Microstructure characterization of poly(2-N-carbazolylethyl acrylate) by two-dimensional NMR spectroscopy

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Received 8 September 2004; revised 15 October 2004

Poly(2-N-carbazolylethyl acrylate) has been synthesized by solution polymerization of 2-N-carbazolylethyl acrylate with 2,2'-azobisisobutyronitrile as free radical initiator. Distortionless Enhancement by Polarization Transfer has been used to distinguish between the overlapping main-chain methine and side-chain methylene resonances in $^{13}$C{$^1$H} NMR spectrum. Configurational assignments of carbon and proton resonances of main-chain methylene group have been done using two-dimensional Heteronuclear Single Quantum Correlation spectroscopy and two-dimensional Total Correlation Spectroscopy. Two and three bond order carbon/proton couplings have been investigated using Heteronuclear Multiple Bond Correlation studies.

IPC Code: Int. Cl.7: C08F 120/18; G01R 33/20

Homo- and co-polyacrylates are of academic and industrial interest because of their wide range of physical and chemical properties that can be controlled by an appropriate choice of pendant group in the polymer and design of copolymer structure. Poly(2-N-carbazolylethyl acrylate) belongs to the class of photoconductive polymers$^{13}$, which finds widespread application in electrophotography, light-emitting diodes, photorefractive materials$^{4,5}$ and photovoltaic devices$^{6,7}$. The photoinduced intrachain charge transfer complexes in a photoconductive polymer ensure efficient charge transport across the polymeric material$^{8}$. Most investigations have concentrated on search for a chromophore that has a high efficiency in forming such charge-transfer complexes. Higher carrier mobility can be expected in polymers where the chromophore is directly linked to the backbone despite the fact that molecular mobility of the chromophore in such cases will be depressed. This insight has given impetus to further research on design of photoconductive polymers in which chromophores are directly linked to main chain through chemical bonding$^{9-11}$. Poly(2-N-carbazolylethyl acrylate)$^{12}$ is an example of photoconductive polymer in which the carbazole moieties appear as pendant groups along the main chain of the polymer.

The determination of microstructure in polymers is useful for establishing the structure-property relationship$^{13,14}$. High-resolution one-dimensional and two-dimensional NMR spectroscopy have proved to be one of the most informative and revealing techniques for the investigation of polymer microstructure$^{15-19}$. Much work has been done to study the photoconductive properties of poly(2-N-carbazolylethyl acrylate) and its copolymers. However, a literature survey reveals that the microstructure of this polymer has not been reported in detail.

In this paper, we report the microstructure of poly(2-N-carbazolylethyl acrylate). Unambiguous assignments have been made with the help of $^{13}$C{$^1$H} NMR, distortionless enhancement by polarization transfer (DEPT), 2D heteronuclear single-quantum correlation (HSQC), total correlation spectroscopy (TOCSY) and 2D heteronuclear multi bond correlation (HMBC) NMR experiments.

Materials and Methods
Carbazole (96%, Aldrich) was recrystallized from methanol. Ethylene carbonate (98%, Aldrich) and sodium hydride (50% oil dispersion, CDH Pvt. Ltd., New Delhi) were used as supplied. Acryloyl chloride (98%, Aldrich) was distilled under reduced pressure and stored at low temperature. AIBN (Fluka) was recrystallized from methanol and stored at low temperature.

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Procedure

Synthesis of monomer, 2-N-carbazolylethyl acrylate

A solution of carbazole (10 g, 0.06 mol) and 4.32 g (0.072 mol) sodium hydride in dry tetrahydrofuran (THF) was vigorously stirred at 0°C. After 2 hours of stirring ethylene carbonate (6.38 g, 0.072 mol) was slowly added and the mixture was stirred at 0°C for 30 min. and then at 40°C for three hours. To the resulting solution ice cold water was added gradually, followed by stirring at 40°C for 3 hours. Finally, work-up of the reaction mixture was done by pouring 200 ml of water and extracting the aqueous mixture with dichloromethane (200 ml x 3). The extract was chromatographed on a silica-gel column. [M. pt. 81-81.5°C (Lit. M. pt. 83-83.5°C). 1H NMR (in CDCl3) δ1.35 (s, 1H, OH), 3.80-3.82 (t, 2H, NCH2), 4.20-4.24 (t, 2H, OCH2), 7.00-7.90 (m, 8H, aromatic).

A solution of acryloyl chloride (5.1 g, 0.057 mol) in 20 ml of dry DCM was added dropwise under vigorous stirring to a mixture of 2-N-(hydroxyethyl) carbazole (10.0 g, 0.047 mol) and 20 ml triethylamine in 200 ml of dry DCM. The mixture was stirred overnight at 0°C. After the Et3N·HCl was filtered off at room temperature, the residue was chromatographed on a silica gel column (7:3:hexane:ethyl acetate). [M.pt. 76°C (lit. M.pt. 75-76°C). 1H NMR (in CDCl3) δ4.50-4.60 (m, 4H, OCH2CH2N), 5.80-6.30 (m, 3H, CH=CH-), 7.00-7.90 (m, 8H, aromatic)].

Polymerization

Poly (2-N-carbazolylethyl acrylate) was prepared by solution polymerization using AIBN (0.05 mol%) initiator in distilled toluene at 60°C. The homopolymer was precipitated in methanol. Further purification was done by reprecipitation in CHCl3/CH3OH solvent system.

NMR studies

NMR experiments were performed in CDCl3 on Bruker 300 MHz DPX spectrometer at a frequency of 300.13 MHz and 75.5 MHz for 1H and 13C 1H NMR respectively using the standard pulse sequences as reported in our earlier publications.20,21

Results and Discussion

13C 1H NMR studies

13C 1H NMR spectrum of poly(2-N-carbazolylethyl acrylate) with assignment of various resonance signals, is shown in Fig. 1. The carbonyl carbon resonates at δ173.25-174.5 ppm showing sensitivity towards configuration. The signals around δ173.25-173.75, δ173.75-174.25 and δ174.25-174.5 ppm are assigned to mm, mr/rm and rr triads respectively. Carbons 3, 5 and 1a of the carbazole ring in the homopolymer were erroneously assigned by Crone and Natansohn.22 Correct assignments of the carbazole ring in poly(N-vinylcarbazole) were reported by Dias et al.23 The aromatic carbons of the pendant group in the investigated poly(2-N-carbazolylethyl acrylate) have been assigned on the basis of investigations reported by Dias et al. The aromatic carbons were found to resonate at δ108.5 (C-1), δ118.0 (C-1), δ119.0 (C-4), δ122.0 (C-4a), δ124.5 (C-3) and δ141.0 (C-1a) ppm. The -OCH2

Scheme 1—Synthesis of 2-N-carbazolylethyl acrylate.
carbon of the side chain appears as a singlet around δ62.5 ppm indicating that it is not sensitive to configurational sequence of the homopolymer.

The spectral region around δ38.8-42.1 ppm is overlapped and can be assigned to backbone methine (-CH) carbon and -NCH$_2$ carbon of the side chain. The overlapped carbon regions can be resolved with the assistance of a DEPT-135 spectrum. The backbone methylene (-CH$_2$) carbon appears as multiplets around δ32.2-38.8 ppm, indicating its sensitivity towards various configurational sequences. This region appears as a broad signal due to the bulky pendant group.

2-D HSQC NMR studies

Investigation of the HSQC spectrum facilitates complete assignment of the $^1$H NMR spectrum. The expanded aliphatic region of the HSQC spectrum is shown in Fig. 2. The methine group appears as a cross peak centered at δ41.13/1.87 ppm. It does not show any kind of configurational sensitivity. The spectral region from δ32.3-38.8/0.7-1.5 ppm represents the β-methylene group. This group shows sensitivity to various configurational sequences. The meso configuration of dyad gives two cross peaks due to two methylene protons having different environment and the racemic configuration gives one crosspeak in between these two crosspeaks. The methylene protons of r dyad and m dyad are depicted in Scheme 2. The cross peaks around δ 34.24/1.28 and δ 34.28/0.74 ppm are assigned to the meso (m) dyad (a and b) and the crosspeak around δ 34.27/1.06 ppm is assigned to the racemic (r) dyad of the methylene region, respectively.

The aromatic region is overlapped in the $^1$H NMR spectrum. The protonated aromatic carbons of the carbazole ring can be resolved with the help of expanded aromatic region of the HSQC spectrum. Hence, peaks centered at δ108.5/7.1, δ119/1.7, δ118/7.8 and δ124.5/7.2 ppm can be assigned to (C-2)-(H-2) [II], (C-4)-(H-4) [IV], (C-1)-(H-1) [I] and (C-3)-(H-3) [III] respectively as shown in Fig. 3.
The overlapped peaks of $-\text{OCH}_2$ and $-\text{NCH}_2$ protons in $^1\text{H}$ NMR spectrum can be resolved with the help of aliphatic region of HSQC spectrum. The $-\text{OCH}_2$ and $-\text{NCH}_2$ are found to resonate at 862.5/4.0 and 842.1/4.15 ppm respectively as shown in Fig. 4.

2-D TOCSY NMR studies

2-D TOCSY NMR enables us to understand the connectivity between the different protons and confirm the various couplings in the polymer chain. The expanded TOCSY spectrum showing the methine and $\beta$-methylene region of the homopolymer is shown in Fig. 5.
The vicinal couplings between the methine protons and the methylene protons in various configurational sequences can be clearly seen in the TOCSY spectrum. The two protons \( H_A \) and \( H_B \) of the \( m \) dyad due to coupling with the methine proton shows two cross-correlation peaks in the TOCSY spectrum centered at \( \delta 1.87/1.3 \) (2) and \( \delta 1.85/0.74 \) (3) ppm respectively. The methylene protons of the \( r \) dyad show a single cross-correlation peak in the TOCSY spectrum in between the two crosspeaks (2) and (3) centered at \( \delta 1.86/1.04 \) (1) ppm.

The geminal coupling between \( \beta \)-methylene protons \( ( H_A \) and \( H_B ) \) of the \( m \) dyad results in a cross-correlation peak centered at \( \delta 0.10/0.7 \) (4) ppm. Thus using HSQC in conjugation with TOCSY enabled to strengthen assignments. Using these assignments \( ^1H \) NMR spectrum was assigned as shown in Fig. 6.

### HMBC NMR studies

The heteronuclear multiple bond correlation (HMBC) experiment proves to be very useful in correlating proton and carbon nuclei via long range couplings. The assignment of the signals of the non-protonated aromatic carbons for the carbazole ring has been achieved by this technique as correlation of these quaternary carbons with protons via \( ^3J_{CH} \) couplings can be easily seen in the HMBC spectrum. The HMBC spectrum of the aromatic region is presented in Fig. 7. It can be clearly seen that each quaternary carbon correlates with protons via \( ^3J_{CH} \) couplings.

The non-protonated carbons were found to be positioned at \( \delta 122.0 \) and \( \delta 141.0 \) ppm using \( ^{13}C \{^1H\} \) NMR and DEPT studies. HMBC studies further confirm the positions of the respective quaternary carbons C-4a and C-1a. C-4a centered at \( \delta 122.0 \) ppm is found to couple with H-4, H-3 and H-1, while C-1a shows coupling with H-4 (11), H-2 (12) and side-chain \(-\text{NCH}_{2}\) (13) protons. The coupling of C-1a with side chain \(-\text{NCH}_{2}\) protons confirms that this non-protonated carbon is the one adjacent to 'N' atom of carbazole ring. The protonated carbon C-2 shows connectivity with H-4 (1) and H-1 (2), C-1 with H-2 (4) and H-3 (3), C-4 with H-2 (6) and H-3 (5), C-5 with H-4 (7), H-3 (9) and H-1 (8) and C-3 with H-4 (10) protons. Henceforth, this further confirms the position of the various protonated carbons of the carbazole ring.

### Acknowledgement

The authors wish to thank the CSIR, New Delhi and DST, New Delhi, India for providing the financial support to carry out this work.

### References