copolymers: The synthesis of copolymers carried out in two steps. A stirred mixture of α -N-methacrylamide- β -naphthol, acrylic ester monomers and AIBN in acetone were added into a 100 mL glass reactor in two lots. The reactive mixture was put into a thermostatic oil-bath on the oscillator and kept oscillating at 80 °C for 0.5 h until the reagents dissolved in acetone. The rest of the mixture dropped stepwise in 0.5 h. The temperature controlled 80 °C and went on oscillating for another 5 h. The products were treated with coating, drying and grinding for recognition studies. ((C₁₄H₁₃NO₂)_{0.25}(C₄H₆O₂)_{0.75})_n, IR (KBr, pellet, cm^{-1}): 3364 ν (N-H), 1733 ν (C=O-O) 1637, 1521, 1442 ν (C=C), 1521 δ (N-H), 2949 ν (C-H), 1230 ν (C-O), 1378 δ_s (CH₃), 2949 ν_{as} (CH₃), 2851 ν_s (CH₃). ((C₁₄H₁₃NO₂)_{0.25}(C₇H₁₂O₂)_{0.75})_n, IR (KBr, pellet, cm^{-1}): 3373 ν (N-H), 1730 ν (C=O-O), 1514 δ (N-H), 1644, 1514, 1466 ν (C=C), 2958 ν (C-H), 1238 ν (C-O), 1382 δ_s (CH₃), 2958 ν_{as} (CH₃), 2870 ν_s (CH₃). ((C₁₄H₁₃NO₂)_{0.25}(C₅H₈O₂)_{0.75})_n: IR (KBr, pellet, cm^{-1}): 3372 ν (N-H), 1730 ν (C=O-O), 1517 δ (N-H), 1641, 1517, 1441 ν (C=C), 2994 ν (C-H), 1236 ν (C-O), 1388 δ_s (CH₃), 2950 ν_{as} (CH₃), 2838 ν_s (CH₃). ((C₁₄H₁₃NO₂)_{0.25}(C₈H₁₄O₂)_{0.75})_n, IR (KBr, pellet, cm^{-1}): 3365 ν (N-H), 1723 ν (C=O-O), 1518 δ (N-H), 1644, 1518, 1467 ν (C=C), 2952 ν (C-H), 1238 ν (C-O), 1382 δ_s (CH₃), 2952 ν_{as} (CH₃). ((C₁₄H₁₃NO₂)_{0.8}(C₂₁H₄₀O₂)_{0.2})_n, IR (KBr, pellet, cm^{-1}): 3293 ν (N-H) 1736 ν (C=O-O) 1526 δ (N-H) 1634, 1526, 1460 ν (C=C), 3063 ν (C-H) 1227 ν (C-O) 1376 δ_s (CH₃) 2851 ν_s (CH₃) 1460 δ_s (CH₂) 2917 ν_{as} (CH₂). ((C₁₄H₁₃NO₂)_{0.8}(C₂₂H₄₂O₂)_{0.2})_n, IR (KBr, pellet, cm^{-1}): 3265 ν (N-H) 1720 ν (C=O-O) 1514 δ (N-H) 1628, 1514, 1464 ν (C=C) 3069 ν (C-H) 1230 ν (C-O) 1381 δ_s (CH₃) 2847 ν_s (CH₂) 2920 ν_{as} (CH₃) 1464 δ_s (CH₂).

RESULTS AND DISCUSSION

Optimized of molecular structure: Fig. 1 showed the fully optimized low energy conformation of fluorescent monomer.

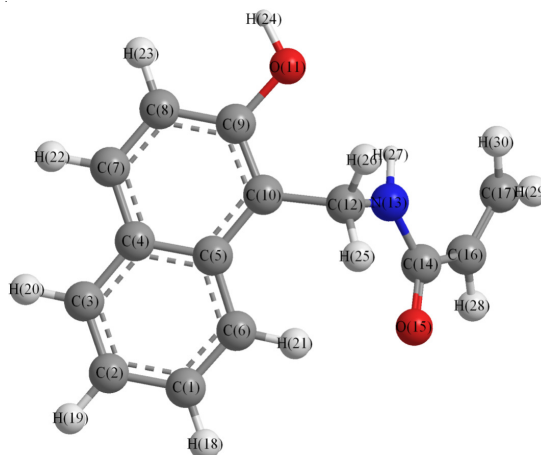


Fig. 1. Fully optimized low energy conformation of α -N-methacrylamide- β -naphthol

Table-1 showed that the bond lengths of C₉-C₁₀ (1.386587 Å), C₁₀-C₁₂ (1.517526 Å) and C₁₄-C₁₆ (1.491762) were shorter than standard bond length of C-C (1.54 Å). The C₁₄-O₁₅ (1.259708 Å) bond was longer than standard bond C=O (1.2 Å). The reason was conjugated effect existed between these atoms. The bond lengths of C₁₂-N₁₃ (1.470209 Å) and N₁₃-C₁₄ (1.368336 Å) were much shorter than standard bond C-N (1.49 Å), which explained part of delocalization. Bond angles and dihedral angles revealed that C₉, O₁₁, C₁₀, N₁₃, C₁₄, O₁₅ were *sp*² hybridization. The molecular had good coplanarity and delocalization resulted in good fluorescence.

Optimal reactive conditions: The optimal reactive condition of polymers listed in Table-2.

Reactant mole ratio, solid content, initiator content, temperature and time were the important factors on the synthesis of polymers. Temperature affected thermodynamics and dynamics of reactions. The molecular thermodynamic movement speeded up when temperature went up, which accelerated the probability of molecular collision resulted in the increasing of the probability of implosion. Inappropriate reactive conditions resulted in poor adhesion or implosion.

UV-Visible absorption spectroscopy: Fig. 2 showed the absorption spectra of monomer α -N-methacrylamide- β -naphthol and its polymers in THF. In all cases, prominent peaks were observed near 280 and 330-340 nm. The peaks were assigned arising from the π - π^* transition of the naphthalene backbone resulted in similar peak shape. In the same solvent and concentration, the absorbance of autopolymer was higher than the others. According to Lambert-Beer law, the molar absorption coefficient of autopolymer was the maximum among all compounds due to the increase of conjugated effect. However, copolymers were smaller than α -N-methacrylamide- β -naphthol because of steric hindrance effect.

Fluorescence spectroscopy: The fluorescence emission spectra of α -N-methacrylamide- β -naphthol and polymers in solvent THF was shown in Fig. 3. The prescanning datas by fluorescent spectrometer showed the maximum excitation of

TABLE-1
SELECTED BOND LENGTHS AND ANGLES FOR α -N-METHACRYLAMIDE- β -NAPHTHOL

Bond lengths (Å)	Bond angles (°)	Dihedral angles (°)
d(C ₉ -C ₁₀) 1.3866	\angle (C ₁ -C ₂ -C ₃) 119.7748	D(6,1,2,19) -179.6962
d(C ₁₀ -C ₁₂) 1.5175	\angle (C ₈ -C ₉ -O ₁₁) 120.8486	D(4,5,10,12) 175.5396
d(C ₁₂ -N ₁₃) 1.4702	\angle (C ₉ -C ₁₀ -C ₁₂) 118.2175	D(7,8,9,11) 179.0852
d(C ₁₄ -C ₁₆) 1.4917	\angle (C ₁₂ -N ₁₃ -C ₁₄) 122.4953	D(10,9,11,24) -174.3455
d(C ₁₆ -C ₁₇) 1.3396	\angle (O ₁₅ -C ₁₄ -C ₁₆) 119.9694	D(25,12,13,27) -170.6512
d(C ₁₄ -O ₁₅) 1.2597	\angle (C ₁₇ -C ₁₆ -H ₂₈) 120.8579	D(12,13,14,16) -178.5436
d(C ₉ -O ₁₁) 1.4031	\angle (C ₁₄ -C ₁₆ -C ₁₇) 126.194	D(14,16,17,29) 177.9048
d(N ₁₃ -C ₁₄) 1.3683	\angle (C ₁₆ -C ₁₇ -H ₃₀) 122.7671	D(28,16,17,30) -176.3823

TABLE-2
OPTIMAL REACTIVE CONDITIONS OF POLYMERS

Polymer	Mole ratio	Solid content (%)	Initiator content (%)	Temperature (°C)	Time (h)
Autopolymer	—	30	5	80	6
NMAMN + MA	1:3	20	5	80	6
NMAMN + MMA	1:3	20	5	80	6
NMAMN + BA	1:3	20	5	80	6
NMAMN + BMA	1:3	20	5	80	6
NMAMN + SA	4:1	35	5	80	6
NMAMN + SMA	4:1	35	5	80	6

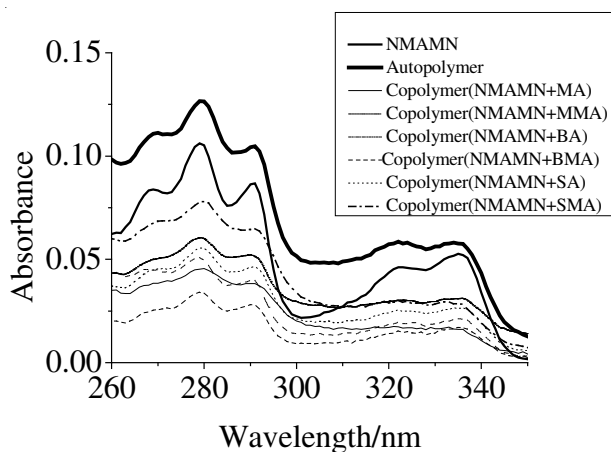


Fig. 2. Absorption spectra of α -N-methacrylamide- β -naphthol and its polymers in THF ($M = 1 \times 10^{-5}$ mol/L)

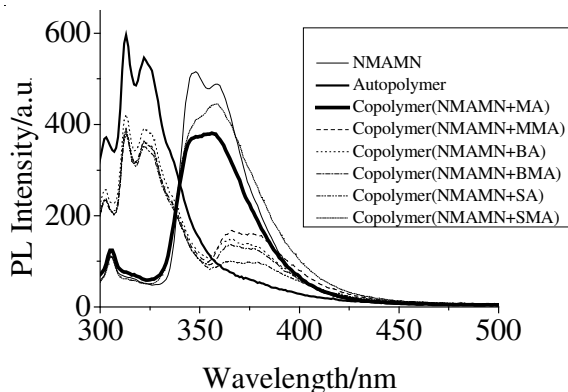


Fig. 3. Fluorescence spectra of α -N-methacrylamide- β -naphthol and polymers in THF ($M = 1 \times 10^{-5}$ mol/L)

α -N-methacrylamide- β -naphthol and polymers in THF. The emission spectra and fluorescent intensity of compounds were performed at their own maximum excitation wavelength. In all compounds, four emission peaks were observed with peaks at about 300 and 360 nm. It is noteworthy that the intensity

enhancement and absorbance follow the same trend. The fluorescent intensity sequence of the compounds showed: autopolymer was enhanced significantly, monomer was the second and the copolymers lower. Fortunately fluorescent intensities of soft monomers were higher than others among the copolymers. Copolymers of soft monomers made the materials not only flexible but also high fluorescence property.

Thermodynamic stability: The TGA curve of α -N-methacrylamide- β -naphthol and polymers was shown in Fig. 4. From the TGA curve, we found the thermal stability of α -N-methacrylamide- β -naphthol was similar to polymers and no weight loss was observed before 200 °C. It showed good thermodynamic stability.

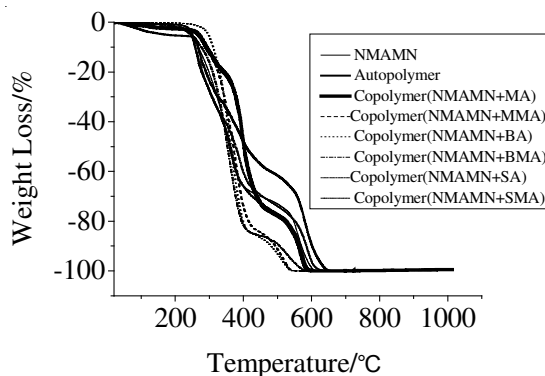


Fig. 4. TGA curves of α -N-methacrylamide- β -naphthol and polymers

Conclusion

α -N-methacrylamide- β -naphthol was synthesized and incorporated into its polymers. Through the fully optimized low energy conformation and measurement of spectroscopic properties, the compounds showed good fluorescence property. The TGA curve showed good thermodynamic stability. Moreover, copolymers of soft monomers made the materials not only flexible but also high fluorescence property. The difunctional compounds may be useful in urban beautification,

electro-luminescence devices, antifouling coating and serve as base compounds for other fluorescent brightening agents in the future.

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