

Microstructure Determination and Thermal Studies of *N*-acryloylcarbazole/Vinyl Acetate Copolymers

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ABSTRACT: Copolymers of *N*-acryloylcarbazole (A) and vinyl acetate (V) were synthesized by bulk polymerization using benzoyl peroxide (BPO) as free-radical initiator at 65°C in different in-feed ratios. The composition of the copolymer was determined by ¹H-NMR spectrum. The comonomer reactivity ratios, determined by Kelen–Tudos (KT) and nonlinear error-in-variables (EVM) methods, were $r_A = 16.75 \pm 1.38$, $r_V = 0.015 \pm 0.002$, and $r_A = 16.36$, $r_V = 0.015$, respectively. Complete spectral assignments of the ¹H and ¹³C{¹H} NMR spectra of the copolymers were done by the help of distortionless enhancement by polarization transfer (DEPT) and two-dimensional NMR techniques such as heteronuclear single quantum coherence (HSQC) and total correlation spectroscopy (TOCSY). The methine and methylene

carbon resonances were found to be compositional as well as configurational sensitive. The signals obtained were broad pertaining to the restricted rotation of bulky carbazole group. The thermal stability and glass-transition temperatures (T_g) of the copolymers were found to be dependent on polymer composition and characteristic of rotational rigidity of the polymer chain. Variation in the values of T_g with the copolymer composition was found to be in good agreement with theoretical values obtained from Johnston and Barton equations. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2720–2733, 2007

Key words: *N*-acryloylcarbazole/vinyl acetate copolymer; microstructure; TGA; DSC; NMR

INTRODUCTION

Carbazole-based polymers have created a class of its own in photosensitive/photorefractive systems, which are used in recording media for holographic storage and real time processing, as they have shown excellent photoconductive, photorefractive, and hole transporting properties.^{1–4} The impetus has been put into designing carbazole-based polymers with tailor-made properties. Carbazole has been derivatized, and carbazole containing monomers have been copolymerized to achieve the desired results, as the photoconductivity depends mainly on the kind of overlap between carbazole moieties.⁵ It has been reported that it is ideal for the photorefractive (PR) polymers to possess a low glass-transition temperature (T_g), so that the “orientational effect” of dipoles due to photoinduced space charge field can be utilized to enhance the PR performances.^{6–8} Low T_g also allows easy preparation of thick films for holographic studies.⁹ It has also been reported that copolymerization greatly effects the glass-transition temperature of the polymers.¹⁰ Moreover, while methyl methacrylate has been reported to

be more reactive towards vinyl ketones,¹¹ the thermal stability of poly(vinyl acetate) has been reported to be more. Also, the T_g of poly(vinyl acetate) is comparable to poly(methyl methacrylate). Thus, it is more feasible and economical to make copolymers of vinyl acetate, more so, when the vinyl ketones are costly.

Determination of microstructure and reactivity ratios of copolymers is of great value in establishing structure–property relationship.¹² It has been reported that the determination of reactivity ratios in the cases where the difference in reactivity is large is difficult due to errors involved in their estimation.¹³ The contribution of ¹³C{¹H} NMR and two-dimensional (2D) NMR spectroscopy to the study of polymer microstructure has been universally recognized.^{14–23}

Glass-transition temperature (T_g), which represents the molecular mobility of polymer chains, is an important phenomenon that influences the material properties and potential applications of a given polymer.²⁴ The thermal studies of poly(*N*-acryloylcarbazole)²⁵ has already been reported.

Microstructure determination of poly(*N*-acryloylcarbazole),²⁵ poly(vinylacetate),^{26,27} and *N*-acryloylcarbazole/methyl methacrylate²⁸(A/M) copolymers by NMR has already been reported. Brar et al.^{29–32} have reported comonomer sequence and cotacticity of vinylacetate copolymers. To the best of our knowledge, the microstructure and thermal studies of *N*-acryloylcarbazole/vinyl acetate (A/V) copolymers

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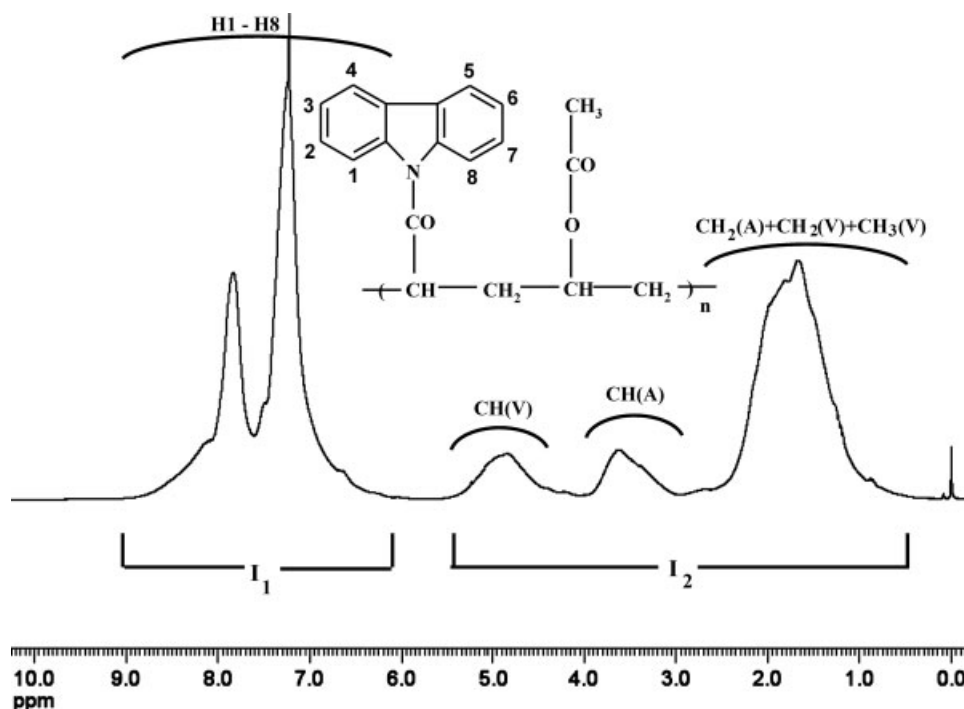


Figure 1 The $^1\text{H-NMR}$ spectrum of A/V copolymer ($F_A = 0.50$) recorded in CDCl_3 at 25°C .

have not been reported so far. In this article, we report the complete compositional and configurational assignments of A/V copolymers with the help of distortionless enhancement by polarization transfer (DEPT) and 2D NMR (HSQC and TOCSY) spectroscopy. These assignments are quite different and better resolved in 1D and 2D NMR than A/M copolymers. Reactivity ratios for comonomers are calculated using Kelen–Tudos (KT) method and the nonlinear error-invariable method (EVM) from the compositional data obtained from $^1\text{H-NMR}$ spectra. We also report the analysis of thermal stability and glass-transition temperatures of A/V copolymers.

EXPERIMENTAL

N-acryloylcarbazole was prepared in a two-step synthesis as reported in our earlier publications.^{25,28}

Vinyl acetate (Merck, Germany, 99%) was washed successively with 10% NaOH, dried over Na_2SO_4 , distilled under reduced pressure, and then stored below 5°C . It was purged with nitrogen gas for 30 min before use. Then, a series of copolymers of *N*-acryloylcarbazole (A) and vinyl acetate (V), containing different mole fractions, were prepared by bulk polymerization using benzoyl peroxide (BPO) as free-radical initiator. The polymerization temperature was kept at 65°C . The conversion was kept below 10% by quenching the reaction in methanol. The resulting copolymers were purified by repeated dissolution in dichloromethane, followed by subsequent precipitation in methanol to remove vinyl acetate. It was further purified by repeated dissolution in dichloromethane, followed by precipitation in ether to remove *N*-acryloylcarbazole. The copolymers were dried under vacuum at 78°C for 24 h.

TABLE I
Copolymer Composition Data of the A/V Copolymers (<10% Conversion) and Their Glass Transition and Thermal Degradation Temperatures

Sample no.	<i>N</i> -acryloylcarbazole mole fraction in-feed (F_A)	<i>N</i> -acryloyl-carbazole mole fraction in copolymer (F_A)	Decomposition temperature (T_d) (K)	Glass-transition temperature (T_g) (K)
1	1	1.00	639	430.4
2	0.10	0.72	637	403.0
3	0.07	0.65	635	397.9
4	0.05	0.59	634	389.2
5	0.03	0.50	631	377.4
6	0.02	0.44	629	368.3
7	0.00(PVA)	0.00	615	304.5

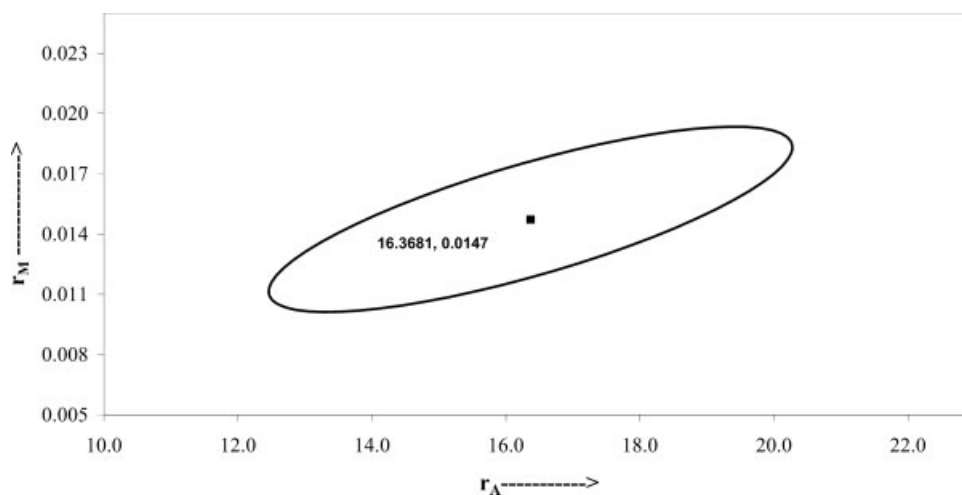


Figure 2 The 95% posterior probability contour for A/V comonomer pair.

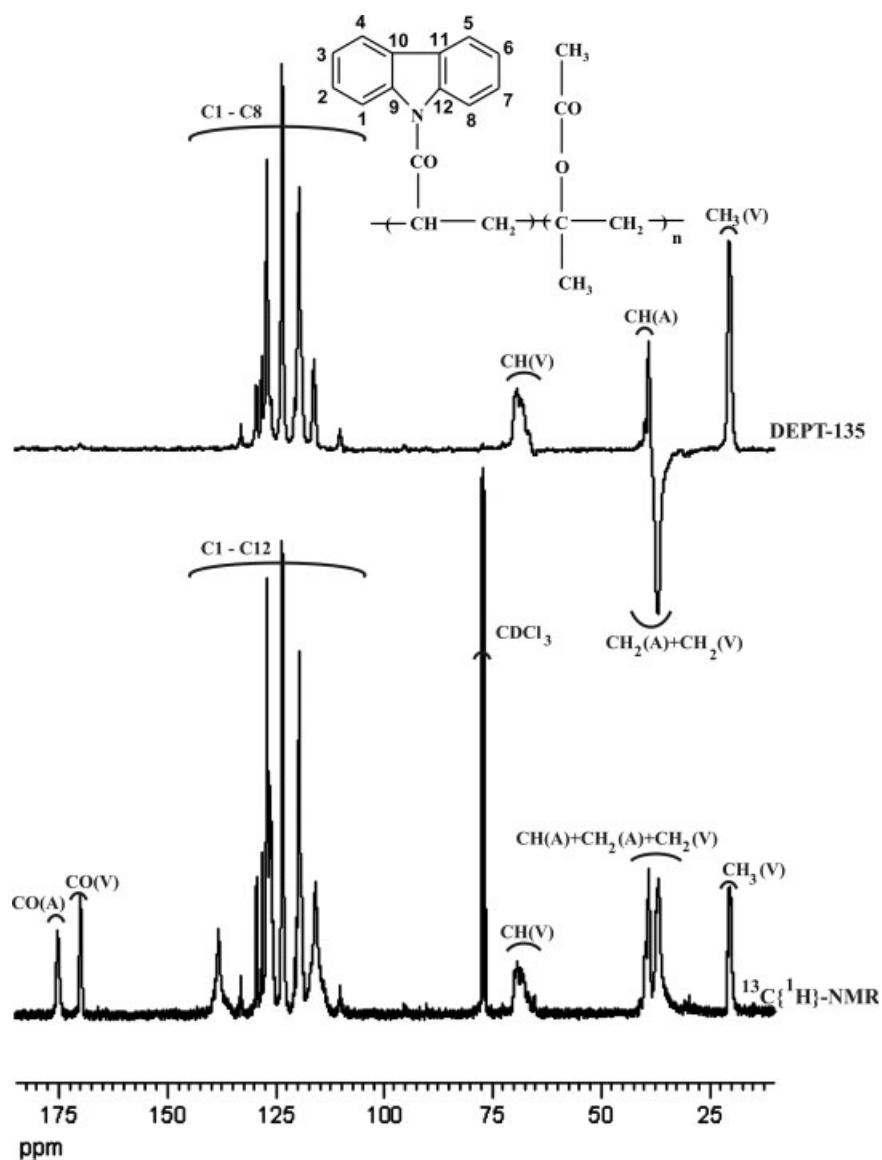


Figure 3 The $^{13}\text{C}\{^1\text{H}\}$ and DEPT-135 NMR spectrum of the A/V copolymer ($F_A = 0.50$) recorded in CDCl_3 at 25°C .

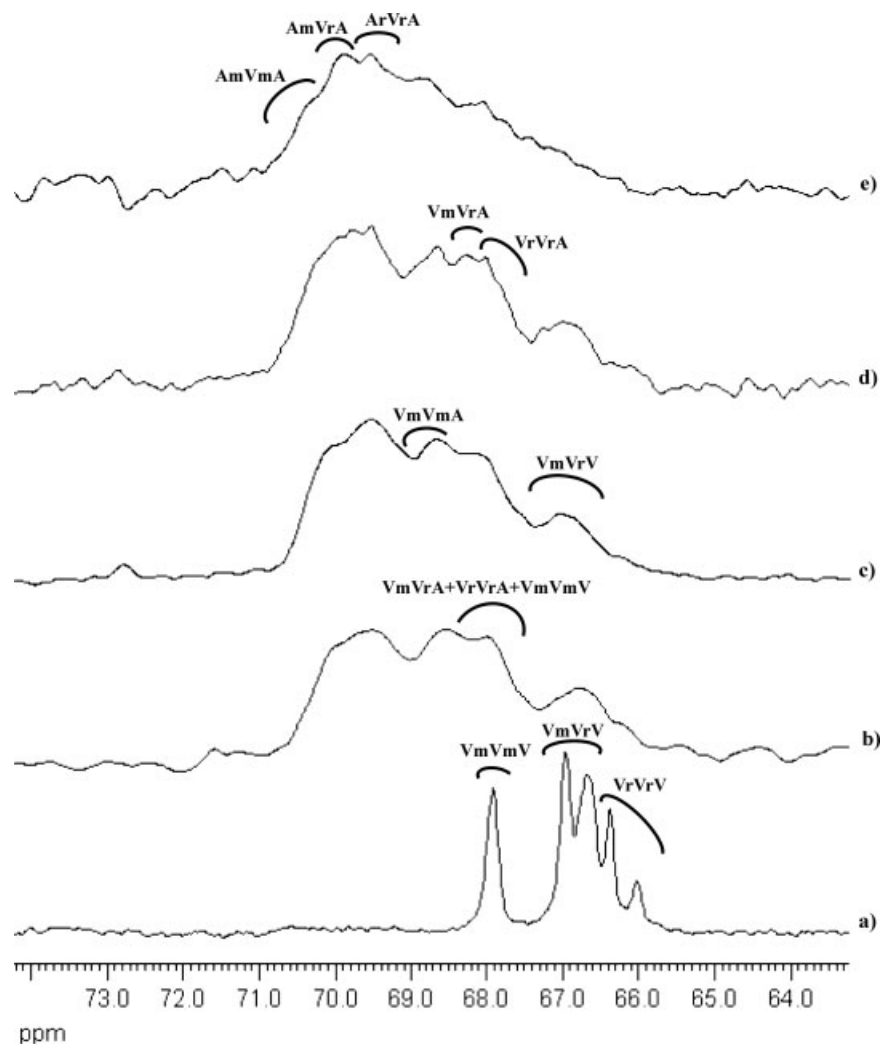


Figure 4 The expanded methine carbon signals of the V unit in the DEPT-90 NMR spectra of the A/V copolymers recorded in CDCl_3 at 25°C : (a) poly(vinylacetate), (b) $F_A = 0.44$, (c) $F_A = 0.50$, (d) $F_A = 0.59$, and (e) $F_A = 0.65$.

The details of recording of NMR spectra and thermal studies of the copolymer samples have been described in our earlier publications.^{25,28}

RESULTS AND DISCUSSION

$^1\text{H-NMR}$ studies

The completely assigned $^1\text{H-NMR}$ spectrum of A/V copolymer ($F_A = 0.50$), recorded in CDCl_3 , is shown in Figure 1. The spectrum is quite complex and overlapping. Nevertheless, the signals have been resolved with the help of 2D NMR techniques such as heteronuclear single quantum coherence (HSQC) and total correlation spectroscopy (TOCSY). The composition of the copolymer has been calculated from the $^1\text{H-NMR}$ spectrum. The relative intensities of the aromatic (I_1) and aliphatic (I_2) proton resonances were calculated, and then the composition of the

A/M copolymer was calculated according to the following equation:

$$F_A = \frac{I_1/8}{I_1/8 + (I_2 - 3I_1/8)/6}$$

where F_A is the mole fraction of *N*-acryloyl carbazole (A) monomer in the copolymer.

The feed mole fraction and copolymer composition data are given in Table I.

Determination of reactivity ratios

The initial estimate of the reactivity ratios was done by the Kelen–Tudos³³ (KT) method with the help of copolymer composition data as obtained from $^1\text{H-NMR}$ spectrum. The values of the terminal reactivity ratios obtained from the KT plot were: $r_A = 16.75 \pm 1.38$ and $r_V = 0.015 \pm 0.002$. These values along

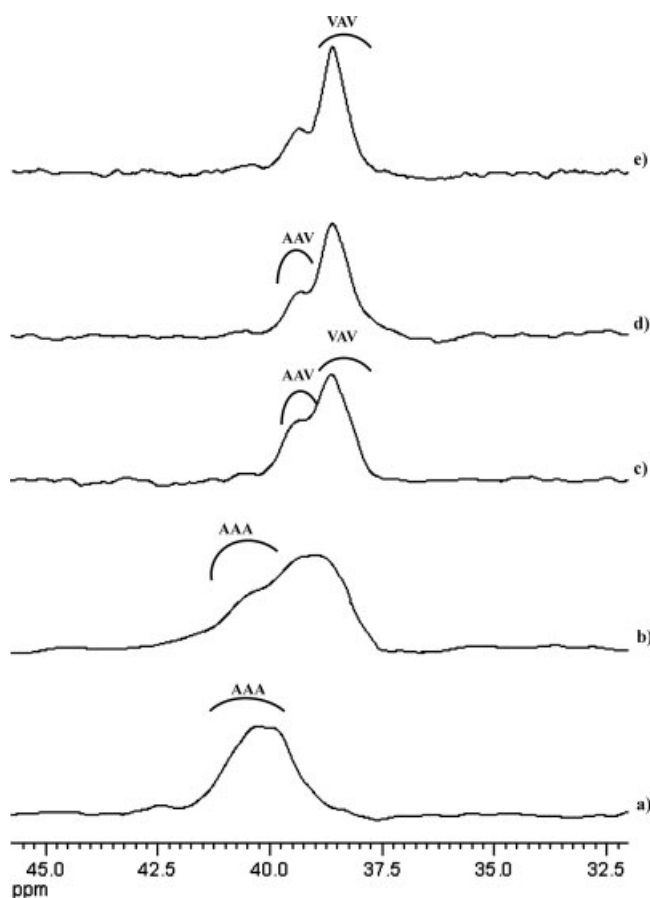


Figure 5 The expanded methine carbon signals of the A unit in the DEPT-90 NMR spectra of the A/V copolymers recorded in CDCl_3 at 25°C : (a) poly(*N*-acryloylcarbazole), (b) $F_A = 0.72$, (c) $F_A = 0.65$, (d) $F_A = 0.59$, and (e) $F_A = 0.44$.

with the copolymer composition data were used to calculate the reactivity ratios using the nonlinear error-in-variables^{34,35} method, using RREVM computer program. The values of reactivity ratios obtained from this method were $r_A = 16.36$ and $r_V = 0.015$, respectively. The 95% posterior probability contour for A/V comonomer pair is shown in Figure 2. The values of reactivity ratios obtained from Kelen–Tudos and nonlinear error-in-variables methods are found to be in good agreement with each other. Moreover, the expensive *N*-acryloylcarbazole was found to be much less reactive towards vinyl acetate than methyl methacrylate ($r_A = 1.05$ and $r_M = 0.90$).

$^{13}\text{C}\{^1\text{H}\}$ NMR studies

The complete assignment of the resonance signals in the $^{13}\text{C}\{^1\text{H}\}$ NMR and DEPT-135 spectrum of the A/V copolymer ($F_A = 0.50$) is shown in Figure 3. The assignments have been done by comparison of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the copolymer with the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the corresponding homo-

polymers, DEPT-135 NMR spectrum, in which, the methylene signals appear in the negative phase and the methine and methyl signals appear in the positive phase, and DEPT-90 NMR spectrum, in which, only methine signals are observed. The carbonyl carbon signals arising from A-unit resonate around $\delta 176.1$ – 173.5 ppm and those from V-unit resonate around $\delta 170.7$ – 169.0 ppm. The aromatic carbons of A-unit resonates from $\delta 142$ – 111 ppm and various assignments of these aromatic carbons have already been reported.^{25,28} The signals around $\delta 21.5$ – 19.2 ppm are assigned to methyl carbon of V unit and the signals around $\delta 70.9$ – 65.6 ppm are assigned to methine carbon of V unit. The spectral region around $\delta 43$ – 30 ppm is quite complex and overlapping, and includes methine of A unit and methylene of both the units. The methine region of A unit has been differentiated with the help of DEPT-90 NMR spectrum.

The methine carbon of V-unit resonates around $\delta 70.9$ – 65.6 ppm and is sensitive to compositional as well as compositional sequences. On the basis of variation in the composition of the copolymers, and on comparison with the corresponding homopolymer, the various triad sequences in the methine carbon resonance signals were assigned. A comparison of the methine carbon resonances (of V unit from DEPT-90 NMR spectrum) for different compositions of A/V copolymers with poly(vinyl acetate) in DEPT-90 spectra is shown in Figure 4. By observing the change in intensities of the signals with the increase in A content in the copolymers, the resonance signals around $\delta 70.9$ – 67.7 , 69.7 – 69.2 , and 69.2 – 68.8 ppm are assigned to AmVmA, AmVrA, and ArVrA triads, respectively. The resonance signals around $\delta 68.8$ – 68.2 , 68.2 – 67.7 , and 67.7 – 67.2 ppm are assigned to VmVmA, VmVrA, and VrVrA triads, respectively. The resonance signals around $\delta 68.1$ – 67.6 , 67.1 – 66.5 , and 66.5 – 65.5 ppm are assigned to VmVmV, VmVrV, and VrVrV triads, respectively.

The methine carbon of A-unit resonates around $\delta 41.3$ – 37.9 ppm and is also sensitive to compositional sequences. A comparison of the methine carbon resonances (of A unit from DEPT-90 NMR spectrum) for different compositions of A/V copolymers with poly(*N*-acryloylcarbazole) is shown in Figure 5. On the similar basis, the various triad sequences in the methine carbon resonance signals were assigned. The resonance signals around $\delta 41.3$ – 39.7 , 39.7 – 39.0 , and 39.0 – 37.9 ppm are assigned to AAA, AAV, and VAV triads, respectively.

Two-dimensional HSQC studies

The 2D HSQC spectrum further confirms the assignments of the various resonance signals in $^{13}\text{C}\{^1\text{H}\}$ and ^1H -NMR spectra. Various assignments of the ar-

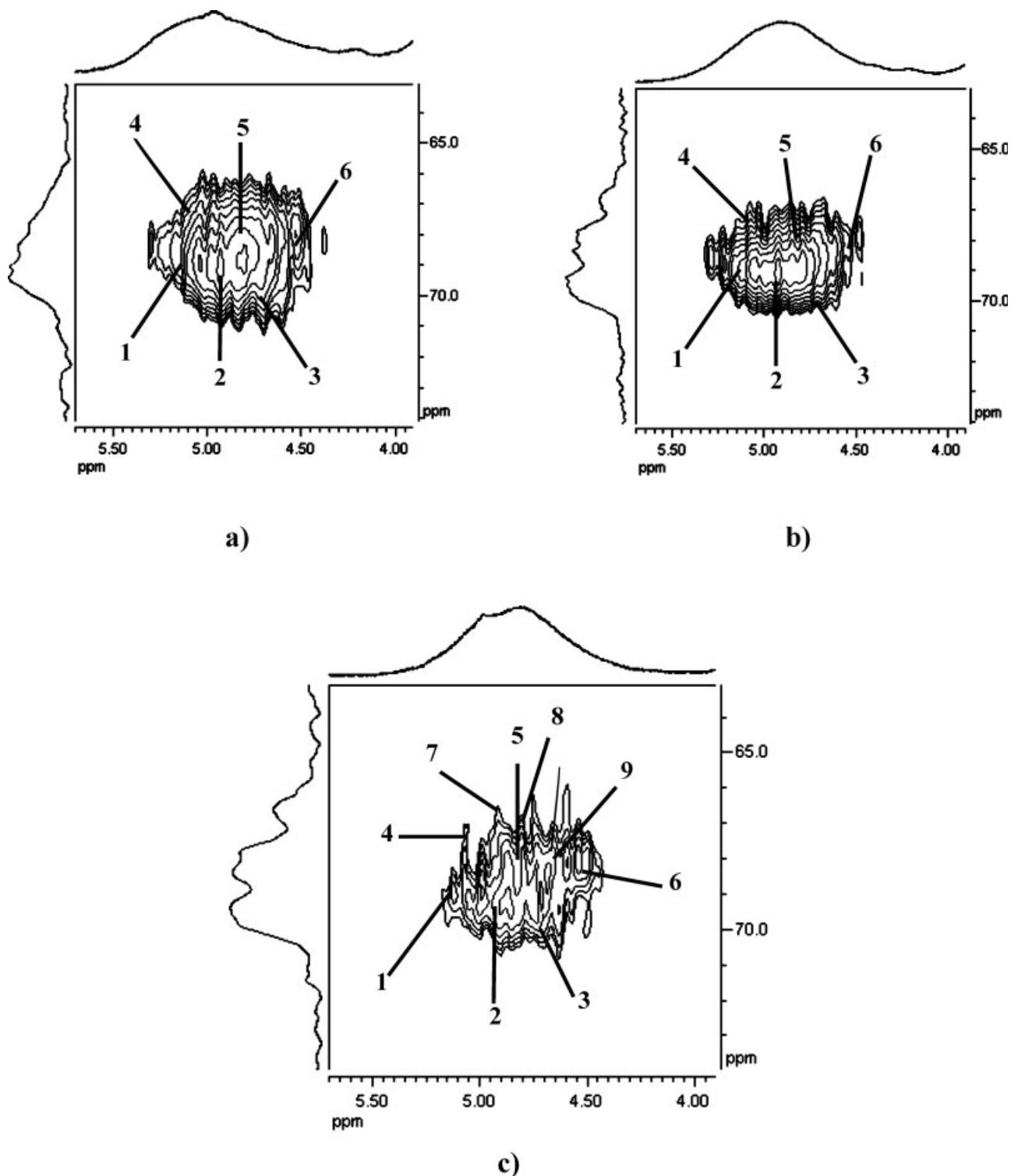


Figure 6 The expanded 2D HSQC spectra of the methine region of V unit of A/V copolymer recorded in CDCl_3 at 25°C : (a) $F_A = 0.65$, (b) $F_A = 0.59$, and (c) $F_A = 0.44$.

omatic region have already been reported.^{25,28} The expanded 2D HSQC spectrum of the methine region of V unit of A/V copolymer is shown in Figures 6(a)–6(c) ($F_A = 0.65$, 0.59 , and 0.44) along with the complete signal assignments. The methine group of the V unit shows compositional as well as configura-

tional sensitivity. The cross peaks 1, 2, 3, 4, 5, 6, 7, 8, and 9 centered at $\delta_{69.0/5.13}$, $69.4/4.93$, $70.0/4.71$, $67.4/5.08$, $68.0/4.82$, $68.4/4.53$, $66.4/4.92$, $66.9/4.80$, and $68.0/4.67$ ppm are assigned to triad compositional sequences ArVrA, AmVrA, AmVmA, VrVrA, VrVmA, VmVmA, VrVrV, VrVmV, and VmVmV,

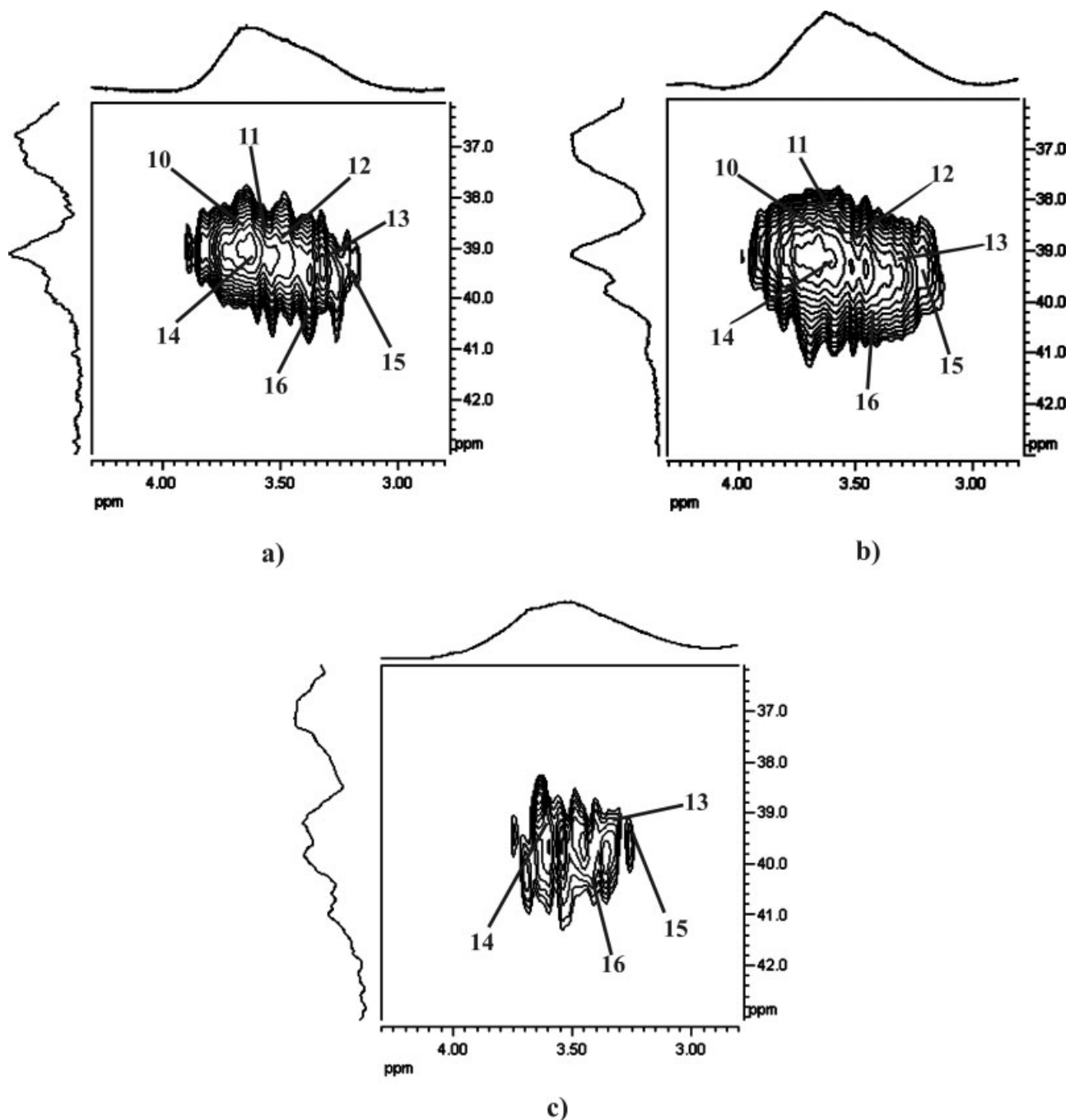


Figure 7 The expanded 2D HSQC spectra of the methine region of A unit of A/V copolymer recorded in CDCl_3 , at 25°C : (a) $F_A = 0.44$, (b) $F_A = 0.59$, and (c) $F_A = 0.72$.

respectively, on the basis of change in intensity with the change in copolymer composition.

The expanded 2D HSQC spectrum of the methine region of A unit of A/V copolymer is shown in Figures 7(a)–7(c) ($F_A = 0.44$, 0.59 , and 0.72) along with the complete signal assignments. The methine group of the A unit shows compositional sensitivity towards ^{13}C -axis and configurational sensitivity towards ^1H -axis. The cross peaks 10, 11, 12, 13, 14,

15, and 16 centered at $\delta 38.6/3.65$, $38.7/3.57$, $38.8/3.50$, $39.2/3.32$, $39.2/3.60$, $39.3/3.21$, and $40.3/3.42$ ppm are assigned to triad compositional sequences VrArV, VmArV, VmAmV, VrArA, VmAA(Hb), VmAA(Hb'), and AAA respectively, on the basis of change in intensity with the change in copolymer composition.

The expanded 2D HSQC spectrum of the methylene region of A/V copolymer is shown in Figures

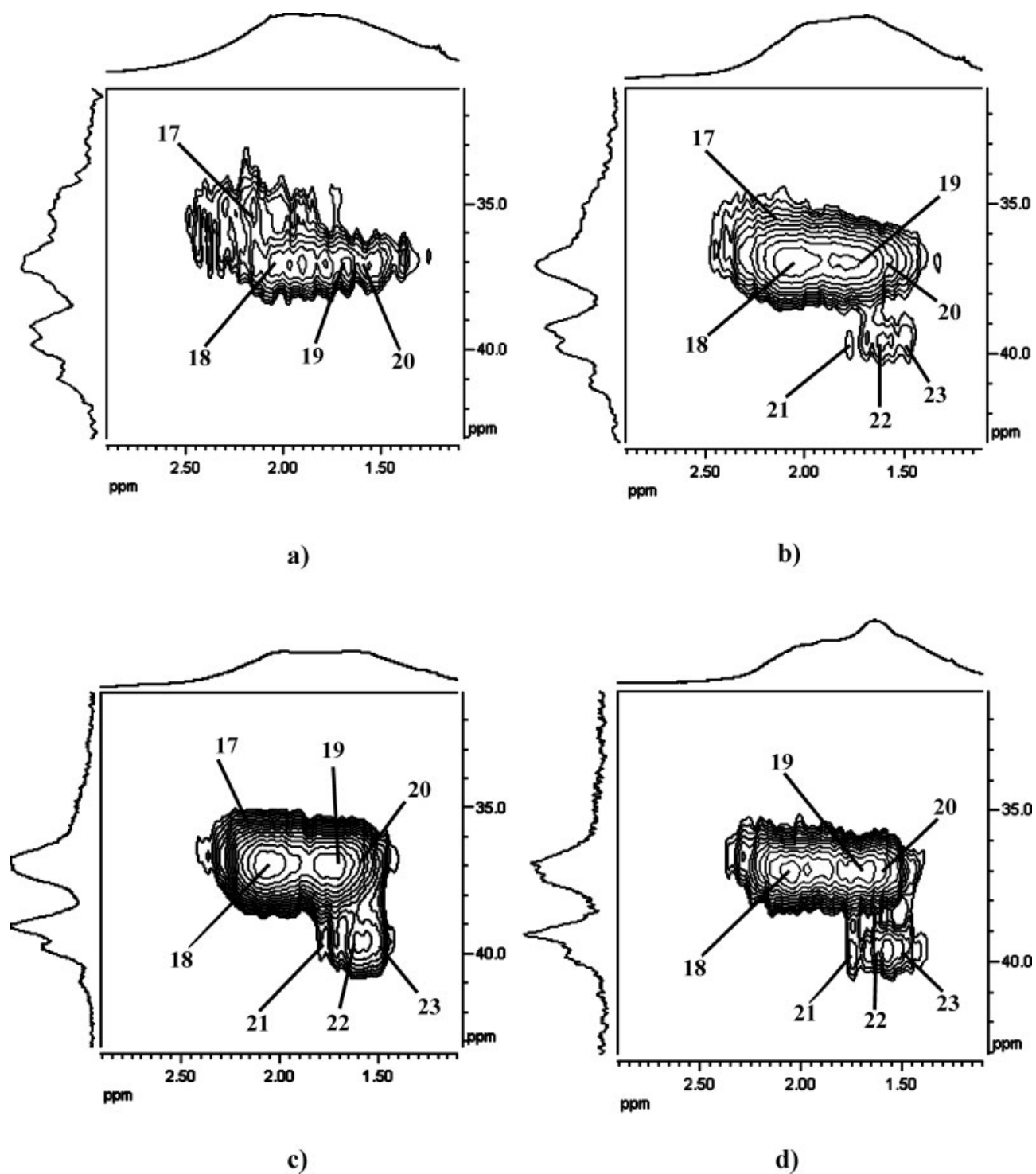


Figure 8 The expanded 2D HSQC spectra of the methylene region of A/V copolymer recorded in CDCl_3 , at 25°C : (a) $F_A = 0.72$, (b) $F_A = 0.65$, (c) $F_A = 0.59$, and (d) $F_A = 0.44$.

8(a)–8(d) ($F_A = 0.72, 0.65, 0.59$, and 0.44) along with the complete signal assignments. The methylene groups of both (A and V) units show dyad compositional sensitivity along carbon axis and configurational sensitivity along proton axis. The region is quite complex and overlapped and can only be

assigned with the help of 2D HSQC spectra. On the basis of variation in intensity of signals with the change in copolymer composition, various dyad compositional sequences in the methylene region are assigned to AA, AM, and MM. The cross peaks 17, 18, 19, 20, 21, 22, and 23 centered at $\delta_{35.5/2.15}$,

TABLE II
Spectral Assignments of A/V Copolymers
Based on 2D HSQC Spectra

Peak no.	Assignments	Chemical shift (ppm)
1	ArVrA	69.0/5.13
2	ArVmA	69.4/4.93
3	AmVmA	70.0/4.71
4	VrVrA	67.4/5.08
5	VrVmA	68.0/4.82
6	VmVmA	68.4/4.53
7	VrVrV	66.4/4.92
8	VrVmV	66.9/4.80
9	VmVmV	68.0/4.67
10	VrArV	38.6/3.65
11	VrAmV	38.7/3.57
12	VmAmV	38.8/3.50
13	VrAA	39.2/3.32
14	VmAA	39.2/3.60
15	VmAA	39.3/3.21
16	AAA	40.3/3.42
17	AA	35.5/2.15
18	AmV	37.0/2.05
19	ArV	37.0/1.69
20	AmV	37.0/1.60
21	VmV	39.7/1.76
22	VrV	39.7/1.63
23	VmV	39.7/1.49

37.0/2.05, 37.0/1.69, 37.0/1.60, 39.7/1.76, 39.7/1.63, and 39.7/1.49 ppm are assigned to AA, AmV(Hb), ArV, AmV(Hb'), VmV(Ha), VrV, and VmV(Ha'), respectively. These dyads could not be assigned further due to the restricted rotation of bulky carbazole group, which make the signals broad. The assignments made in HSQC spectra have been tabulated in Table II.

Two-dimensional TOCSY studies

The 2D TOCSY spectrum of A/V copolymer ($F_A = 0.50$) with low mixing time is shown in Figure 9 along with the complete signal assignments. Assignments of aromatic protons have been reported earlier.^{25,28} Figure 9(a) shows the aliphatic region. The region I is the cross-correlations of methine protons of A unit with methylene protons, and region II is the cross-correlations of methine protons of V unit with methylene protons. The cross peaks 24 and 25 centered at $\delta 2.05/1.60$ and $1.76/1.49$ ppm is due to the geminal coupling of methylene protons in AmV and VmV dyads, respectively.

Figure 9(b) shows the expanded 2D TOCSY spectrum of region I. The central methine proton in VAV triad, as shown in Scheme 1, can show different vicinal couplings with methylene protons in AV dyads. The cross peak 26 centered at $\delta 3.65/1.69$ ppm is assigned to the vicinal coupling of methine protons in VrArV triad with the methylene protons in ArV

dyad. Similarly, the central methine proton in AAV triads, as shown in Scheme 2, can show different vicinal coupling with methylene protons in AV dyads. Thus, the cross peak 27 centered at $\delta 3.32/1.69$ ppm is assigned to the vicinal coupling of methine protons in AArV triad with the methylene protons in ArV dyad and the cross peaks, 28 and 29, centered at $\delta 3.60/2.05$ and $3.21/1.60$ ppm, are assigned to the vicinal coupling of methine protons in AAmV triad with the methylene protons in AmV dyads (with Hb and Hb', respectively), respectively. The cross peak 30 centered at $\delta 3.42/2.15$ ppm is assigned to the vicinal coupling of methine protons in AAA triad with the methylene protons in AA dyad.

Figure 9(c) shows the expanded 2D TOCSY spectrum of region II. As shown in Scheme 1, the central methine proton in VVA triad can show different vicinal coupling with methylene protons in AV and VV dyads. Thus, the cross peak 31 centered at $\delta 4.82/1.63$ ppm is assigned to the vicinal coupling of methine protons in VrVmA triad with the methylene protons in VrV dyad, and the cross peak 32 centered at $\delta 4.82/1.69$ ppm is assigned to the vicinal coupling of methine protons in VmVrA triad with the methylene protons in VrA dyad. The cross peak 33 centered at $\delta 5.08/1.69$ ppm is assigned to the vicinal coupling of methine protons in VrVrA triad with the methylene protons in VrA dyad. Similarly, the central methine proton in AVA triad, as shown in Scheme 2, can also show different vicinal couplings with methylene proton in AV dyads. Thus, the cross peaks 34 and 35 centered at $\delta 4.71/2.05$ and $4.71/1.60$ ppm are assigned to the vicinal coupling of methine protons in AmVmA triad with the methylene protons in VmA dyad (Hb and Hb', respectively) and the cross peak 36 centered at $\delta 4.93/1.69$ ppm is assigned to the vicinal coupling of methine protons in AmVrA triad with the methylene protons in VrA dyad. The cross peaks 37 and 38 centered at $\delta 4.93/2.05$ and $4.93/1.60$ ppm are assigned to the vicinal coupling of methine protons in AmVrA triad with the methylene protons in VmA dyad (Hb and Hb', respectively), and the cross peak 39 centered at $\delta 5.13/1.69$ ppm is assigned to the vicinal coupling of methine protons in ArVrA triad with the methylene protons in VrA dyad. The assignments made in TOCSY (low mixing time) spectra have been tabulated in Table III.

The 2D TOCSY NMR spectrum of A/V copolymer ($F_A = 0.50$) with high mixing time recorded in $CDCl_3$ is shown in Figure 10. Figure 10(a) shows the aliphatic region. The cross peak 40 centered at $\delta 2.05/1.60$ ppm is due to the four bond coupling of methylene protons in AmV dyad (Scheme 2). The region III shows the relay couplings (four bond) of methine protons of A unit with methine protons of V unit. Figure 10(b) shows the expanded 2D TOCSY

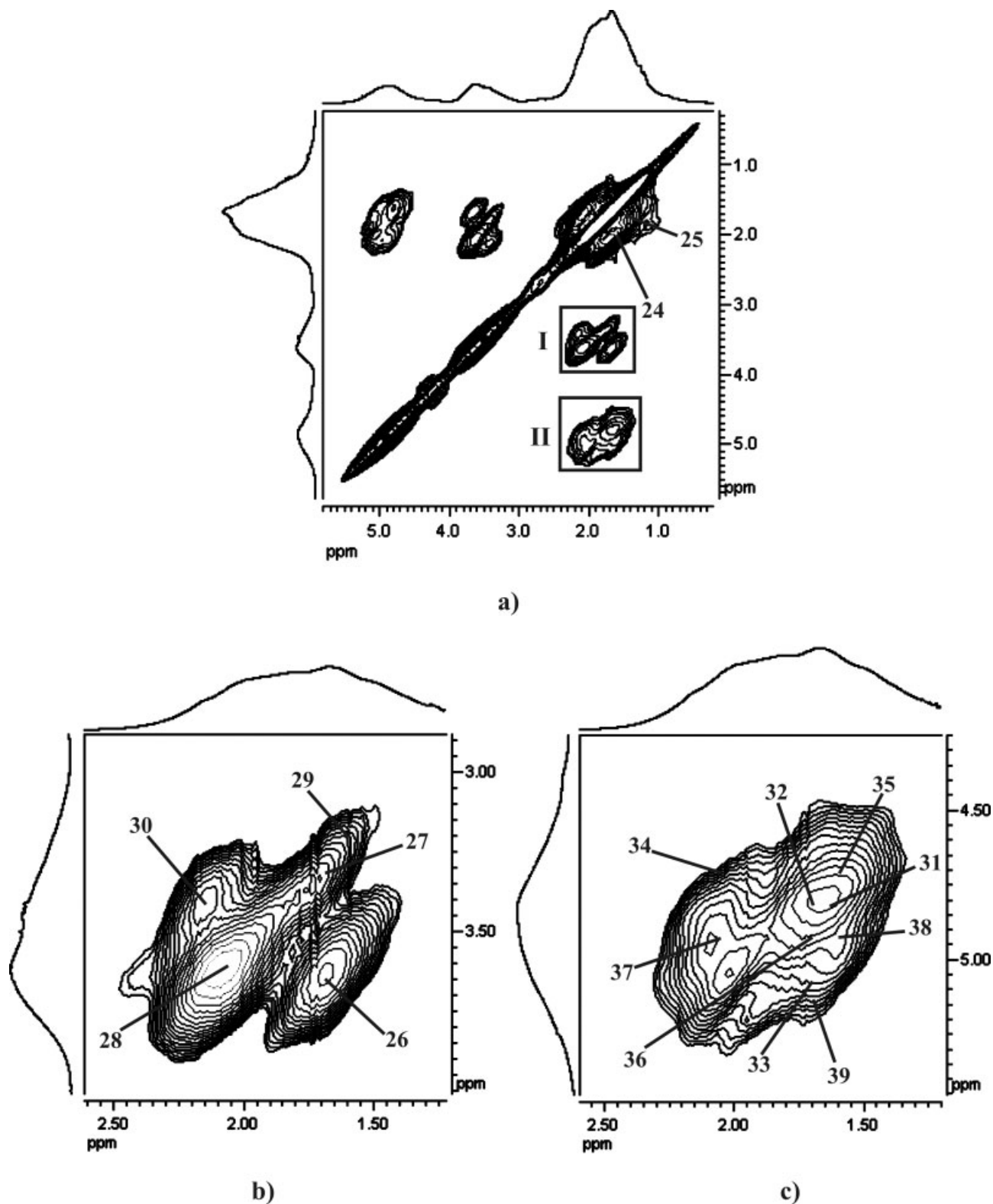
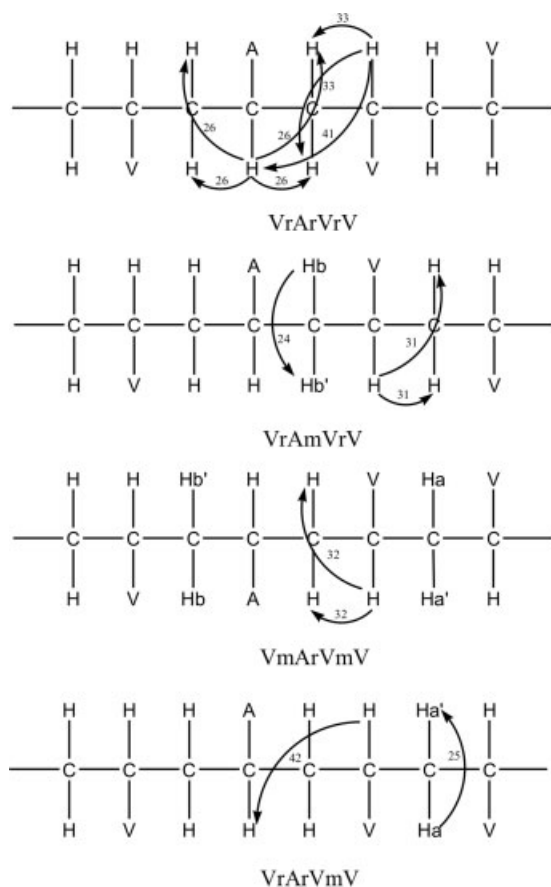


Figure 9 The expanded 2D TOCSY spectrum of A/V copolymer ($F_A = 0.50$) with low mixing time recorded in CDCl_3 , at 25°C : (a) aliphatic region, (b) region I, and (c) region II.

spectrum of region III. As shown in Schemes 1 and 2, the central methine proton in VVA and AVA triads can show various relay couplings with methine

proton in VAV and AAV triads, respectively. Thus, the cross peaks 41 and 42 centered at $\delta 5.08/3.65$ and $4.82/3.65$ ppm are assigned to the relay coupling of

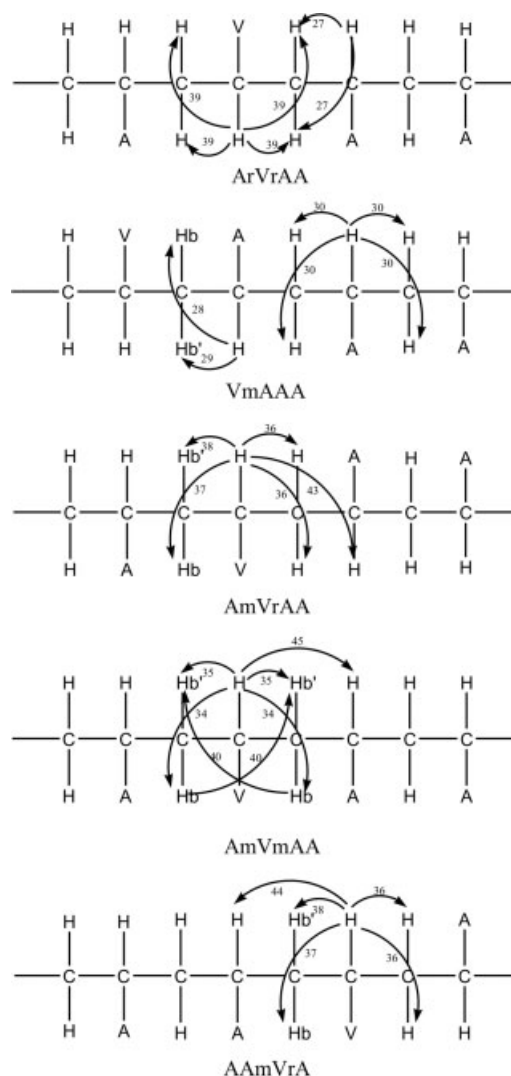


Scheme 1 Various couplings between nonequivalent protons observed in TOCSY spectra (where V = OOCCH₃ and A = OC-carbazole).

methine protons in VrVrA and VmVrA triads with the methine protons in VrArV triad, respectively. The cross peaks 43 and 44 centered at δ 4.93/3.32 and 4.93/3.60 ppm are assigned to the relay coupling of methine protons in AmVrA triad with the methine protons in AArV and AAmV triads, respectively. The cross peak 45 centered at δ 4.71/3.60 ppm is assigned to the relay coupling of methine protons in AmVmA triad with the methine protons in AAmV triad. The assignments made in TOCSY (high mixing time) spectra have been tabulated in Table IV.

Thermal studies

The glass-transition temperature (T_g) of a copolymer is one of the most important phenomenon that determine its physical properties. Out of the numerous theoretical models^{36–40} to calculate T_g by considering the dyad distribution in the copolymers, the theoretical models derived by Johnston³⁹ and Barton,⁴⁰ have been found to exhibit better agreement with experimental T_g .⁴¹ The dependence of the T_g on composition in these copolymers has been analyzed by using



Scheme 2 Various couplings between nonequivalent protons observed in TOCSY spectra (where V = OOCCH₃ and A = OC-carbazole).

TABLE III
Spectral Assignment of A/V Copolymers Based on 2D TOCSY (Low Mixing Time) Spectra

Peak no.	Type of proton	Coupled to	Chemical shift (ppm)
24	AmV(Hb)	AmV(Hb')	2.05/1.60
25	VmV(Ha)	VmV(Ha')	1.76/1.49
26	VrArV	ArV	3.65/1.69
27	AArV	ArV	3.32/1.69
28	AAmV	AmV(Hb)	3.60/2.05
29	AAmV	AmV(Hb')	3.21/1.60
30	AAA	AA	3.42/2.15
31	VrVmA	VrV	4.82/1.63
32	VmVrA	VrA	4.82/1.69
33	VrVrA	VrA	5.08/1.69
34	AmVmA	VmA(Hb)	4.71/2.05
35	AmVmA	VmA(Hb')	4.71/1.60
36	AmVrA	VrA	4.93/1.69
37	AmVrA	VmA(Hb)	4.93/2.05
38	AmVrA	VmA(Hb')	4.93/1.60
39	ArVrA	VrA	5.13/1.69

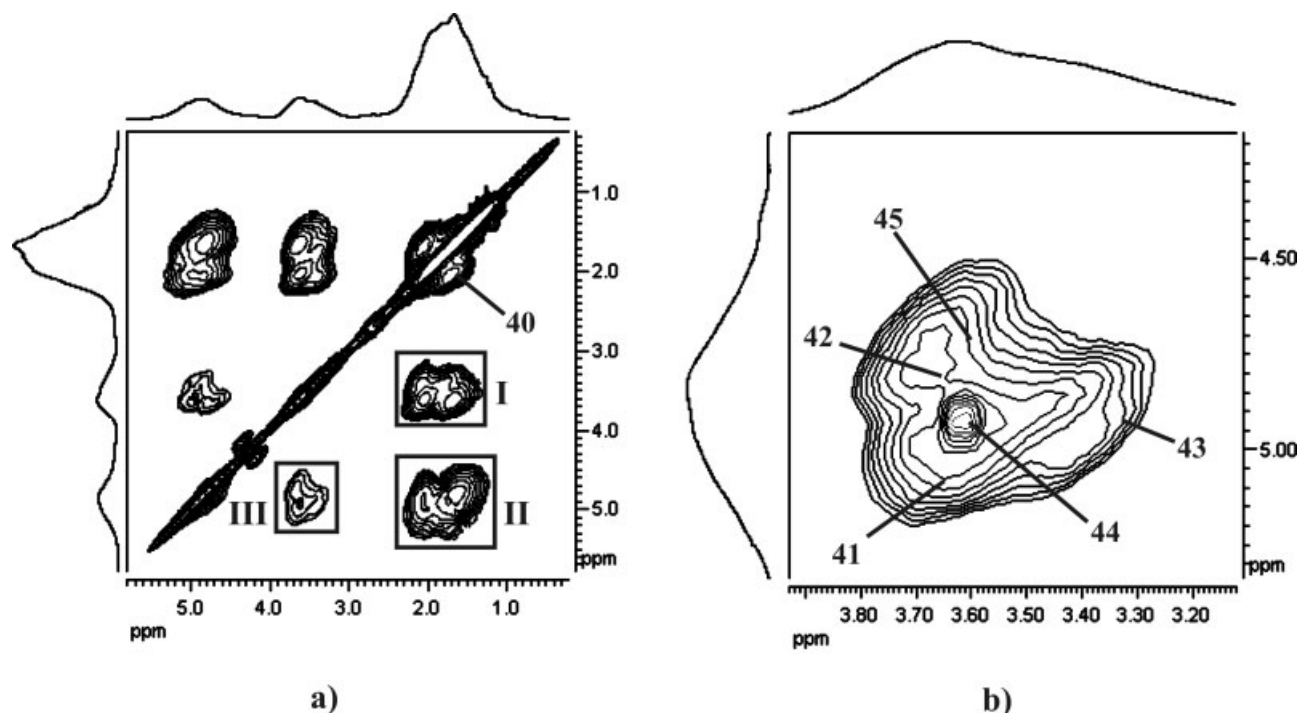


Figure 10 The expanded 2D TOCSY NMR spectrum of A/V copolymer ($F_A = 0.50$) with high mixing time recorded in CDCl_3 , at 25°C : (a) aliphatic region and (b) region III.

Johnston and Barton equations as reported in our earlier publication.²⁸ The value of T_{gAM} of the copolymer system was determined by computerized multiple regression analysis using Microsoft excel worksheet and taking into account the T_g 's of the homopolymers and the series of copolymers. The T_g of the A/V copolymers and the homopolymers are shown in Table I. The copolymerization of *N*-acryloylcarbazole with vinylacetate leads to the lowering of T_g . Figure 11 shows the comparison of the experimental and theoretical T_g values calculated using Johnston equation with the weight fraction of monomer A (W_A). Figure 12 shows the comparison of the experimental and theoretical T_g values calculated using Barton equation with the mole fraction of monomer A (F_A). These models show good agreement with the experimental data.

TABLE IV
Spectral Assignment of A/V Copolymers Based on 2D TOCSY (High Mixing Time) Spectra

Peak no.	Type of proton	Coupled to	Chemical shift (ppm)
40	AmV(Hb)	AmV(Hb')	2.05/1.60
41	VrVrA	VrArV	5.08/3.65
42	VmVrA	VrArV	4.82/3.65
43	AmVrA	AArV	4.93/3.32
44	AmVrA	AAmV	4.93/3.60
45	AmVmA	AAmV	4.71/3.60

The decomposition temperatures (T_d) of A/V copolymers are shown in Table I. The T_d of both the homopolymers are high. We have already reported the decomposition of poly (*N*-acryloylcarbazole).²⁵ Moreover, as expected, from the thermal decomposition data of A/V copolymers (Table I) and A/M copolymers,²⁸ it can be concluded that the A/V copolymers are thermally much more stable.

CONCLUSIONS

The reactivity ratios of monomers are $r_A = 16.75 \pm 1.38$, $r_V = 0.0153 \pm 0.0023$, and $r_A = 16.36$, $r_V = 0.0147$, respectively, by KT and EVM methods. The complex ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of copolymer is assigned with the help of DEPT, HSQC, and TOCSY. The methine and methylene signals have been found to be compositional and configurational sensitive, which has been well resolved with the help of HSQC and TOCSY. The DSC studies are used to study the rigidity of the chain. The value of T_g varies from 430 K [poly(*N*-acryloylcarbazole)] to 304 K [poly(vinylacetate)] with the variation in copolymer composition. The dependence of the T_g on the composition of the copolymers is analyzed by using different theories that take into account the sequence distribution in the copolymer. The copolymers were found to be thermally stable.

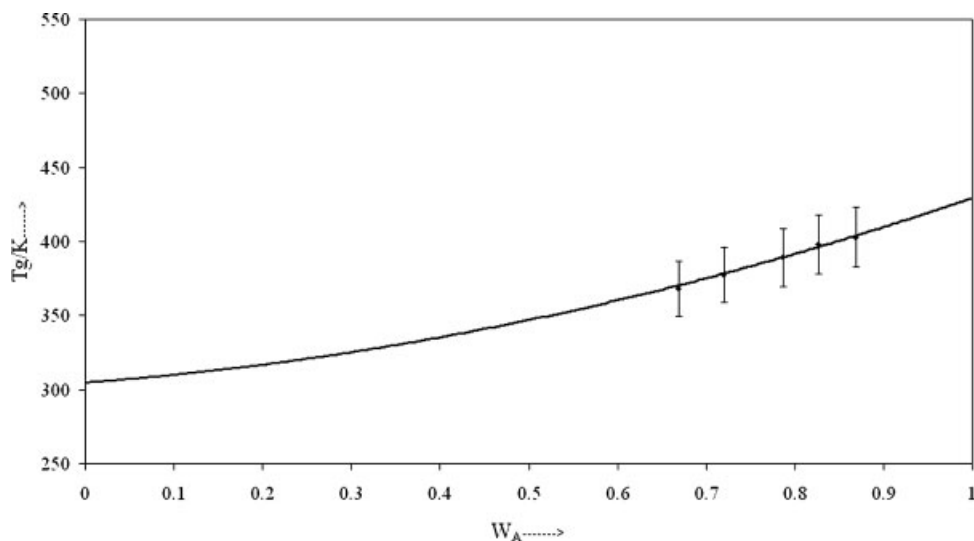


Figure 11 Comparison of experimental glass-transition temperature values with theoretical values for A/V copolymers calculated from Johnston equation.

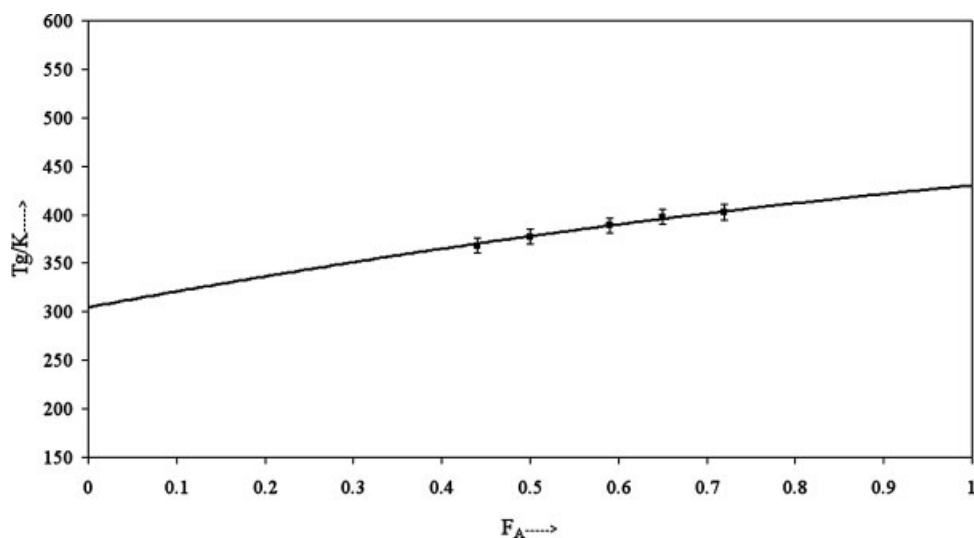


Figure 12 Comparison of experimental glass-transition temperature values with theoretical values for A/V copolymers calculated from Barton equation.

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