

Synthesis and Characterization of PMMA with 4 - Carbazole Chromophore Substitution

Keyanpour-Rad, Mansoor**

Materials and Energy Research Center, P. O. Box 14155-4777, Tehran, I. R. IRAN

ABSTRACT: *A new carbazole- containing polymer has been synthesized for further photophysical studies. Efficient synthesis of the substituted methyl methacrylate has been accomplished via microwave assisted synthesis of 1 - chloro - 4 - carboxy - 5, 6, 7, 8- tetrahydrocarbazole followed by further steps, such as reduction of the 4-substituted methyl carboxylate, dechlorination of the ring and at last, the reaction of the 4 - hydroxymethyl - 9 - ethyl carbazole with methacryloyl chloride.*

The resulting monomer was then polymerized free-radically to form the polymer, having a distribution M_w/M_n of 2.6.

KEY WORDS: *Microwave promoted synthesis, Carbazole-containing polymethylmethacrylate, Carbazole chromophores, 4- substituted carbazoles, Free radical polymerization.*

INTRODUCTION

Carbazole derived monomers and polymers have been extensively studied for their good photoconductive properties [1-2]. Properties of these materials, such as good optical photorefractive and charge transporting, combined with ease of processing have stimulated a tremendous amount of new researches in different areas of material science [3-4]. A general method of synthesis to prepare the monomers by treating an aromatic or heterocyclic compounds containing a hydroxyl group with acryloyl and methacryloyl chloride in the presence of an acid binding substance, preferably a tertiary amine, was then suggested. In order to polymerize these monomers via radical polymerization, only, azobisisobutyronitrile (AIBN) has been acted as the satisfactory initiator [5-6].

The syntheses of some carbazole - containing

methacrylate polymers, except the 4-substituted carbazole methacrylate, have been reported by Keyanpour, et al. [7] for their photophysical studies. The reason for the absence of the 4 - substituted carbazole containing methacrylate among the other substituted ones, was the tedious works of the steps in the synthesis and also the very low yields of some steps for preparation of poly (N - ethyl - 4 - vinylcarbazole).

For example, the aromatization reaction of the tetrahydrocarbazole (4) was reported to afford a poor yield of the product [8], but it was successfully accomplished in high yield via a microwave promoted synthesis in a very short time [9].

Based on successful aromatization reaction of 4-substituted carbazoles, we tried to synthesis and

* To whom correspondence should be addressed.

+ E-mail: mankian_rad@yahoo.com

1021-9986/05/2/11

5/\$/2.50

polymerization of [4-(9-ethyl) carbazole] methyl methacrylate, by using microwave irradiation for the ring closure step to have the tetrahydrocarbazole (2) in quantitative yield. The photophysical properties of this polymer will be further studied in a same fashion as accomplished for the same compounds [7,10].

EXPERIMENTAL

Materials

Azobisisobutyronitrile (AIBN), which obtained from Aldrich Chemical Company, was recrystallized from absolute ethanol, and stored at zero degree in the dark.

Commercial methacryloyl chloride (95%) obtained from Aldrich Chemical Company was distilled at atmospheric pressure (bp 95-96 °C) and freshly used in the monomer synthesis. The starting materials were obtained from Merck Chemical Company and directly used without any purification. The intermediates (1), (3), (4), (6) and (7) (Scheme 1) were prepared according to the procedures reported in the literature [8]. As reported in the literature, the commercial p-chloro -m-aminobenzoic acid was treated with sodium nitrite to form the related diazonium salt which reduced by sulphur dioxide in situ to form (1). The N-ethylation of (2) was synthesized by treatment of (2) with KOH, followed by the addition of ethyl iodide to afford (3). This compound was esterified by methanol to form (4) which was aromatized by microwave irradiation in dry condition, using chloranil as the oxidizing agent. The 4-substituted methyl ester in (5) was successfully reduced by lithium aluminum hydride to give (6) which in turn was dechlorized with Raney nickel to have compound (7). The aromatization of (4) to the intermediate (5) was performed according to the microwave method of synthesis published in our previous publication [9].

Instruments

Mass spectrum was measured by V.G. Micromass 12. Nuclear magnetic resonance spectra were recorded on a Bruker 80 MHz spectrometer, by using CDCl₃ as internal TMS. The chemical shifts are reported as δ (ppm). Infrared spectra was recorded on a Bruker IFS 48 spectrophotometer.

A domestic microwave oven (Butane 245) at 2450 MHz (100w) was used for the synthesis of intermediate (2).

The vacuum line used for polymerization of the monomer was a conventional glass system.

Average molecular weight of the polymer was found by gel permeation chromatography (GPC; Waters 150 C), using tetrahydrofuran (THF) as the solvent. The sample concentration was kept at 0.3 - 0.6 % with a volume of 100-200 ml. The calibration of the instrument was in accordance of universal calibration method, using narrow molecular weight polystyrene standards [11].

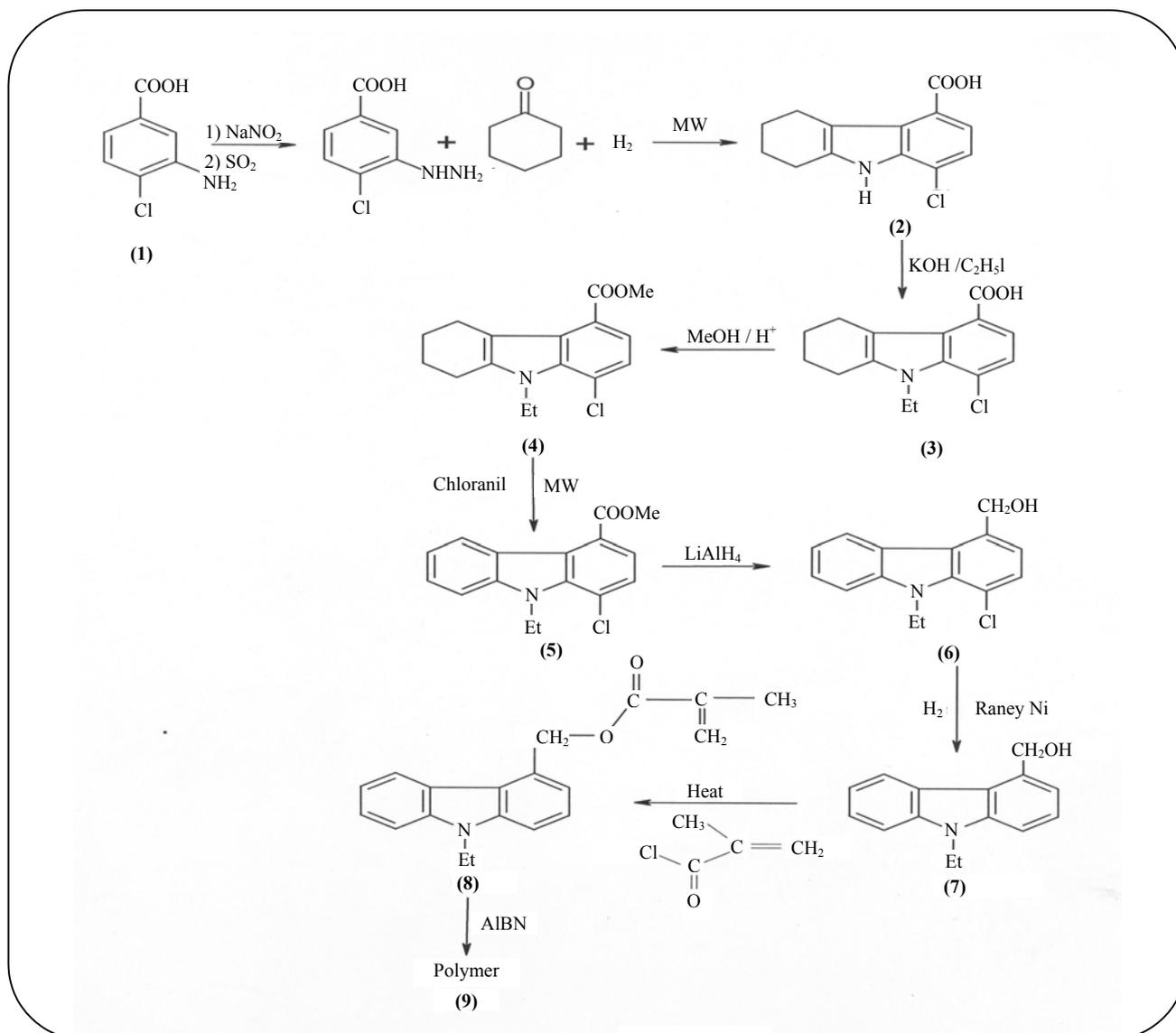
The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed by polymer department of University of Barcelona, Spain.

Microwave assisted synthesis of 1-chloro-4-carboxy-5,6,7,8-tetrahydrocarbazole (4)

A mixture of 10.7g (0.057 mol) of hydrazino hydrochloride (1), 10 ml concentrated H₂SO₄ and 90 ml (0.86mol) of cyclohexanone was placed in the microwave oven and irradiated at 100w for a period of 10 min. the resulting mass was added to cold water, mixed well and filtered, affording, a highly crystalline product which was recrystallized from small amount of glacial acetic acid, yielding 12.8g (90%) of (2), mp 221-223°C dec Lit mp 220-223[7]; ν_{\max} 3340 (NH), 1660 (C=O), 1600 (C=C), 765 and 735 cm⁻¹; δ (D₂O, K₂CO₃) 8.1, 7.7, 7.58, 7.42 (2H, two d, Ar H), 3.3 (4H,m, H for the saturated ring), 2.3 (4H, two d, protons for the saturated ring).

Synthesis of monomer [4-(9-ethyl) carbazolyl] methyl methacrylate (8).

A mixture of 3.0g (0.0133 mol) of (7), dry triethylamine 5.0 ml (0.036 mol) and 30 ml of dioxane was cooled to about 6 °C. The mixture was stirred and a solution of 2.5 ml (0.024 mol) of methacryloyl chloride in 10ml of the same solvent was added dropwise. The resulting heterogeneous mixture stirred at 6 °C for 0.5 hour and allowed to reach the room temperature to complete the reaction. It was then poured into ice-water, and the oily material was extracted into dichloromethane, washed with water and the organic solvent was evaporated. The residue was dissolved in 20 ml of water-ethanol (1:1, v/v), treated with 10 ml saturated sodium bicarbonate solution and left at zero degree, for 15 hours. It was then diluted with water, extracted with dichloro-methane, washed with water, dried with (MgSO₄) and evaporated



Scheme 1

to dryness to give 1.7g (46%) of a colourless oily material which was homogeneous by T.L.C chromatography, (silica gel/ CHCl_3 / R_f 0.6). Found: C, 77.63; H, 6.56. $\text{C}_{19}\text{H}_{19}\text{NO}_2$ requires: C,77.79;H,6.53. ν_{max} (neat film) 2990 (C-H), 1715 (C=O), 1630 (C=C), 1620, 1600, 1580. 1450 (broad), 1440, 1380, 1325, 1295, 1250, 1150, 1110, 1080, 1010, 960, 940, 812, 790, 780, 760, 745, 725 cm^{-1} . δ (CDCl_3 -Int TMS) 8.4 (1H, ArH), 7.6 (6H, complex m. ArH), 6.38 (1H, s, olefinic proton), 6 (2H, s, CH_2), 5.75 (1H, s, olefinic proton) 4.77-4.4 (2H, q, ethyl group), 2.18 (3H, s, CH_3), 1.8-1.3(3H, t, ethyl group), Fig. 1. m/e 293 (M^+ , 100%), 278 (32), 224 (16), 208 (80), 194 (40), 180 (16), 167 (28).

Synthesis of poly [4-(9-ethyl) carbazolyl] methylmethacrylate (9)

A solution of 1.75 g (0.006 mol) of (8), 15 mg of AIBN in 5ml of dichloromethane was degassed and left at 70 °C for 5 hours. The reaction mixture poured into methanol, the resulting polymer was filtered, purified by dissolving into THF and reprecipitating into methanol several times and dried to yield 1.40g (80%) of (9). ν_{max} (Nujol mull) 1730 (broad C=O), 1620, 1600, 1330, 1250, 1150, 950, 925 cm^{-1} δ (CDCl_3 -Int. TMS) 8.0, 7.3, 7.0 (~6H,ArH), 5.5 (3H, shielded ArH, CH_2), 4.1 (2H, CH_2 of ethyl), 1.7,1.1, 0.75 (~8H, CH_3 of ethyl, CH_3 , CH_2), Fig. 2.

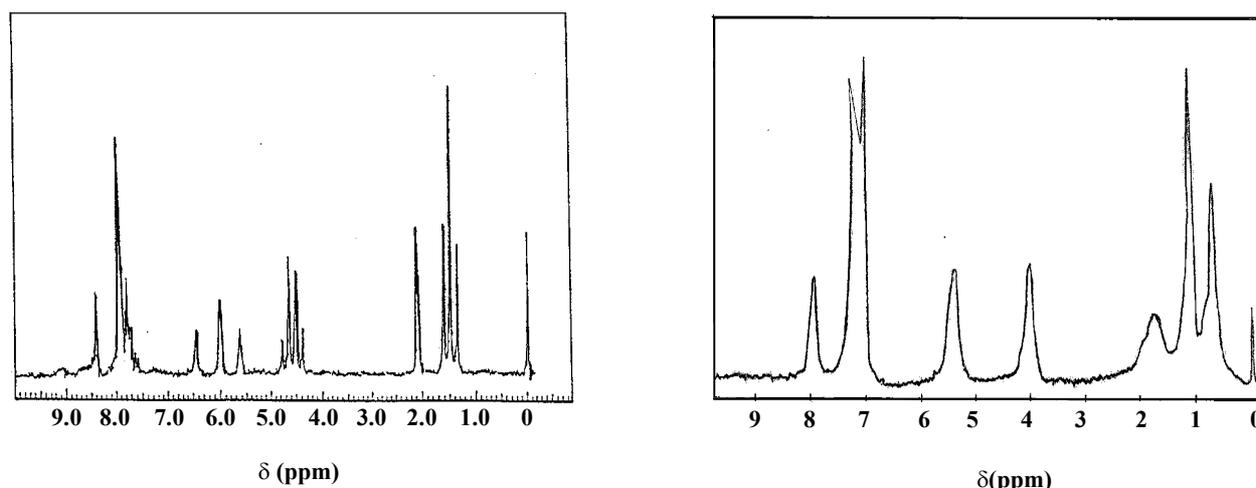


Fig. 1: NMR Spectrum of monomer (8).

RESULTS AND DISCUSSION

The synthesis of the monomer (8), scheme 1, was accomplished similar to the synthesis route of 4-vinylcarbazole, as reported before [8]. The microwave assisted synthesis of the tetrahydrocarbazole (2) amazingly afforded a quantitative yield of pure product, with exactly the same melting point and spectrophotometric characteristic peaks as reported in the literature [8]. Like the synthesis of compound (5) and (9) the preparation of monomer (8) was performed in dry condition, by using microwave irradiation in the two steps, the overall yield of monomer has been increased to an excellent quantity of 45%.

The monomer (8) was oily in nature and showed one spot on TLC and seemed to be stable at ordinary laboratory condition. Monomer (8) was characterized based on different spectroscopic data (UV, IR, NMR and Mass spectroscopy) elemental analysis. The broad and sharp peaks of carbonyl and olefinic peaks, at 1715 and 630 cm^{-1} respectively, are good evidences for successful formation of substituted carbazole methyl methacrylate. In addition, the aryl protons as a singlet at 8.4 ppm and a complex multiplet at 7.6 ppm in the NMR spectrum, (Fig.1) are good evidences for proper substitution at 4-position of carbazole ring. The olefinic protons appeared at 6.38, 6 and 5.75 ppm and the N-ethyl substituted protons appear at 4.77-4.4 and 1.93-1.8 ppm, of the spectrum.

In mass spectrum, the M^+ peak counted at 293 is the molecular weight of the monomer. The loss of a methyl

group results in the formation of the next fragmented ion, which at counted at 278, and the rest of fragmentation pattern is same as all the carbazole compounds [8].

Polymerization reaction of the monomer (8) resulted into a polymer (9) with 80% yield. Purification of this polymer was accomplished by dissolving the polymer precipitate into THF and reprecipitating several times into methanol, leaving behind all the unreacted monomer. The infra-red spectrum of this polymer shows a shift of the carbonyl peaks of the pendant ester groups to 1730 cm^{-1} . The NMR spectrum of the polymer (Fig. 2), was a typical polymeric spectrum. As it is shown in Fig. 2, there are two peaks for the aromatic ring protons, totally counted for 6 protons. The resonance at 5.4 ppm counted approximately for 3 protons, one of which belong to the shielded aromatic proton, and the other two belong to the methylene protons attached to the position 4 of the carbazole ring. The shielded aromatic proton is similar to the one reported for poly (N-Et-4-Vinylcarbazole) [8]. This result presumably reflects an increase in steric hindrance when bonding to the polymer backbone occurs at the 4- position. The rest of the peaks shown in Fig. 2, belong to the aliphatic protons in the polymer.

Average molecular weight studies indicated that the M_w of polymer was 5.2×10^5 and distribution of M_w/M_n of 2.6. The average molecular weights of the other substituted carbazole methylmethacrylate polymers were also recorded to be in the order of 10^5 [6].

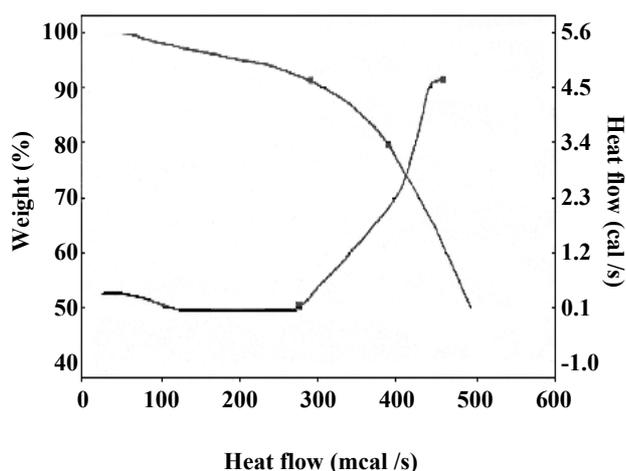


Fig. 3: TGA and DSC Thermograms of Polymer (9).

THERMAL PROPERTIES

Thermal properties of polymer (9) was investigated by (TGA) and (DSC). The representative curves are shown in Fig. 3. As it is shown in Fig. 3, the initial decomposition temperature of polymer (9) has occurred around 275 °C with about 10% loss and the maximum decomposition occurred about 380 °C with about 22 % loss.

As it is indicated in DSC curve, the glass transition temperature, T_g , of polymer (9) ranged from 255-295 °C. The high glass transition temperature of polymer (9) can be attributed to stiffness of the polymer chain due to the presence of bulky carbazole methyl methacrylate-chromophores, and strictly hindered when bonding to the polymer backbone at the 4-position. This could be an interesting property for further investigation on the photophysical studies of this polymer.

CONCLUSIONS

Microwave assisted synthesis of the 4 -carboxy-substituted tetrahydro carbazole resulted in a high yield of pure (2) in only 10 min. Period, the overall yield of monomer (8) has been increased by 45 % if the syntheses of (2) and (5) were accomplished via microwave irradiation procedures. Monomer (8) has been successfully polymerized free radically to form the polymethyl methacrylate with 4-carbazole chromophore substitution, the photoconductive properties of which will be the subject of further studies.

Acknowledgment

I would like to thank Petroleum Research Center for conducting CHN analysis and department of polymer technology of university of Barcelona for the DSC thermal analysis.

Received : 6th March 2004 ; Accepted : 21st September 2004

REFERENCES

- [1] Kalle, A. G., Brit. Patent, 940878 (1967).
- [2] Munder, J. and Sus, O., US. Patent, 3 316087 (1967).
- [3] Bagdal, D, Warzale, M., Piclichowski. J. and Santra. J., *Polimery*, **44**, 14, (1999).
- [4] Bogdal. D., Yaschchuk. V., Piclichowski. J., Ogulchansky, T., Warzala, M. and Kudry, V., *J. App. Polym. Sci*, **84**, p. 650 (2002).
- [5] Longi, P., Pellino, E., Greco, F. and Mazzochi, R., *Chim. Ind.*, **46**, 2, p. 156 (1964).
- [6] Natta, G., Longi, P. and Pellino, E., *Makromol. Chem.*, **71**, p.212 (1964).
- [7] Keyanpour-Rad, M., Ledwith A., Hallamb A, North AM., Breton, M., Hoyle C., and Guillet, JE, *Macromolecules*, **11**, p. 1114, (1978).
- [8] Keyanpour – Rad, M., Ledwith A., Johnson, G. E., *Macromolecules*, **13**, p. 222 (1980).
- [9] Keyanpour-Rad, M., *Indian Journal of Heterocyclic Chemistry*, **10**, p. 319 (2001).
- [10] Keyanpour-Rad, M. and Ledwith A., *Polym. Bulletin*, **1**, p. 337 (1979).
- [11] Deyl, Z., Macek, K. and Janak, J., *Liquid Column Chromatography*, Elsevier, Amsterdam Scientific (1975).