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Microstructure elucidation of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate) using two-dimensional NMR spectroscopy

Ajaib Singh Brar*, Sonia Gandhi, Meghna Markanday

Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

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Abstract

The configurational assignments of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate) prepared by solution polymerization with 2,2'-azobisisobutyronitrile (AIBN) as free radical initiator were studied by combination of one- and two-dimensional NMR spectroscopy. The $-OCH_2$ and $-NCH_2$ carbon resonances were distinguished using Distortionless Enhancement by Polarization Transfer (DEPT) experiments. The configurational assignments for main chain methylene and α -methyl group were done by using 2D HSQC spectroscopy. Various geminal and vicinal couplings within the configurational sequences were assigned with the help of Total Correlation Spectroscopy (TOCSY). Two and three-bond order carbon/proton coupling were observed using Heteronuclear Multiple Bond Correlation (HMBC).

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1. Introduction

Recently homo and copolymer systems based on pendant carbazole units and those with tailored chemical structures have received considerable attention, which is amply justified in view of the unusual electrical, photoelectrical, thermal and other photophysical properties [1,2]. Carbazole derivatives substituted by electron withdrawing groups at 3-position can give rise to charge carriers in the visible region, through an induced intramolecular charge transfer complex. Thus, here photoconductivity combined with Non-Linear Optical (NLO) activity makes it a useful photorefractive material [3-6]. These photorefractive materials have a wide range of applications in the field of image processing techniques, programmable optical interconnection and high-density optical data storage [7-9]. Poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate) is one of such kind of photorefractive material with the pendant group containing carbazole moiety substituted at 3-position by electron withdrawing group. Copolymerization of such systems with monomers having acceptor side groups such as 3,5-dinitrobenzoic derivatives show high degree of charge transfer complexation as well as sensitivity to light. These copolymers in turn show properties like electrochromism and photoconductivity [10–12].

The physical and chemical properties of polymers are influenced by their molecular level microstructure hence its study is useful in establishing structure property relationship [13–15]. 1D and 2D NMR spectroscopy has been found to be most efficient technique for determining the microstructure of polymers [16–24].

In this manuscript, we report the microstructure of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate) using ¹H, ¹³C{¹H} NMR, DEPT, 2D HSQC and TOCSY NMR experiments. The α -CH₃ region was found to be triad sensitive whereas the main chainmethylene was found to be dyad sensitive. Further studies on higher bond order carbon/proton couplings were made possible by 2D HMBC spectroscopy.

^{*} Corresponding author. Tel.: +91 11 26 591 377; fax: +91 11 581 102. *E-mail address:* asbrar@chemistry.iitd.ernet.in (A.S. Brar).

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2. Experimental

2.1. Materials

9-Ethyl carbazole (97%, Aldrich), phosphoryl chloride (98%, Thomas Baker), sodium borohydride (95%, CDH), methacryloyl chloride (97%, Lancaster) were used as purchased. *N*,*N*-dimethylformamide (99%, s.d.Fine-Chem, Ltd, India) was distilled under reduced pressure and 2,2'-azobisisobutyronitrile (Fluka) was recrystallized using methanol and stored at low temperature.

2.2. Synthesis (Scheme 1)

(a) Synthesis of 9-ethyl-3-formylcarbazole (Scheme 1(a)). To 2.5 g (0.034 moles) of *N*,*N*-dimethylformamide cooled to 0 °C, 5.16 g (0.033 moles) of phosphoryl chloride was added dropwise. The above mixture was stirred and heated to 40 °C. To this 6 g (0.03 moles) of 9-ethyl carbazole (I) was added. After 10 h the mixture was poured into 100 mL of water at 45 °C and stirred until the oil phase got crystallized. The reaction mixture was worked up by extracting the aqueous mixture with dichloromethane (100 mL×3). Organic layer

was separated and dried. Column chromatography was carried out on silica gel column (85:15/hexane:ethyl acetate).

Yield: 87%; m.p.: 82 °C (lit 81 °C).

¹H NMR (CDCl₃): δ 10.08 (s, 1H, -CHO), δ 1.45 (t, 3H, -CH₃), δ 4.37 (q, 2H, -CH₂), δ 7.25–8.59 (m, aromatic).

(b) *Synthesis of 9-ethyl-3-methylolcarbazole* (Scheme 1(b)). A solution of 0.56 g of sodium borohydride in 10 mL of 0.4 N sodium hydroxide was added dropwise to a stirred mixture of 5 g (0.023 moles) of 9-ethyl-3-formylcarbazole and 50 mL ethanol. The mixture was stirred below its boiling point for 2 h after it became a clear, colourless solution. White crystals were obtained on cooling. The solvent was then removed at room temperature and the product was filtered, dried and recrystal-lized from cyclohexane/benzene (1:1 mixture)

Yield: 97%; m.p.: 86.5-87 °C.

¹H NMR (CDCl₃): δ 1.77 (s, 1H, -OH), δ 4.83 (s, 2H, -CH₂O), δ 1.41 (t, 3H, -CH₃), δ 4.36 (q, 2H, -CH₂), δ 7.20–8.09 (m, aromatic).

(c) Synthesis of 9-ethyl-3-hydroxymethylcarbazolyl methacrylate (Scheme 1(c)). A mixture of 1.045 g (0.01 moles) of methacryloyl chloride and 10 mL dichloromethane (DCM) was added dropwise (for 15 min) under vigorous stirring to a solution of 2.3 g (0.01 moles) of



Scheme 1. Synthesis of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate).

9-ethyl-3-methylolcarbazole, 50 mL of dry DCM, and 1.01 g (0.01 moles) of triethylamine (cooled at 0 °C). The mixture was stirred overnight and $Et_3NH \cdot HCl$ was filtered off. After removing DCM in vacuo, the product was chromatographed on silica gel column (8:2/hexane:ethyl acetate).

Yield: 81%

¹H NMR: $\delta 5.56$ (s, 1H, CH₂(i)), $\delta 6.15$ (s, 1H, CH₂(ii)), $\delta 1.97$ (s, 3H, CH₃(iii)), $\delta 5.37$ (s, 2H, -CH₂O), $\delta 4.35$ (q, 2H, -NCH₂), $\delta 1.42$ (t, 3H, CH₃(iv)), $\delta 7.23-8.13$ (m, aromatic).

(d) *Polymerization*. Poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate) was prepared by solution polymerization using AIBN (0.05 mole%) in distilled toluene as solvent at 60 °C. The polymer obtained was filtered and dissolved in minimum amount of chloroform. Reprecipitation was further carried out in methanol.

2.3. NMR measurements

NMR spectra were recorded on Bruker DPX-300 spectrometer in CDCl₃. The ¹H and ¹³C{¹H} NMR measurements were made at frequencies of 300.13 and 75.5 MHz, respectively. In ¹³C{¹H} NMR spectra 2K scans

ÇH2CH

were accumulated with 2 s delay time. DEPT measurements were carried using standard pulse sequence with a J modulation time of 3.7 ms (J_{CH} =135 Hz) with 2 s delay time. The pulse sequence invigpt and inv4gplpIrnd of the Bruker software were used to record gradient HSQC and HMBC experiments, respectively. The spectra were acquired with 512 increments in the F1 dimension and 2048 data points in the F2 dimension. Total correlation spectroscopy (TOCSY) experiment was performed using standard pulse sequence. 32 scans were accumulated for 512 experiments with 2 s delay time [25].

3. Results and discussion

3.1. ${}^{13}C{}^{1}H$ NMR studies

The various resonance signal assignments in ${}^{13}C{}^{1}H$ NMR spectrum for poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate) are shown in Fig. 1. The aliphatic unit of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate) has structural similarities to the poly(methyl methacrylate). The carbonyl carbon resonances constituted three envelopes of resonances (as shown by poly(methyl methacrylate)) from





Fig. 2. Expanded ¹³C{¹H} NMR spectrum showing carbonyl carbon resonances of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate).

175.9–176.6, 176.7–177.4 and 177.5–178.5 ppm (Fig. 2) were assigned to mm, mr/rm and rr, respectively [25,26]. The α -methyl region showed splitting into two regions corresponding to rr and mr/rm triads from low to high chemical shift (Fig. 3). Triads rr and mr/rm constituted single peaks at 16.78 and 18.88 ppm, respectively. The methyl (–NCH₂CH₃) group showed an intense resonance at 13.8 ppm (Fig. 1).

The triad concentrations were calculated from the area under these resonance signals. From these triad fractions, using the Bernoullian statistics, the probability of the meso addition to the growing polymer chain ($P_{\rm m}$) was calculated. The average value of $P_{\rm m}$ from the triad fractions is 0.19. The experimentally and statistically determined triad fractions of various carbon resonances are shown in Table 1. The theoretical values were calculated from Bernoullian statistics using $P_{\rm m}$ =0.19 while the experimental values were determined from ¹³C{¹H} NMR spectrum.

The $-CH_2$ resonances were assigned with the help of DEPT-135 experiments as they appear as negative peaks in DEPT-135 spectrum (Fig. 4). The resonances which were

present in ¹³C{¹H} spectrum and absent in DEPT spectrum were assigned to quaternary carbons by the comparison of these two spectra. Quaternary carbon resonances showed configurational sensitivity up to triad level. The peaks centered at 45.03, 45.39 and 45.9 ppm were assigned to rr, rm/mr and mm (as shown by poly(methyl methacrylate)) triads, respectively (Fig. 5). The methylene groups of – OCH₂ and –NCH₂ gave resonances at 67.69 and 37.41 ppm, respectively and the position of the peaks were further confirmed by 2D experiments. The backbone methylene showed configurational sensitivity as it appeared as a multiplet around 52.11–55.77 ppm (Fig. 1).

The aromatic carbons were found to resonate at around 105.53–141.15 ppm where peaks at 122.85, 139.75 and 140.21 ppm were assigned to quaternary carbons C-b, C-3 and C-a, respectively as shown in Fig. 1. The various other assignments for the aromatic carbons C-4 and C-5 were based on the assignments made by Simionescu et al. [27] for the carbazole ring. The aromatic carbons were found to resonate at 108.39 (C-1, C-8), 119.06 (C-2), 120.79 (C-5), 121.46 (C-4), 125.82 (C-6) and 127.02 ppm (C-7), as shown in Fig. 1.



Fig. 3. Expanded ${}^{13}C{}^{1}H$ NMR spectrum showing α -methyl carbon resonances of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate).

Table 1 The experimentally and statistically determined triad fractions of various carbon resonances

Triads	Triad fractions			
	Theoretical	Quaternary carbon	α-Methyl	Carbonyl
rr	0.65	0.67	0.63	0.66
rm(mr)	0.31	0.30	0.33	0.31
mm	0.04	0.03	0.04	0.03

3.2. 2D HSQC NMR studies

2D HSQC enables unambiguous assignments of various resonance signals in ${}^{13}C{}^{1}H{}$ and ${}^{1}H$ NMR spectra. The expanded HSQC for aliphatic is shown in Fig. 6. The crosspeaks 1, 2 and 3 centered at 13.37/1.06, 37.19/3.86 and 67.39/4.66 ppm were assigned to methyl (–NCH₂CH₃), –NCH₂ and –OCH₂, respectively. The α -methyl region was found to be configurational sensitive and crosspeak 4 and 5 centered at 16.37/0.71 and 18.76/0.93 ppm were assigned to rr and rm/mr triads, respectively (Fig. 6).

The backbone β -methylene group showed sensitivity to various configurational sequences resulting in crosspeak 6 (Fig. 6). The two methylene protons of r dyad will be under similar environment giving a single crosspeak in 2D HSQC spectrum, while the two methylene protons of m dyad will give two crosspeaks in 2D HSQC as shown in Fig. 7. The crosspeak 7 centered at 54.71/1.79 ppm is assigned to racemic (r) dyad whereas the crosspeaks 8 and 9 centered at

54.41/1.34 and 54.32/1.99 ppm were assigned to meso (m) dyad arising due to non-equivalent protons H_A and H_B , respectively (Fig. 7).

The various assignments of aromatic region in ¹H NMR and ¹³C{¹H} NMR were done with the help of expanded aromatic region of HSQC spectrum. Hence the crosspeaks 10, 11, 12, 13, 14, 15 and 16 centered at 107.99/6.89, 126.91/7.02, 118.82.7.03, 108.16/7.05, 125.59/7.23, 121.29/7.69 and 120.49/7.86 ppm, respectively can be assigned to C-8, C-7, C-2, C-1, C-6, C-4 and C-5, respectively as shown in Fig. 8.

3.3. 2D TOCSY NMR spectra studies

2D TOCSY NMR is useful in understanding various proton couplings in different configurations of the polymer. The assignments done for $-NCH_2$ and $-OCH_2$ in HSQC spectrum were further confirmed by 2D TOCSY experiments as protons of NCH₂ showed vicinal coupling with methyl ($-NCH_2CH_3$) group resulting in cross-correlation peak 'i' centered at 1.09/3.92 ppm, as shown in Fig. 9.

The geminal coupling between backbone β -methylene protons in meso configuration (H_A and H_B) results in crosscorrelation peak 'ii' centered at 1.99/1.33 ppm (Fig. 9). Hence the assignments done in HSQC spectra were further confirmed by TOCSY experiments.

With the help of all these studies various assignments in ¹H NMR spectrum were done, as shown in Fig. 10.



Fig. 4. DEPT-135 NMR spectrum of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate).



Fig. 5. Expanded ¹³C{¹H} NMR spectrum of quaternary carbon of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate).

3.4. HMBC NMR studies

HMBC NMR spectroscopy can be used to study longrange couplings between proton and carbon nuclei. The tentative assignments done for quaternary and non-protonated aromatic carbons via ${}^{13}C{}^{1}H$ NMR and DEPT experiments were further confirmed by HMBC experiments.

The crosspeak 'a' centered at 37.45/1.12 ppm was assigned to coupling between NCH₂ proton with methyl group. Carbon of $-OCH_2$ group showed coupling with H-4



Fig. 6. Expanded 2D HSQC spectrum showing couplings in the aliphatic region of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate).



Fig. 7. Methylene region in 2D HSQC spectrum of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate).

of aromatic ring resulting in crosspeak 'b' centered at 67.75/7.78 ppm (Fig. 11). This confirms that the substitution is at third position of carbazole ring.

The assignments done for aromatic carbons and protons in ${}^{13}C{}^{1}H$ and ${}^{1}H$ NMR spectra were further

region. The crosspeaks 'c' and 'd' were assigned to couplings of quaternery carbon C a with H 5 and H 6. The

strengthened by the expanded HMBC spectrum of aromatic

of quaternary carbon C-a with H-5 and H-6. The quaternary carbon C-3 couples with H-4 and H-2 giving



Fig. 8. Expanded 2D HSQC spectrum showing couplings in aromatic region.



Fig. 9. 2D TOCSY spectrum showing couplings of -NEt and H_A-H_B protons of m centered methylene dyad of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate).

rise to crosspeaks 'e' and 'f' whereas C-b shows connectivity with H-1, H-4, H-5 and H-8 resulting in crosspeaks 'g', 'h', 'i' and 'j', respectively. The various other carbon–proton couplings in carbazole ring are C1–H2, C2–H1, C5–H6, C7–H5, C6–H8 and C6–H5 resulting in crosspeaks 'k', 'l', 'm', 'n', 'o' and 'p', respectively as shown in Fig. 12.

4. Conclusions

The microstructure of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate) prepared by solution polymerization was analysed by one- and two-dimensional spectroscopy. 1D (¹H, ¹³C{¹H}and DEPT) and 2D (HSQC, TOCSY and HMBC) NMR techniques were studied to assign





Fig. 11. 2D HMBC spectrum showing higher bond order couplings for -NEt and -OCH2 groups.

methylenes, α -methyl and aromatic region of the homopolymer. The backbone methylene and α -methyl were assigned to dyad and triad configurational sequence, respectively. These assignments were further justified with the help of 2D HSQC and TOCSY experiments. The higher carbon/proton bond order couplings for –OCH₂, –NCH₂ and aromatic region were studied by HMBC. Explicit assignments of carbon/proton resonances and the analysis of



Fig. 12. Expanded 2D HMBC spectrum for the aromatic region of poly(9-ethyl-3-hydroxymethylcarbazolyl methacrylate).

different connectivities were done using 2D NMR spectroscopy thus establishing the microstructure of the homopolymer.

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