

Synthesis and Characterization of *N*-Acryloylcarbazole/Methyl Methacrylate Copolymers

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ABSTRACT: Copolymers of *N*-acryloylcarbazole (A) and methyl methacrylate (M) were synthesized in different in-feed ratios. The composition of the copolymer was determined by the help of ^1H NMR spectrum. The comonomer reactivity ratios determined by Kelen-Tudos (KT) and nonlinear error-in-variables methods were $r_A = 1.12 \pm 0.16$, $r_M = 0.94 \pm 0.14$, and $r_A = 1.05$, $r_M = 0.90$, respectively. Complete spectral assignments of the ^1H and ^{13}C ^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), total correlation spectroscopy (TOCSY), and heteronuclear multiple bond correlation (HMBC). The methine, α -methyl, and carbonyl carbon resonances were found to be sequence sensitive. The signals obtained were broad because of the restricted rotation of

bulky carbazole group and the quadrupolar effect of nitrogen present in carbazole moiety. Glass transition temperatures (T_g) were determined by differential scanning calorimetry and were found to be characteristic of copolymer composition. As the *N*-acryloylcarbazole content increases, the T_g increases from 378.3 K for poly(methyl methacrylate) to 430.4 K for poly(*N*-acryloylcarbazole). Variation in T_g with the copolymer composition were found to be in good agreement with theoretical values obtained from Johnston and Barton equations. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2667–2676, 2006

Key words: differential scanning calorimetry; microstructure; *N*-acryloylcarbazole/methyl methacrylate copolymer; NMR; reactivity ratios

INTRODUCTION

Polymers derived from carbazole containing monomers have generated a lot of interest in the recent past due to their photoconductive, photorefractive, and hole transporting properties.^{1–4} Considerable efforts have been made to make various derivatives of carbazole to enhance these properties. It is a well-known fact that the photoconductivity of carbazole containing substances depends mainly on the type of overlap between carbazole moieties.⁵ A better overlap can be realized by bringing some flexibility in the chain, which can be done either by copolymerizing *N*-acryloylcarbazole with comonomers such as methyl methacrylate, acrylonitrile, and so forth, that contains small pendent group or by increasing the length of the spacer between the main chain and the carbazole moiety.

NMR spectroscopy is probably the most effective technique to determine the intramolecular (sequence determination and tacticity) and intermolecular (chemical composition) chain structure of the poly-

mers.^{6–10} This provides useful information regarding the monomer addition process, that is, the preference of monomer to add in iso or syndio configurations in a given type of polymerization process. Complete assignment of NMR resonances of copolymers is usually complicated because of overlapping signals, arising from the diverse range of microenvironments present.^{11–13} Thus, it is often observed that the sequence determination by one dimensional (1-D) NMR techniques (^1H , ^{13}C $\{^1\text{H}\}$ NMR, and DEPT) alone is quite difficult due to the large overlap of signals. Two dimensional (2D) NMR techniques,^{14–16} especially the heteronuclear single quantum coherence (HSQC) and total correlation spectroscopy (TOCSY) simplify the task as one can obtain the compositional and configurational sequence assignments of the copolymers. Long range carbon-proton couplings can be obtained from heteronuclear multiple bond correlation (HMBC)^{17,18} technique.

Polymer glass transition temperature, which represents the molecular mobility of polymer chains, is an important phenomenon that influences the material properties and potential applications of a given polymer.¹⁹

To the best of our knowledge, the NMR and thermal studies of these copolymers have not been reported so far. In this study, we report the complete assignments of ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectra of A/M copolymers

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with the help of DEPT, 2D HSQC, TOCSY, and HMBC NMR experiments. We also report the analysis of glass transition temperatures of these copolymers.

EXPERIMENTAL

Materials

Toluene was distilled over sodium/benzophenone. Carbazole (Aldrich, Germany; 96%) was recrystallized from dichloromethane. 3-Chloropropionyl chloride (Aldrich, Germany; 98%) and sodium acetate (CDH) were used as received. Ethanol was dried over sodium and distilled. Benzoyl peroxide (BPO) was recrystallized from chloroform. Methyl methacrylate (Merck, Germany; 99%) was passed through a column of basic alumina and distilled under vacuum, which was then stored at 0°C and purged with nitrogen before use.

Synthesis of *N*-acryloylcarbazole

N-Acryloylcarbazole was synthesized from carbazole via a two-step synthetic scheme. Carbazole (1 equiv) was stirred in dry toluene in nitrogen atmosphere for 5 min and heated to 100°C. A solution of 3-chloropropionylchloride (2 equiv; bp = 144°C) in dry toluene was then injected to the above solution through septum,²⁰ and the reaction was allowed to proceed for 22 h. The reaction mixture was cooled to room temperature and quenched with methanol. The solvents were removed under reduced pressure and the slurry obtained was triturated and recrystallized from methanol to obtain *N*-(3-chloropropionyl) carbazole (Yield = 87.2%; mp = 124°C).

¹H NMR (CDCl₃): δ 3.59(t, 2H, CH₂), δ 4.05 (t, 2H, CH₂Cl), δ 7.39 (t, 2H, aromatic{3,6}), δ 7.47 (t, 2H, aromatic{2,7}), δ 7.97 (d, 2H, aromatic{4,5}), δ 8.16 (d, 2H, aromatic{1,8}).

N-(3-Chloropropionyl) carbazole (1 equiv), synthesized by the aforementioned procedure, and sodium acetate (2 equiv) were refluxed for 4 h²¹ in absolute ethanol. Then, the solvent was removed under reduced pressure and the viscous liquid thus obtained was poured into distilled water and extracted with ether. The organic layer was then dried over anhydrous sodium sulfate. Ether was then removed under reduced pressure and resulting product thus obtained was purified by repeated dissolution in boiling hexane, followed by subsequent precipitation by cooling the solution in liquid nitrogen to obtain *N*-acryloylcarbazole (Scheme 1). (Yield: 71.7%; mp = 52°C).

¹H NMR (CDCl₃): δ = 6.03(d, 1H, CH₂), 6.65 (d, 1H, CH₂), 7.07 (dd, 1H, CH), 7.34 (t, 2H, aromatic{3,6}), 7.43 (t, 2H, aromatic{2,7}), 7.94 (d, 2H, aromatic{4,5}), 8.08 (d, 2H, aromatic{1,8}).

Polymerization by free radical mechanism

A series of copolymers of *N*-acryloylcarbazole (A) and methyl methacrylate (M) containing different mole fractions were prepared by solution polymerization in benzene using BPO as the initiator while maintaining the polymerization temperature at 70°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 methyl methacrylate. It was further purified by repeated dissolution in dichloromethane, followed by precipitation in ether to remove *N*-acryloyl carbazole. The copolymers were dried under vacuum at 78°C for 24 h.

NMR measurements

All the NMR spectra were recorded in CDCl₃ at 25°C on a Bruker DPX-300 NMR spectrometer operating at 300.13 and 75.48 MHz for ¹H and ¹³C nuclei, respectively, using the standard pulse sequences.^{22,23} Gradient heteronuclear single quantum coherence (HSQC) experiment was performed by using the standard Bruker *invigptp* pulse sequence. The spectrum was obtained with 512 increments in the *F*₁ dimension and 2048 data points in the *F*₂ dimension. Total correlation spectroscopy (TOCSY) experiment was carried out using standard pulse sequence. A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the 512 *t*₁ experiments (where *t*₁ is the increment in evolution time between pulses). Gradient heteronuclear multiple bond correlation (HMBC) experiment was performed by using the standard Bruker *inv4gplprnd* pulse sequence.

Differential scanning calorimetry

The glass transition temperatures (*T*_g) of the copolymers were recorded on differential scanning calorimeter, Pyris Diamond (Perkin–Elmer) DSC with a water circulating system. The temperature scale was calibrated from the melting point of standard samples (Indium and Zinc). DSC scans were recorded in N₂ atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

¹H NMR studies

The ¹H NMR spectrum along with complete signal assignments is shown in Figure 1 (*F*_A = 0.51). The spectral region around δ 0.15–1.21 ppm is assigned to α-methyl protons, the region around δ 1.21–2.56 ppm is assigned to methylene protons of both (M and A) units, the region around δ 2.56–4.21 ppm is assigned to methine proton of A unit and methoxy protons of M

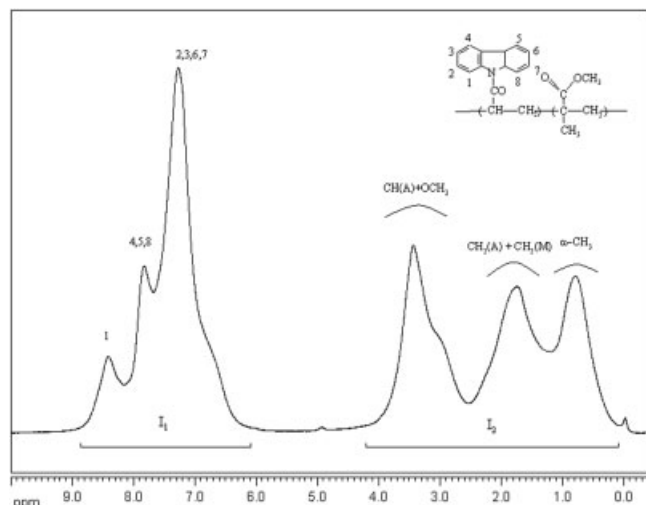


Figure 1 ^1H NMR spectrum of the A/M copolymer ($F_A = 0.51$) in CDCl_3 at 25°C .

unit, and region around δ 6.1–8.8 ppm is assigned to aromatic protons of the carbazole ring. The composition of the copolymer was calculated from the ^1H NMR spectrum, which gives the relative intensities of the aromatic (I_1) and aliphatic (I_2) proton resonances. I_1 region consists of eight protons of carbazole moiety of A unit, whereas the I_2 region consists of three protons of A unit and eight protons of M unit. Thus, the composition of the A/M copolymer was calculated according to the following equation:

$$F_1 = \frac{I_1/8}{I_1/8 + (I_2 - 3I_1/8)/8}$$

where F_1 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-Tudos (KT)²⁴ method with the help of copolymer composition data. The values of the terminal

TABLE I
Copolymer Composition Data of the M/A Copolymers (<10% Conversion)

Sample no.	Mole fraction in-feed (f_A)	Mole fraction in copolymer (F_A)
1	0.21	0.23
2	0.30	0.32
3	0.50	0.51
4	0.60	0.62
5	0.80	0.82

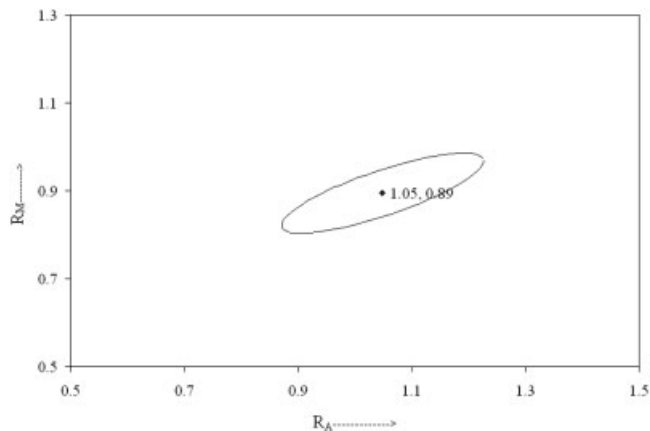


Figure 2 Ninety five percent posterior probability contour for A/M comonomer pair.

reactivity ratios obtained from relevant plots were $r_A = 1.12 \pm 0.16$ and $r_M = 0.94 \pm 0.14$. These values along with the copolymer composition data were used to calculate the reactivity ratios by the nonlinear error-in-variables^{25,26} method using RREVM computer software. The values of reactivity ratios obtained from this method were $r_A = 1.05$ and $r_M = 0.90$, respectively. The 95% posterior probability contour for A/M comonomer pair is shown in Figure 2. The values of reactivity ratios obtained from KT and nonlinear error-in-variables methods are in good agreement with each other.

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

The complete assignment of the resonance signals in the ^{13}C $\{^1\text{H}\}$ NMR spectrum of the M/A copolymer ($F_A = 0.51$) in CDCl_3 is shown in Figure 3. The car-

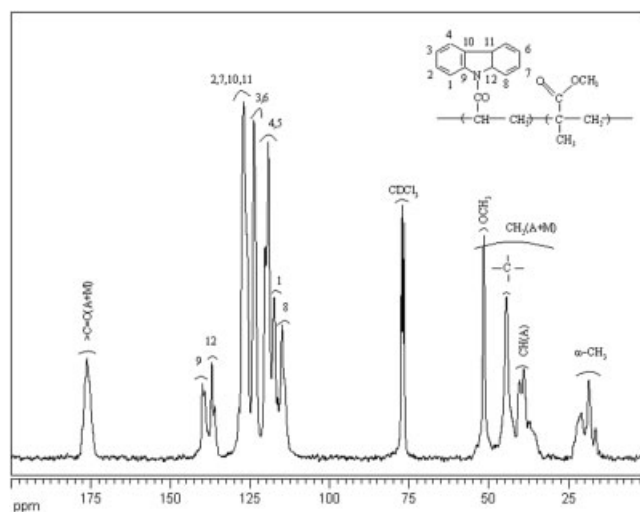


Figure 3 ^{13}C $\{^1\text{H}\}$ NMR spectrum of the A/M copolymer ($F_A = 0.51$) in CDCl_3 at 25°C .

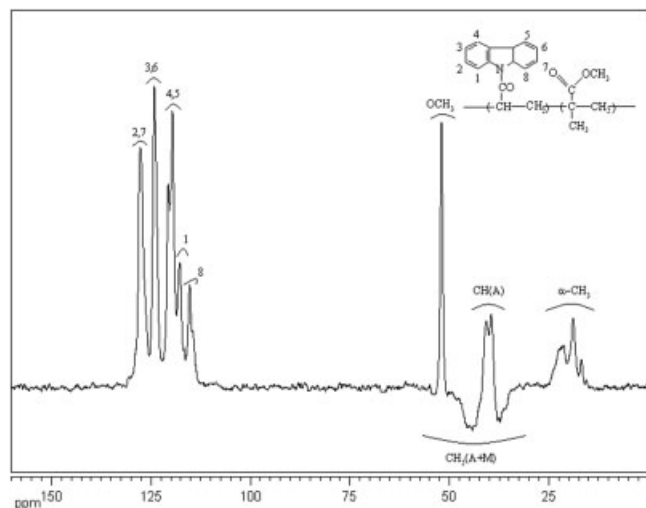


Figure 4 DEPT-135 NMR spectrum of the A/M copolymer ($F_A = 0.51$) in CDCl_3 at 25°C .

bonyl carbon signals arising from both (A and M) units resonate around δ 173.3–178.3 ppm. Despite the fact that the carbazole moiety belongs to C_{2v} symmetry group; yet, the two benzene rings are magnetically

nonequivalent resulting in an asymmetric spectrum. This observation has been attributed to restricted rotation of the bulky carbazole combined with the ring current effects of the neighboring rings.²⁷ The aromatic carbons of A unit resonate from δ 112 to 142 ppm. The peaks at δ 117.4, 114.9, 119.2, 123.8, and 127.0 ppm are assigned to C-1; C-8; C-4, 5; C-3, 6; and C-2, 7, respectively. Various assignments of the Quaternary carbons of the aromatic region in the ^{13}C $\{^1\text{H}\}$ NMR spectrum were done with the help of DEPT-135 NMR spectrum. Figure 4 shows the DEPT-135 NMR spectrum of the A/M copolymer ($F_A = 0.51$) in CDCl_3 . The peaks at δ 138.2–140.8, 134.9–137.8, and 124.8–126.5 ppm are assigned to C-9; C-12; and C-10, 11, respectively. The signals around δ 15.6–24.2 ppm are assigned to α -methyl carbon of M unit. The spectral region around δ 33.5–55.5 ppm is complex and overlapping and thus could not be assigned further with the ^{13}C $\{^1\text{H}\}$ NMR spectrum alone and with the help of DEPT-90 NMR spectrum, and methine carbon signals of A unit has been distinguished from this region.

The methine carbon of A unit resonates around δ 37.6–41.7 ppm and is sensitive to compositional sequences. The expanded region of methine carbon res-

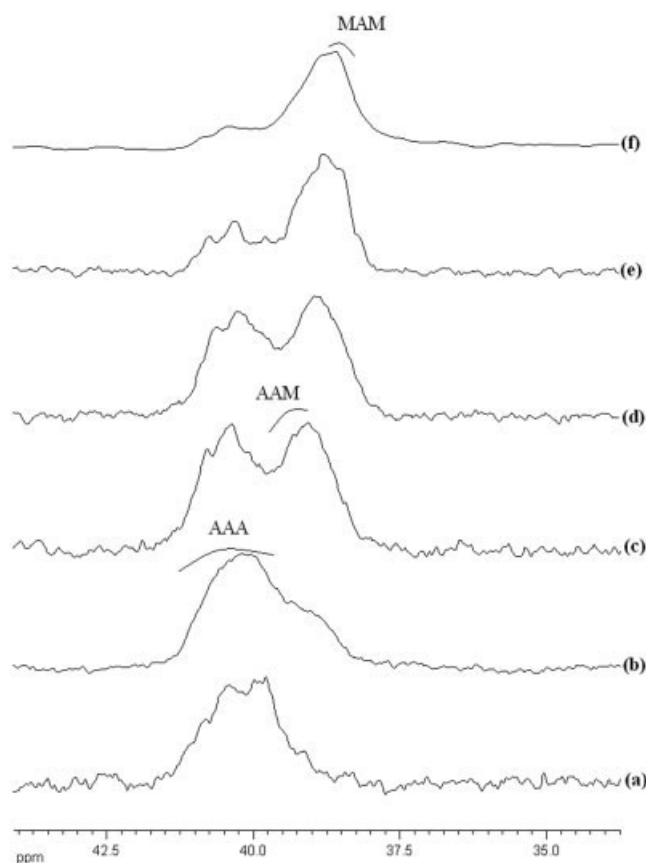


Figure 5 Expanded Methine carbon signals of the A unit in the DEPT-90 NMR spectra of the A/M copolymer in CDCl_3 at 25°C : (a) poly(*N*-acryloylcarbazole), (b) $F_A = 0.82$, (c) $F_A = 0.62$, (d) $F_A = 0.51$, (e) $F_A = 0.32$, and (f) $F_A = 0.23$.

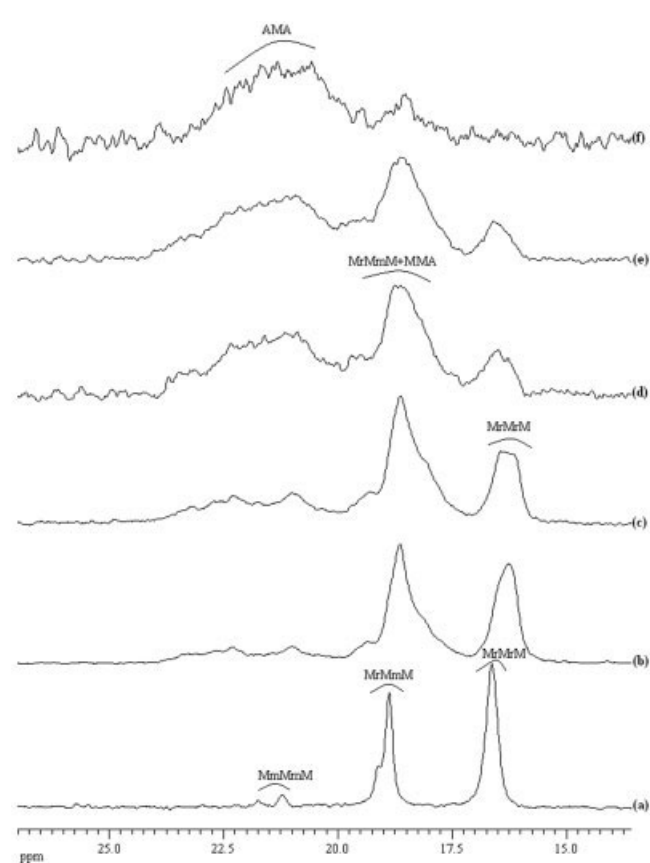


Figure 6 Expanded α -methyl carbon signals of the M unit in the ^{13}C $\{^1\text{H}\}$ NMR spectra of the A/M copolymer in CDCl_3 at 25°C : (a) poly(methyl methacrylate), (b) $F_M = 0.77$, (c) $F_M = 0.68$, (d) $F_M = 0.49$, (e) $F_M = 0.38$, and (f) $F_M = 0.18$.

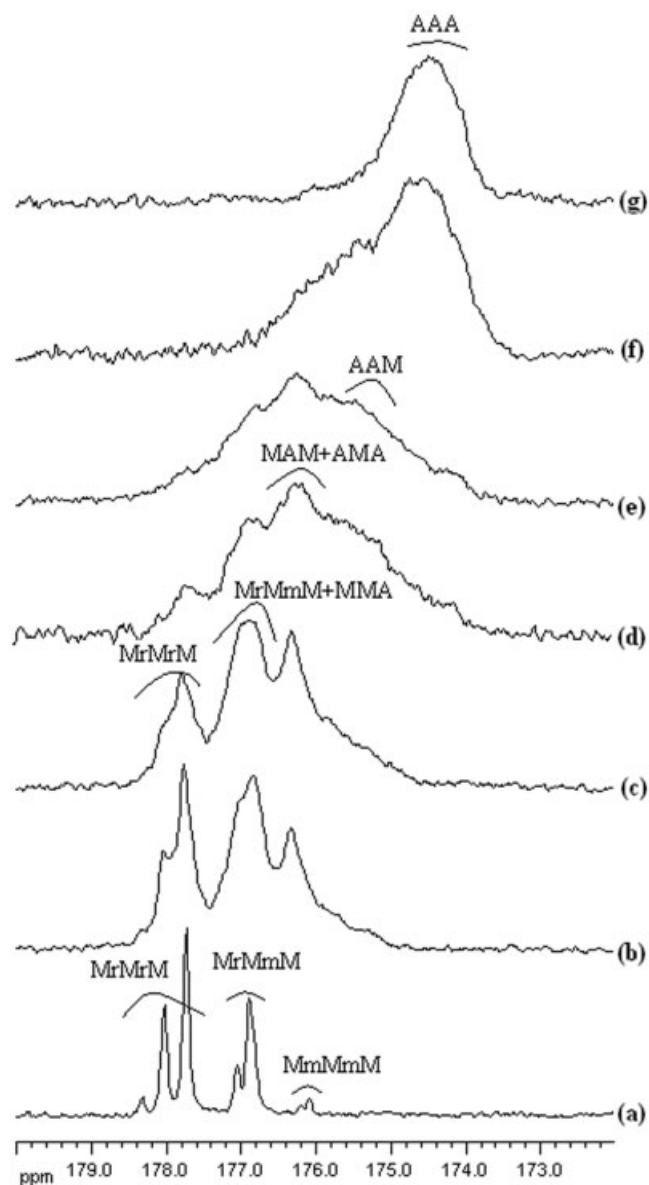


Figure 7 Expanded carbonyl carbon signals of both (A and M) units in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the A/M copolymer in CDCl_3 at 25°C : (a) poly(methyl methacrylate), (b) $F_M = 0.77$, (c) $F_M = 0.68$, (d) $F_M = 0.49$, (e) $F_M = 0.38$, (f) $F_M = 0.18$, and (g) poly(*N*-acryloylcarbazole).

onances in the DEPT-90 NMR spectra of A/M copolymers with different mole fractions of A and the corresponding homopolymer is shown in Figure 5. On the basis of variation in the composition of the copolymers, and on comparison with the spectrum of corresponding homopolymer, the various triad sequences in the methine carbon resonance signals were assigned. The resonance signals around δ 42.1–39.9, 39.9–38.7, and 38.7–37.2 are assigned to AAA, AAM, and MAM triads, respectively.

The α -methyl carbon of M unit resonates around δ 15.6–24.1 ppm and is also sensitive to compositional sequences. The expanded region of α -methyl carbon

resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of A/M copolymers with different mole fractions of M and the corresponding homopolymer (M) is shown in Figure 6. On the similar basis, the various triad sequences in the α -methyl carbon resonance signals were assigned. The resonance signals around δ 15.6–17.1, 17.1–19.9, and 19.9–24.0 ppm were assigned to MrMrM, AMM + MmMrM, and AMA triads, respectively.

The carbonyl carbons of both (M and A) units resonate around δ 173.6–178.5 ppm and are also sensitive to compositional sequences. The expanded region of carbonyl carbon resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of A/M copolymers with different mole fractions of M and the homopolymers (A and M) is shown in Figure 7. On the similar basis, the various triad sequences in the carbonyl carbon resonance signals were assigned. The resonance signals from δ 173.6 to 175.3 ppm are assigned to AAA triad, from δ 175.3 to 175.8 ppm are assigned to AAM triad, from δ 175.8 to 176.6 ppm are assigned to MAM + AMA triads, from δ 176.6 to 177.4 ppm are assigned to MMA + MmMrM triad, and from δ 177.4 to 178.5 ppm are assigned to MrMrM triad.

Two dimensional HSQC studies

2D HSQC NMR spectrum further confirms the various assignments made in $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra. The 2D HSQC NMR spectrum of A/M copolymer ($F_A = 0.51$) recorded in CDCl_3 is shown in Figure 8 along with the complete signal assignments. Various assignments of the aromatic region of the ^1H NMR spectrum

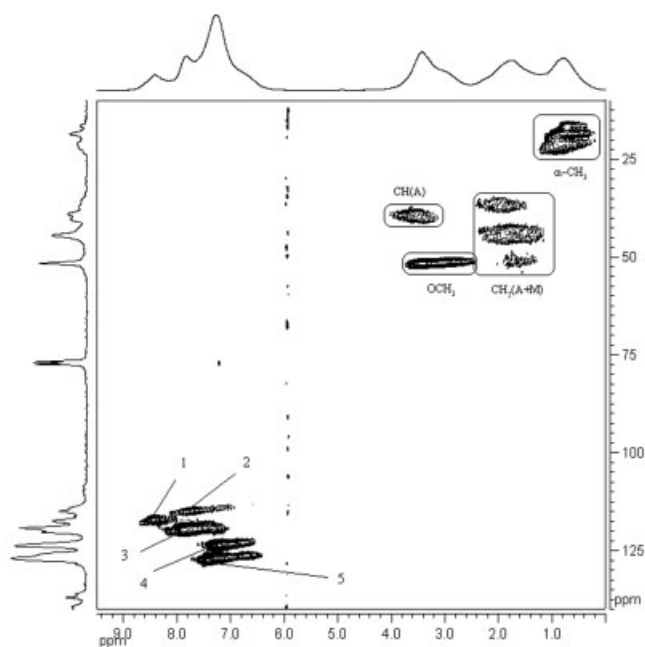


Figure 8 2D HSQC NMR spectrum of A/M copolymer ($F_A = 0.51$) in CDCl_3 at 25°C .

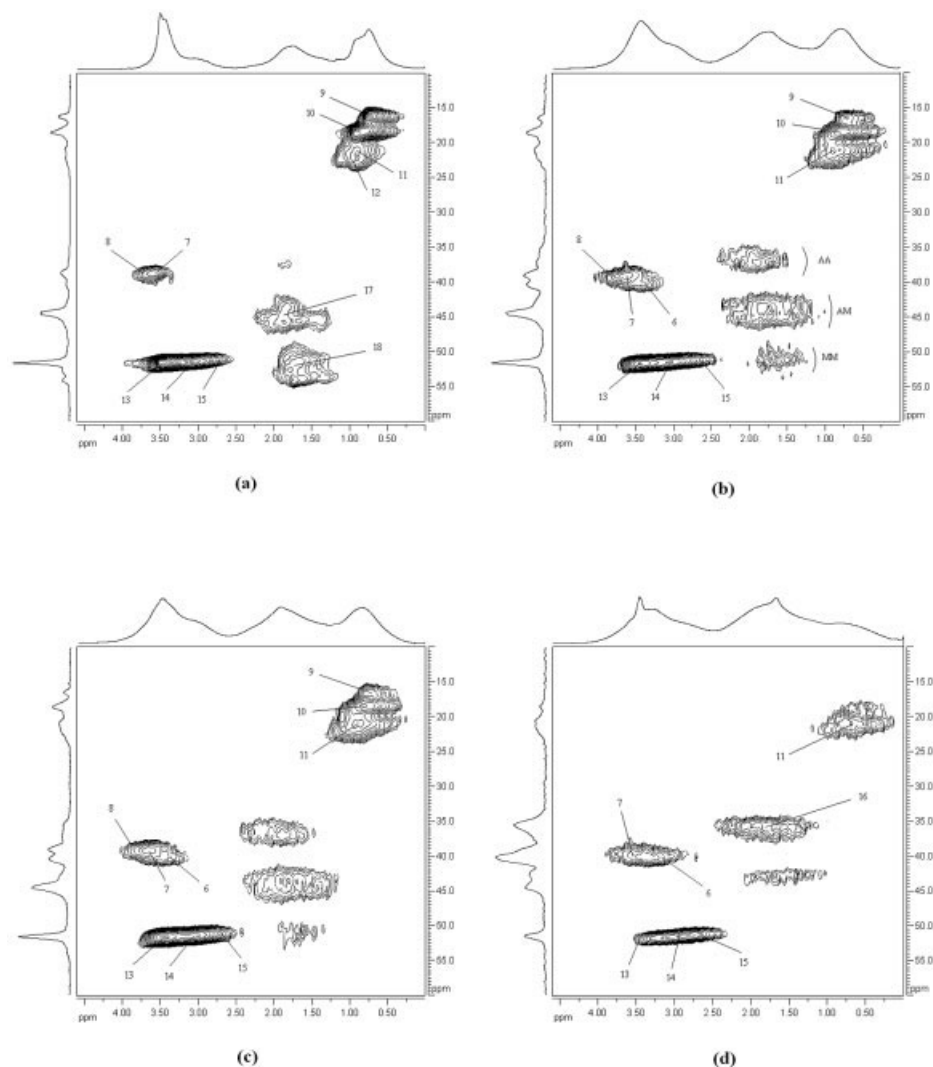


Figure 9 Expanded 2D HSQC NMR spectrum of A/M copolymer of composition (a) $F_A = 0.32$, (b) $F_A = 0.51$, (c) $F_A = 0.62$, and (d) $F_A = 0.82$; in CDCl_3 at 25°C .

were done with the help of HSQC spectrum. The crosspeaks 1, 2, 3, 4, and 5 centered at δ 117.4/8.46, 114.9/7.76, 119.2/7.9, 123.8/7.30, and 127.0/7.34 ppm are assigned to C-1; C-8; C-4, 5; C-3, 6; and C-2, 7, respectively.

The expanded two dimensional HSQC NMR spectra are shown in Figures 9(a)–9(d) ($F_A = 0.32, 0.51, 0.62$, and 0.82). The methine group of the A unit shows compositional sensitivity. On the basis of change in intensity with the change in copolymer composition, the cross peaks 6, 7, and 8 centered at δ 40.6/3.36, 39.0/3.62, and 38.0/3.79 ppm are assigned to triad compositional sequences AAA, AAM, and MAM, respectively. The α -methyl region of the M unit shows compositional sensitivity along carbon axis. The cross peaks 9, 10, 11, and 12 centered at δ 16.4/0.78, 18.5/0.82, 18.6/0.90, and 21.4/0.94 are assigned to triad compositional sequences MrMrM, MmMrM, MMA, and AMA, respectively, on the basis of change in intensity with the change in copolymer composition.

The methoxy region of the M unit in the ^{13}C $\{^1\text{H}\}$ NMR spectrum is quite complex and overlapped with methylene carbon of M unit and can only be assigned with the help of two dimensional HSQC NMR spectra (Fig. 9). This region shows compositional sensitivity along proton axis. The cross peaks 13, 14, and 15 centered at δ 51.5/3.42, 51.5/3.05, and 51.4/2.65 ppm are assigned to triad compositional sequences MMM, MMA, and AMA, respectively, on the basis of change in intensity with the change in copolymer composition.

The methylene groups of both (M and A) units show dyad compositional sensitivity along carbon axis. The region is quite complex and overlapped and can only be assigned with the help of 2D HSQC NMR spectra (Fig. 9). 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 16, 17, and 18 centered at δ 37.5/1.90,

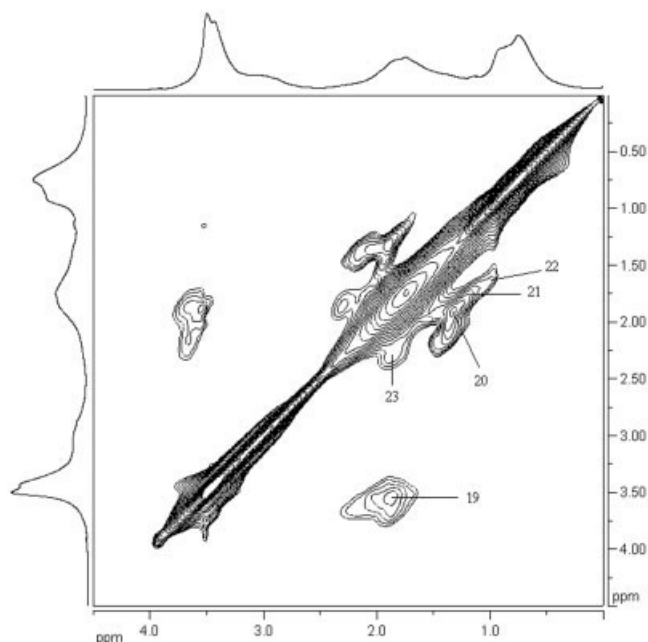


Figure 10 Expanded 2D TOCSY NMR spectrum (low mixing time) showing aliphatic region of A/M copolymer ($F_A = 0.32$) in CDCl_3 at 25°C .

43.8/1.79, and 52.7/1.89 ppm are assigned to AA, AM, and MM, respectively. These dyads could not be assigned further due to the restricted rotation of bulky carbazole group and the quadrupolar effect of nitrogen present in carbazole moiety, which make the signals broad.

Two dimensional TOCSY studies

Once the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum is assigned completely, the various overlapping resonance signals in the ^1H NMR spectrum are assigned by one-to-one correlation between carbon and proton with the help of 2D HSQC NMR spectrum. To understand the connectivity and to confirm the various couplings in the polymer chain, the TOCSY spectra of the copolymers of various compositions were recorded. The expanded 2D TOCSY spectrum of A/M copolymer ($F_A = 0.32$) recorded in CDCl_3 is shown in Figure 10 along with the complete signal assignments. Although the presence of bulky and rigid carbazole moiety and the quadrupolar effect of nitrogen make the signals broad, still the vicinal coupling between the methine and the methylene protons can be clearly observed.

The cross peak 19 centered at δ 1.90/3.56 ppm is due to the vicinal coupling of methylene protons in AA dyad with the methine protons in AAA triad. The cross peaks 20, 21, and 22 centered at δ 1.34/1.90, 1.22/1.74, and 1.05/1.62 ppm are due to the geminal coupling of methylene protons of MM dyad in different environments. The cross peak 23 centered at δ

1.90/2.26 ppm is due to the geminal coupling of methylene protons in AA dyad.

The assignment of the various aromatic ring protons in the ^1H NMR spectrum is shown in Figure 11. The cross peaks 24 and 25 centered at δ 7.36/8.38 and 7.36/7.80 ppm are assigned to the coupling between protons 1–2 and 3–4, respectively. The cross peaks 26 and 27 centered at δ 7.36/7.70 and 7.28/7.85 ppm are assigned to the coupling between protons 5–6 and 7–8, respectively.

Two dimensional HMBC studies

The 2D heteronuclear multiple bond correlation (HMBC) NMR experiment is a powerful technique to observe the long range couplings. The expanded 2D HMBC NMR spectrum of A/M copolymer ($F_A = 0.23, 0.32, \text{ and } 0.51$) recorded in CDCl_3 showing carbonyl carbon region is shown in Figures 12(a)–12(c). The cross peak 28 centered at δ 177.3/3.52 ppm is assigned to the coupling of carbonyl carbon in MrMrM triad to the methoxy protons in MMM triad. The cross peaks 29 and 30 centered at δ 176.6/3.52 and 175.8/3.12 ppm are assigned to the coupling of carbonyl carbon in MMA + MmMrM and MAM triads with methoxy protons in MMM and MMA triads, respectively. The cross peaks 31 and 32 centered at δ 177.0/0.85 and 176.4/1.00 ppm are assigned to the coupling of carbonyl carbon in MrMrM and MMA + MmMrM triads with α -methyl protons in MrMrM and MMA + MmMrM triads, respectively. The cross peaks 33

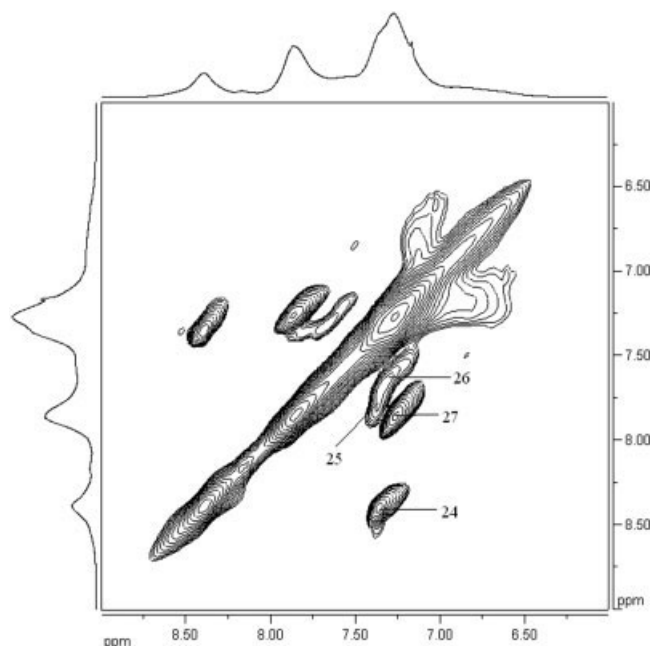


Figure 11 Expanded 2D TOCSY NMR spectrum (low mixing time) showing aromatic region of A/M copolymer ($F_A = 0.32$) in CDCl_3 at 25°C .

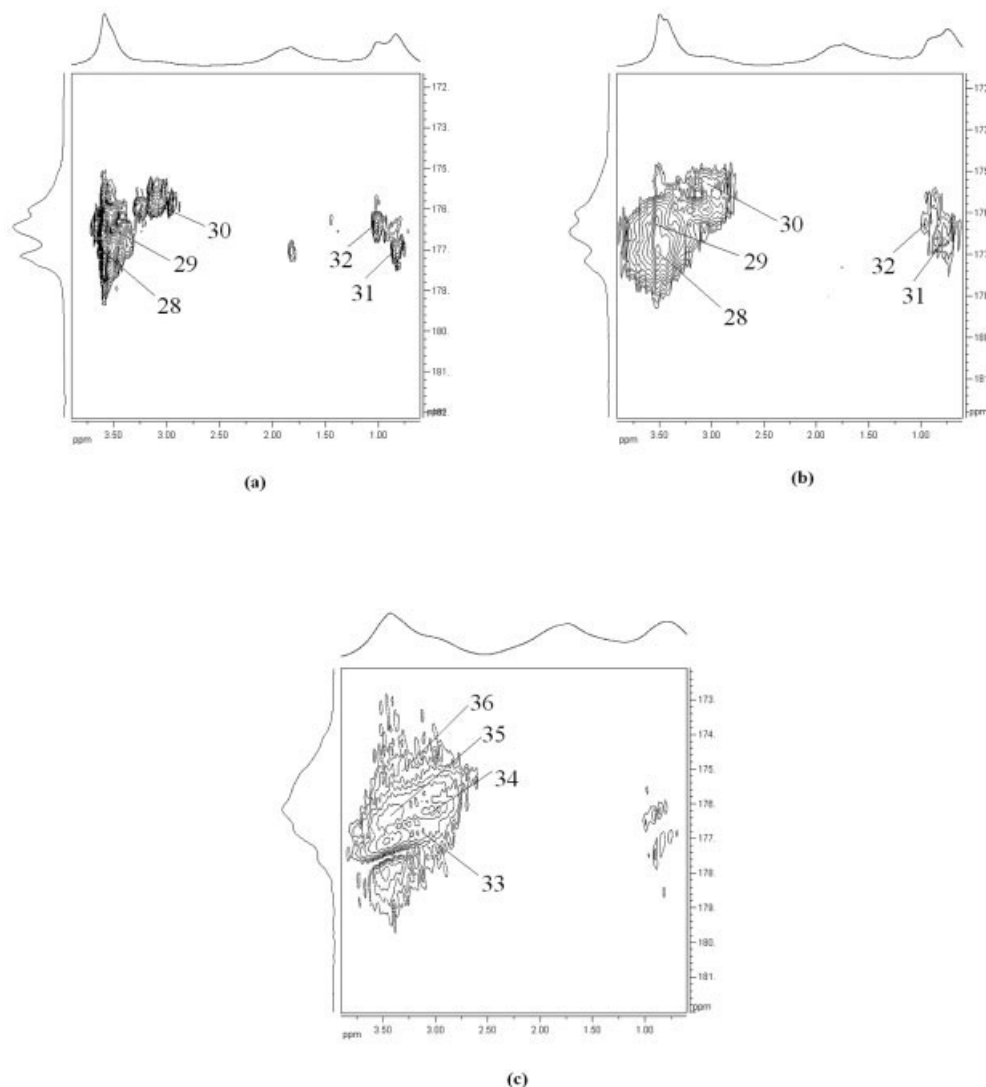


Figure 12 Expanded 2D HMBC NMR spectrum of A/M copolymer of composition (a) $F_A = 0.23$, (b) $F_A = 0.32$, and (c) $F_A = 0.51$ in CDCl_3 at 25°C .

and 34 centered at δ 177.2/3.12 and 176.2/3.10 ppm are assigned to the coupling of carbonyl carbon in MMA and MAM triads with methoxy protons in MMA triads. The cross peaks 35 and 36 centered at δ 176.2/3.48 and 175.1/3.32 ppm are assigned to the coupling of carbonyl carbon in AMA and AAM triad with methine protons in AAM and AAA triads, respectively.

DSC studies

Physical properties of a copolymer are determined by its glass transition temperature (T_g). Simple additive relations describing the T_g of the copolymers based on thermodynamic theory (Gibbs and DiMarzio²⁸) and free volume theory (Fox and Flory²⁹) often failed in predicting accurate T_g of the copolymers as they neglect the effect of chemical nature and organization of

the monomers on the mobility of a polymer chain. Several models^{30–32} have been proposed that take into consideration the effect of sequence distribution of the monomer units on glass transition temperature. Among these the one derived by Johnston³¹ and Barton,³² which correlate T_g to the dyad distribution in the copolymers, exhibit better agreement with experimental T_g .³³ The dependence of the T_g on composition in these copolymers is analyzed by using Johnston and Barton equations. The Johnston equation³¹ is as follows:

$$\frac{1}{T_g} = \frac{W_A P_{AA}}{T_{gAA}} + \frac{W_A P_{AM} + W_M P_{MA}}{T_{gAM}} + W_M P_{MM} T_{gMM}$$

where, w_A and w_M are weight fractions of the monomers A and M, respectively, and P_{AA} , P_{AM} , P_{MA} , and

TABLE II
Glass Transition and Thermal Degradation Temperatures of M/A Copolymers

Sample no.	N-acryloylcarbazole mole fraction in-feed (f_A)	N-acryloylcarbazole mole fraction in copolymer (F_A)	Glass transition temperature
1	1.00 (A)	1.00	430.4
2	0.80 (A1)	0.82	416.6
3	0.60 (A2)	0.62	410.8
4	0.50 (A3)	0.51	409.3
5	0.30 (A4)	0.32	404.4
6	0.21 (A5)	0.23	390.3
7	0.00 (M)	0.00	378.3

P_{MM} are the probabilities of AA, AM, MA, and MM dyads, respectively, and $q = f_A/f_M$ is the monomer feed ratio and r_A and r_M are reactivity ratios for A and M, respectively.

The Barton equation³² is as follows:

$$T_g = F_{AA}T_{gAA} + F_{MM}T_{gMM} + (F_{AM} + F_{MA})T_{gAM}$$

where F_{AA} , F_{AM} , F_{MA} , and F_{MM} are the mole fractions of AA, AM, MA, and MM dyads, respectively.

The value of T_{gAB} of the copolymer system was determined by computerized multiple regression analysis, using T_g of the homopolymers and the series of copolymers.

The T_g of the M/A copolymers and the homopolymers are shown in Table II. The copolymerization of *N*-acryloylcarbazole with methyl methacrylate leads to the lowering of T_g of the poly(*N*-acryloylcarbazole). The T_g of the poly(*N*-acryloylcarbazole) was found to be 430.4 K, which is almost 155 K higher than its alkyl homologue (polyvinylketone).³⁴ It indicates that the rigid carbazole ring hinders the rotation around the bond in the chain. The Figures 13 and 14 show the

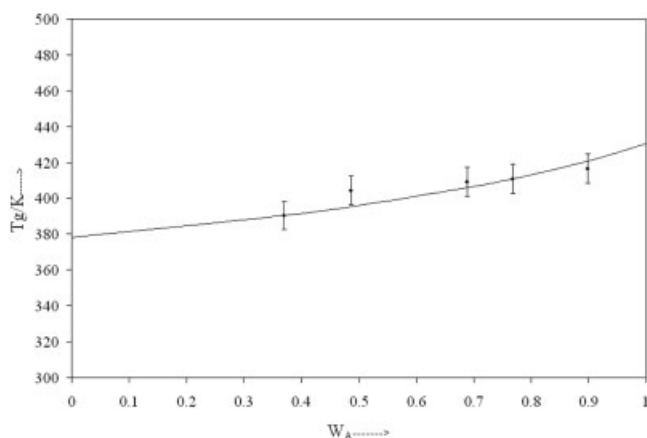


Figure 13 Comparison of experimental glass transition temperature values with theoretical values for A/M copolymers calculated from Johnston equation.

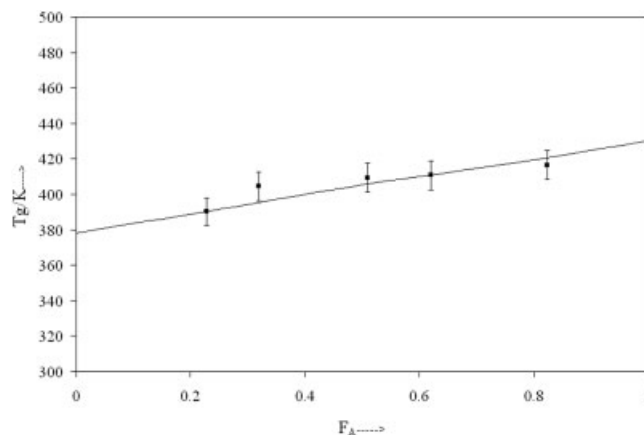


Figure 14 Comparison of experimental glass transition temperature values with theoretical values for A/M copolymers calculated from Barton equation.

comparison of the experimental and theoretical T_g values calculated using Johnston and Barton equations, respectively. These models show good agreement with the experimental data.

CONCLUSIONS

To conclude, the reactivity ratios of monomers are $r_A = 1.12 \pm 0.16$, $r_M = 0.94 \pm 0.14$, $r_A = 1.05$, and $r_M = 0.90$ by KT and error-in-variables methods, respectively. The methine, α -methyl, and carbonyl carbon resonances are assigned to triad compositional sequences, but quantitative calculations could not be done as signals obtained are very broad. The broadening is due to the restricted rotation of bulky carbazole group and the quadrupolar effect of nitrogen present in carbazole moiety. The complex ^1H NMR spectrum of copolymer is assigned with the help of HSQC and HMBC. The complex ^{13}C NMR spectrum is resolved by the help of DEPT, HSQC, and HMBC. The DSC studies are used to study the rigidity of the chain. The T_g varies with the variation in copolymer composition. As the amount of *N*-acryloylcarbazole increases, the T_g increases from 378.3 K for poly(methyl methacrylate) to 430.4 K for poly(*N*-acryloylcarbazole). 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 theoretical values obtained by these equations are found to be in good agreement with the experimental data.

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