

# Structural Investigations of (9-Ethyl-carbazol-6-yl) Methyl Methacrylate/Methyl Acrylate Copolymers Using Two-Dimensional NMR Spectroscopy

Ajaib Singh Brar, Sonia Gandhi

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

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**ABSTRACT:** (9-Ethyl-carbazol-6-yl) methyl methacrylate/methyl acrylate (E/A) copolymers of different compositions were prepared by solution polymerization by varying the molar infeed ratio, using AIBN as initiator at 60°C. The reactivity ratios calculated by Kelen–Tudos (KT) method were found to be  $r_E = 1.16 \pm 0.02$  and  $r_A = 0.69 \pm 0.01$  whereas those calculated from RREVM method were found to be  $r_E = 1.18$  and  $r_A = 0.68$ . The molecular weights ( $M_w$ ) and polydispersity index (PDI,  $M_w/M_n$ ) were determined using gel permeation chromatography (GPC). Glass transition temperatures ( $T_g$ ) for different compositions of E/A copolymers were determined using differential scanning calorimetry (DSC). Copolymer molar outfeed ratio ( $F_E$ ) was calculated from  $^1\text{H}$  NMR spectra. The  $\alpha$ -methyl, methine, backbone methylene, and quaternary carbon resonance signals of the

copolymers were distinguished using  $^{13}\text{C}\{^1\text{H}\}$ , DEPT-45, -90, and -135 NMR techniques. The  $\alpha$ -methyl and  $\beta$ -methylene showed compositional and configurational sensitivity up to pentad and tetrad level, respectively, whereas methine showed only compositional sensitivity up to pentad level. Unambiguous assignments for  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were done by correlating 1D ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , DEPT) and 2D (HSQC, TOCSY) NMR data. The spectral assignments for carbonyl region were done by studying higher bond order couplings by heteronuclear multibond correlation (HMBC) spectra. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5595–5606, 2006

**Key words:** microstructure; nuclear magnetic resonance spectroscopy (NMR); photorefractive polymers; (9-ethyl-carbazol-6-yl) methyl methacrylate

## INTRODUCTION

Owing to their special photophysical properties, copolymers containing carbazole-based chromophores are good electron donors and possess outstanding electrical and photoelectrical properties.<sup>1</sup> Various N- and C-substituted carbazole containing polymers have been synthesized and studied.<sup>2</sup> The copolymers containing ring-substituted carbazolyl pendant groups have been found to show enhanced photorefractivity because of the ability of these chromophores to form charge carriers in the visible region through an induced intramolecular charge transfer complex.<sup>3–8</sup> These copolymers can be used in photonic applications because their photoconductivity combined with nonlinear optical activity (NLO) makes them good photorefractive material.<sup>8–13</sup> This property makes them a versatile material for optical storage and optical processing applications.<sup>14–17</sup> (9-Ethyl-carbazol-6-yl) methyl

methacrylate/methyl acrylate (E/A) copolymer belongs to the class of photorefractive materials. These polymers are the combination of electron donor and acceptor groups and the references cited depicts their ability to act as photorefractive materials and other properties related to it.<sup>18–22</sup>

Because of the presence of bulky carbazole moiety, the E-based polymers are brittle and possess high glass transition temperature because of which their processing becomes difficult. Hence copolymerization is a useful method to improve physical and chemical properties of these polymers.<sup>23,24</sup>

Copolymerization with acrylate-based monomers such as methyl acrylate (A), ethyl acrylate, butyl acrylate, etc., can result in copolymers with improved physical and chemical properties. Increasing A content in copolymers such as poly((9-ethyl-carbazol-6-yl) methyl methacrylate-co-methyl acrylate) decreases the glass transition temperature ( $T_g$ ) thereby improves processability.<sup>25,26</sup> Copolymerization also influences the photoconductive and photorefractive properties of these copolymers, which results in copolymers having tailored properties.

These physical and chemical properties of the copolymers are influenced by their microstructure, which is defined as the local structural information,

Correspondence to: A.S. Brar (asbrar@chemistry.iitd.ernet.in).

Contract grant sponsor: Department of Science and Technology (DST), New Delhi, India.

TABLE I  
Theoretical and Experimental  $F_M$ , Molecular Weight Distribution, % Conversion, and  $T_g$  of E/A Copolymers

Infeed molar fraction ( $f_E$ )	Conversion (wt %)	Outfeed molar fraction ( $F_E$ )		Molecular weight $M_w$ ( $10^{-4}$ g/mol)	PDI	Glass transition temperature $T_g$ ( $^{\circ}\text{C}$ )
		Experimental	Theoretical			
1.0	–	–	–	7.38	1.65	141
0.8	3.4	0.86	0.84	11.8	1.68	123
0.5	4.4	0.55	0.56	10.4	1.56	113
0.3	4.2	0.37	0.37	7.79	1.51	78
0.2	2.9	0.26	0.26	4.85	1.37	62

i.e., the microenvironment at the level of short-chain segments, which is a few monomeric unit long. Hence, determining the microstructure is a crucial step for studying various thermal and photophysical properties of the copolymers.<sup>27,28</sup> High-resolution 2D NMR spectroscopy was found to be the most efficient technique for determining the microstructure of the copolymers.<sup>29–33</sup> Microstructures of various (meth)acrylate copolymer systems have been studied by Brar et al., using various NMR techniques, and these studies have further helped in knowing the tacticity for various methacrylate–acrylate copolymer systems.<sup>34–36</sup> In our earlier publication, the tacticity of poly((9-ethyl-carbazol-6-yl) methyl methacrylate) was reported,<sup>37</sup> and using this knowledge, the microstructure of E/A copolymers have been investigated.

In this article, we report the microstructure of (9-ethyl-carbazol-6-yl) methyl methacrylate/methyl acrylate (E/A) copolymers using 1D ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , DEPT) and 2D (HSQC, TOCSY, HMBC) NMR spectroscopic techniques.<sup>34–36,38,39</sup> The various compositional and configurational sensitivity of  $\alpha\text{-CH}_3$ ,  $\beta\text{-methylene}$ , and methine in  $^{13}\text{C}\{^1\text{H}\}$  NMR were unambiguously assigned by 2D NMR. The long range couplings between carbonyl carbon with  $\alpha\text{-CH}_3$  and methylene protons were investigated using 2D HMBC NMR studies.<sup>40,41</sup> Variation in the glass transition temperature ( $T_g$ ) for different compositions of E/A copolymers was also studied.

## EXPERIMENTAL

### Materials

(9-Ethyl-carbazol-6-yl) methyl methacrylate (E) was prepared as reported in an earlier publication,<sup>37</sup> methyl acrylate (A, Merck, 98% pure) was dried over  $\text{CaH}_2$ , vacuum distilled, and kept at temperatures below  $5^{\circ}\text{C}$  before use. 2,2'-Azobisisobutyronitrile (AIBN, Fluka) was recrystallized using methanol and stored at low temperature.

### Polymerization

Poly((9-ethyl-carbazol-6-yl) methyl methacrylate-co-methyl acrylate) was synthesized by solution poly-

merization using AIBN (0.05%) as initiator at  $60^{\circ}\text{C}$  in distilled toluene as solvent. E/A copolymers with different molar infeed ratios were synthesized (Table I). The copolymer obtained was filtered and dissolved in minimum amount of chloroform. Re-precipitation was further carried out in methanol and was repeated several times to purify the copolymers obtained.

The polymerization was carried out in such a manner that the conversion was kept below 5% to avoid compositional drift. The conversion was controlled by monitoring the change in viscosity of the reaction mixture with time. Precipitation was carried out in methanol as the reaction mixture became slightly viscous so that the gel point is not reached. Percentage conversion was then determined gravimetrically.

### Characterization

Various 1D ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , DEPT) and 2D (HSQC, TOCSY, HMBC) NMR spectra for different copolymer compositions were recorded on a Bruker DPX-300 spectrometer in  $\text{CDCl}_3$ . Copolymer compositions were calculated from  $^1\text{H}$  NMR spectra. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR measurements were made at frequencies of 300.13 and 75.5 MHz, respectively, at  $25^{\circ}\text{C}$  with standard pulse sequence, as reported in our earlier publications.<sup>42,43</sup> Measurements were done on 10% (w/v) polymer solution.

Percentage conversion was determined gravimetrically. The weight-average molecular weight ( $M_w$ ) and polydispersity index (PDI,  $M_w/M_n$ ) were measured using gel permeation chromatography (GPC) system equipped with a Waters 501 pump with a guard column and a Waters 410 RI detector against polystyrene standards. Measurements of the glass transition temperature ( $T_g$ ) for different compositions of copolymers were done by differential scanning calorimetry (DSC) on Perkin–Elmer DSC-7 with a heating rate of  $10^{\circ}\text{C min}^{-1}$ . About 13–14 mg of the samples was sealed in aluminum pans and was subjected to repeated heating/cooling cycles.

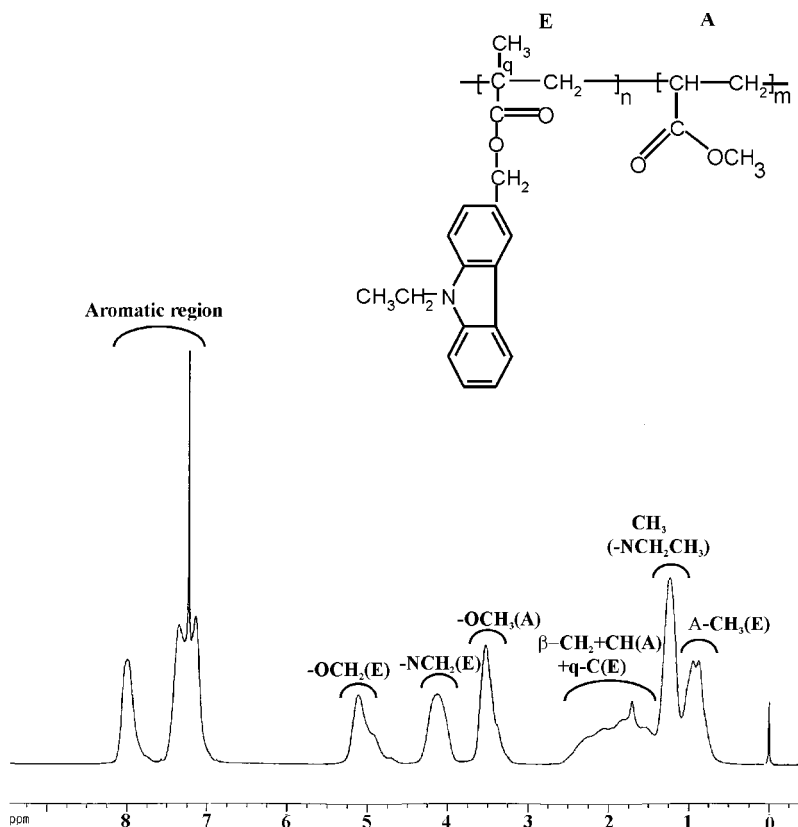


Figure 1  $^1\text{H}$  NMR spectrum of E/A copolymer for  $F_E = 0.55$  in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Copolymer composition and reactivity ratio determination

$^1\text{H}$  NMR data for the copolymer was used to determine the copolymer composition. As shown in Figure 1, the resonances for the  $-\text{OCH}_3$  (A unit) and  $-\text{NCH}_2$  (E unit) are well separated; hence, their relative resonance areas can be measured and used to calculate the mole fraction of (9-ethyl-carbazol-6-yl) methyl methacrylate ( $F_E$ ) in E/A copolymers using the following equation:

$$F_E = \frac{I(\text{NCH}_2)/2}{I(\text{OCH}_3)/3 + I(\text{NCH}_2)/2}$$

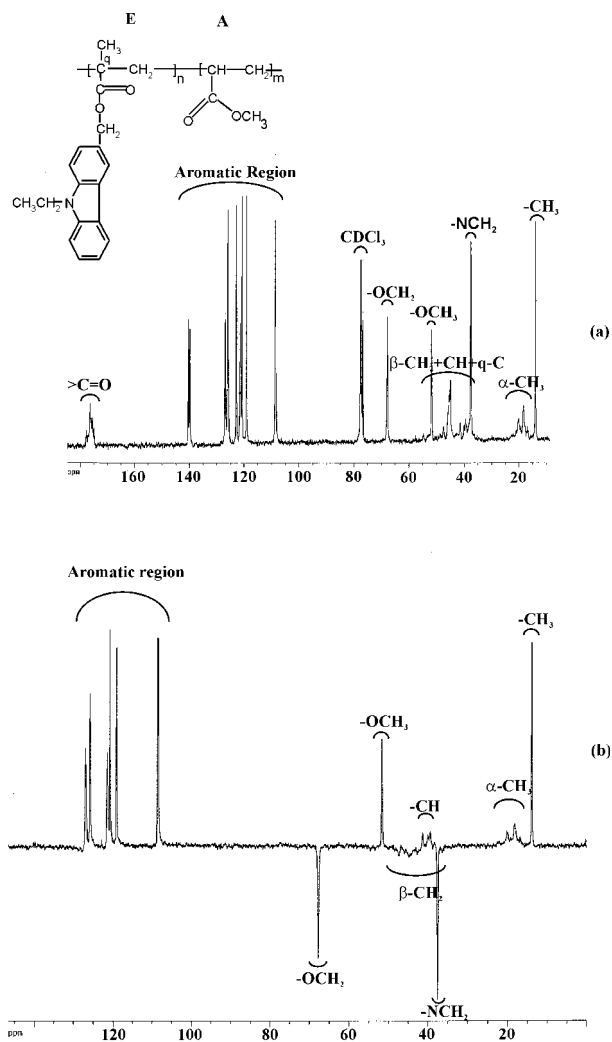
where,  $I(\text{NCH}_2)$  is the area under the resonance signal of  $-\text{NCH}_2$  protons of the E unit and  $I(\text{OCH}_3)$  is the area under the resonance signal of  $-\text{OCH}_3$  proton of A unit. Table I shows theoretical and experimental molar outfeed ( $F_E$ ) of various E/A copolymers along with their molecular weight distribution ( $M_w$ ), PDI, and  $T_g$ . Theoretical  $F_E$  for various copolymers were determined as reported by Brar et al.<sup>34</sup> The reactivity ratios for the monomers in the E/A copolymers were calculated by Kelen–Tudos (KT) method<sup>44</sup> and nonlinear error-in-variable (RREVM)

method.<sup>45</sup> The reactivity ratios determined by KT and RREVM methods were found to be  $r_E = 1.16 \pm 0.02$ ,  $r_A = 0.69 \pm 0.01$  and  $r_E = 1.18$ ,  $r_A = 0.68$ , respectively. It could be seen from the values of the reactivity ratios that E is more reactive than A unit hence at low conversion the E/A copolymer will have more of E content.

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

Various resonance signal assignments in  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum for E/A copolymers having  $F_E = 0.55$  are shown in Figure 2(a). As evident, by comparing the  $^{13}\text{C}\{^1\text{H}\}$  NMR data of poly((9-ethyl-carbazol-6-yl) methyl methacrylate) and poly(methyl acrylate) with their copolymers, the resonances of carbonyl, methine,  $\alpha$ -methyl,  $-\text{OCH}_2$ , and  $-\text{OCH}_3$  are observed in the same region as in the homopolymers. Besides these resonances, signals that are not present in the homopolymer spectrum also appear, which provide information regarding how the monomer units are arranged along the copolymer chain.

The methylene, methoxy, and methine resonances were differentiated and assigned by comparing  $^{13}\text{C}\{^1\text{H}\}$  and DEPT experimental data. The resonances that were present in  $^{13}\text{C}\{^1\text{H}\}$  spectrum and absent in DEPT-135 were assigned to quaternary carbons,



**Figure 2** (a)  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of E/A copolymer ( $F_E = 0.55$ ). (b) DEPT-135 NMR spectrum of E/A copolymer ( $F_E = 0.55$ ) in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .

by the comparison of these spectra. By using DEPT-135 and 90 NMR data, the highly overlapped  $\beta$ -methylene and methine regions could be resolved as all  $\text{CH}_2$  resonances appear in the negative phase in DEPT-135 [Fig. 2(b)] and DEPT-90 shows only CH resonances.

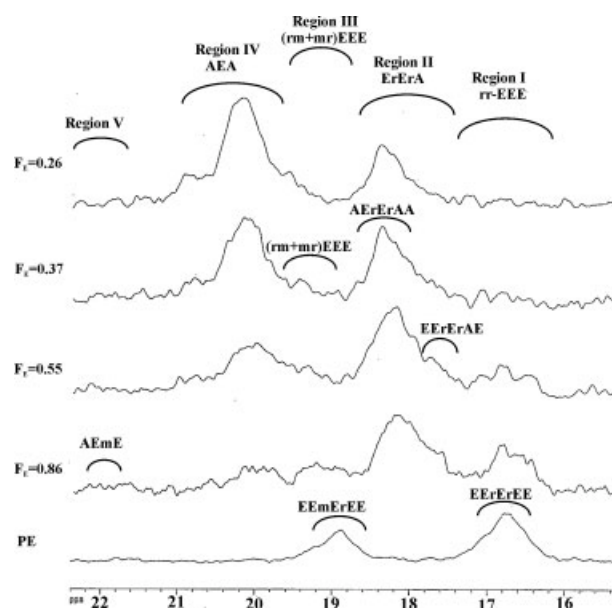
In Figure 2(a), the singlets centered at 14.91, 38.75, 67.93, and 52.61 ppm showed no compositional and configurational sensitivity and were assigned to the carbons of methyl ( $-\text{NCH}_2\text{CH}_3$  of E unit),  $-\text{NCH}_2$  (E unit),  $-\text{OCH}_2$  (E unit), and  $-\text{OCH}_3$  (A unit), respectively. The carbonyl carbon resonances of both E and A unit constituted the region around 175.0–179.0 ppm. The  $\alpha$ -methyl region of E unit shows compositional and configurational sensitivity and is assigned to the region around 16.0–21.0 ppm. The complex and overlapped region around 35.0–55.0 ppm were found to constitute the  $\beta$ -methylene (of both E and A unit), methine (A unit), and quater-

nary (E unit) carbon resonances. The region around 45.10 ppm was assigned to the quaternary carbon resonances of E unit. The region around 39.0–42.0 ppm was assigned to methine of A unit and its complexity was attributed to it being compositional sensitive. The  $\beta$ -methylene region of both E and A units were found to show both compositional and configurational sensitivity.

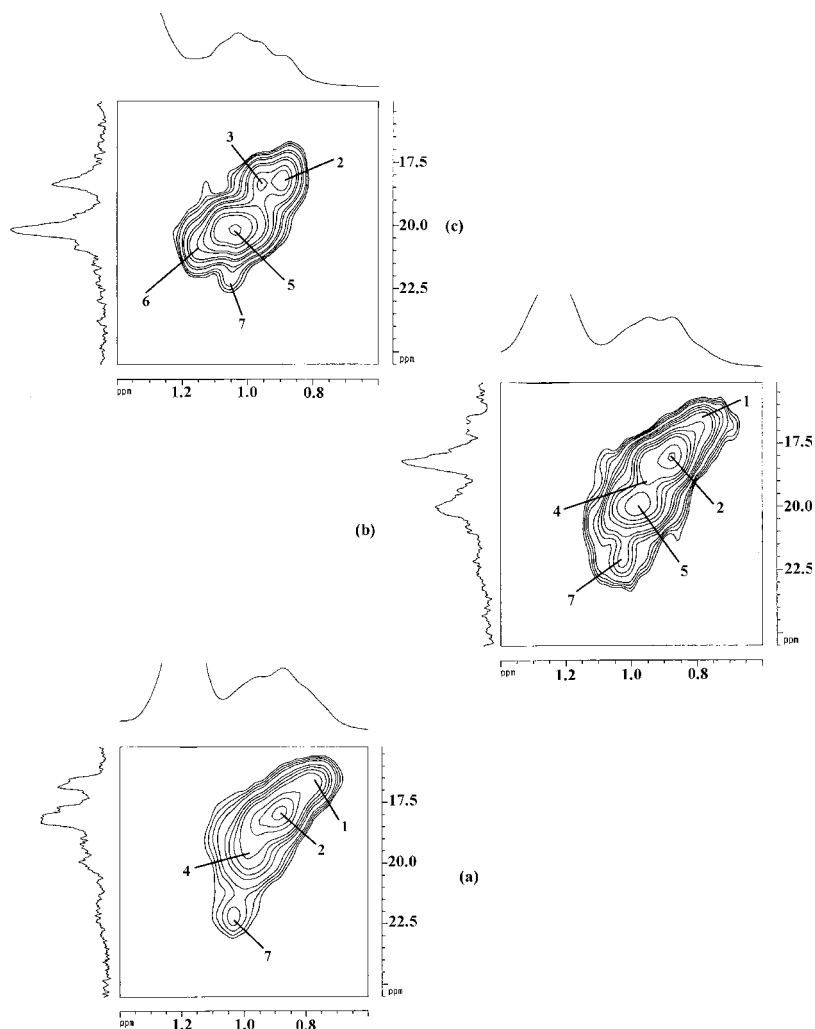
The carbon resonances in the region 108.0–144.0 ppm are due to the aromatic rings present in the E unit and they have been already assigned in the earlier publication for the homopolymer.<sup>37</sup>

### Spectral analysis of $\alpha$ -methyl region

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra for the  $\alpha$ -methyl region of various E/A copolymer compositions and poly((9-ethyl-carbazol-6-yl) methyl methacrylate) are compared in Figure 3. The  $\alpha$ -methyl region for the homopolymer showed splitting into two regions corresponding to rr and mr/rm triads from low to high chemical shifts at around 16.80 and 18.90 ppm, respectively, with very low mm content. Using this information, the assignments for the  $\alpha$ -methyl region of the copolymer were done, which was further confirmed by 2D HSQC experiments. The region around 16.90–17.10 ppm (Region I) was assigned to rr-EEE triad sequence, whose intensity decreases with decreasing E content. The region II was assigned to  $r(\text{EEA} + \text{AEE})$  triad sequence, which was found to show further compositional sensitivity up to pentad level. The regions III and IV at around 19.50 and



**Figure 3** Expanded  $\alpha$ -methyl carbon resonance patterns of PE and E/A copolymer with decreasing  $F_E$  in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .



**Figure 4** 2D HSQC NMR spectra of E/A copolymers showing the  $\alpha$ -methyl region in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ : (a)  $F_E = 0.86$ , (b)  $F_E = 0.55$ , and (c)  $F_E = 0.26$ .

20.20 ppm were assigned to (rm + mr) EEE and AEA triad sequence, respectively.

These tentative assignments were further confirmed by using 2D HSQC experiments. The crosspeak 1 centered at 16.81/0.79 ppm [Fig. 4(a,b)] is assigned to ErErE triad corresponding to region I in  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum. The crosspeaks 2 and 3 centered at 18.0/0.90 and 18.35/0.96 ppm were assigned to EErErAE and AErErAA pentads (Fig. 4), respectively, corresponding to region II in Figure 3. The region III corresponding to ErEmE triad sequence results in crosspeak 4 centered at 19.43/0.99 ppm [Fig. 4(a,b)].

The crosspeaks 5 and 6 centered at 20.29/1.04 and 20.80/1.15 ppm, respectively, are assigned to AEA triads [Fig. 4(c)] corresponding to region IV in Figure 3. The region V (Fig. 3) assigned to AEmE resulted in crosspeak 7 centered at 22.01/1.03 ppm (Fig. 4) in 2D HSQC NMR spectra.

Table II shows the spectral assignments of  $\alpha$ -methyl carbon resonances. Table III shows the theoretical and experimental E-centered triad fractions determined from  $\alpha$ -methyl carbon resonance patterns using reactivity ratios. First-order Markov statistical model was used to calculate the triad fractions.<sup>34</sup>

### Spectral analysis of methine region

The comparison of methine region of E/A copolymers and the homopolymer poly(methyl acrylate)<sup>29</sup> in  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra is shown in Figure 5. On the basis of variation in the E content, the methine carbon signals can be divided into three regions VIII, VII, and VI from 38.80–39.80, 39.8–40.6, and 41.20–41.80 ppm, which are assigned to EAE, AAE, and AAA triads, respectively. These assignments were done on the basis of change in the intensity of various peaks with the variation in the copolymer

**TABLE II**  
Spectral Assignments of  $\alpha$ -Methyl Carbon Resonances Based on  $^{13}\text{C}\{^1\text{H}\}$  NMR and 2D HSQC Spectra

Peak	Peak assignments	Peak position ( $^{13}\text{C}\{^1\text{H}\}$ NMR; ppm)	Peak position (2D HSQC; $^{13}\text{C}/^1\text{H}$ ; ppm)
1	ErErE	16.81	16.81/0.79
2	EErErAE	17.89	18.0/0.90
3	AErErAA	18.35	18.35/0.96
4	ErEmE	19.43	19.43/0.99
5	AEA	20.29	20.29/1.04
6	AEA	20.80	20.80/1.15
7	AEmE	22.01	22.01/1.03

composition and it is evident from Figure 5 that methine region shows only compositional sensitivity. Further, splitting within EAE and AAE triads was assigned to EEAE, AEAE, EAAEA, and EAAEE pentads centered at around 39.1/2.32 (8), 39.4/2.35 (9), 40.01/2.27 (10), and 40.41/2.35 (11) ppm, respectively (Fig. 6). Each of the regions is tentatively assigned to higher compositional sequences up to pentad level in  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum, which are further confirmed by 2D HSQC NMR studies. The peak centered at 41.30/2.27 ppm (12) was assigned to AAA triad sequence.

Figure 6 shows the 2D HSQC spectra for three different compositions of E/A copolymers and all the spectral assignments are collated in Table IV. On the basis of these assignments, it is evident that the methine proton lies in the narrow range of 2.30–2.40 ppm in the  $^1\text{H}$  NMR spectrum (Fig. 1). Table V lists the theoretical and experimental A-centered triad fractions determined from methine carbon resonance patterns showing a good agreement between these values.

The 2D TOCSY NMR studies are further used to study 1,3 bond order couplings between methine protons of the A unit in AAE- and EAE-centered triads with methylene protons of ArE, AmA, and AmE dyads in the copolymers. Figure 7 shows the 2D TOCSY spectra for three different compositions of the E/A copolymers.

Table IV enlists the various spectral assignments for the methine region on the basis of  $^{13}\text{C}\{^1\text{H}\}$  and 2D HSQC NMR studies.

**TABLE III**  
Theoretical and Experimental E-Centered Triad Fractions Determined from  $\alpha$ -Methyl Carbon Resonance Patterns

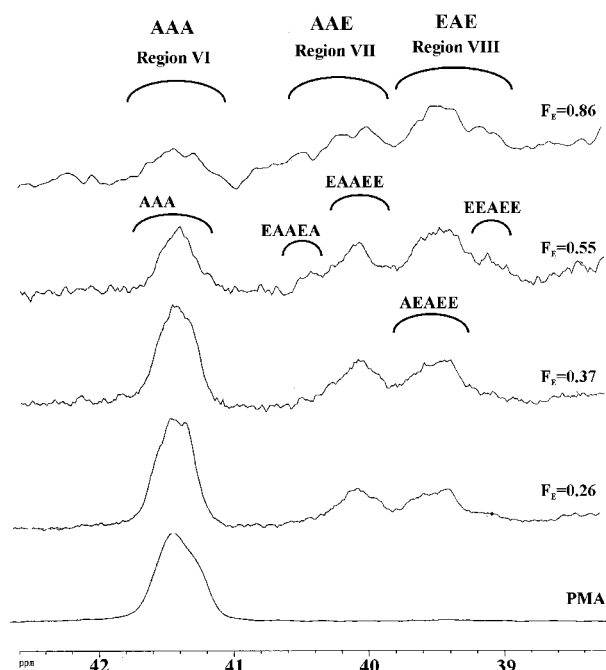
$F_M$	Triad fractions					
	Calculated			Experimental		
	EEE	EEA + AEE	AEA	EEE	EEA + AEE	AEA
0.86	0.68	0.29	0.03	0.65	0.30	0.04
0.55	0.29	0.50	0.21	0.30	0.48	0.23
0.37	0.11	0.45	0.44	0.11	0.46	0.43
0.26	0.05	0.35	0.60	0.03	0.35	0.58

### Spectral analysis of backbone methylene region

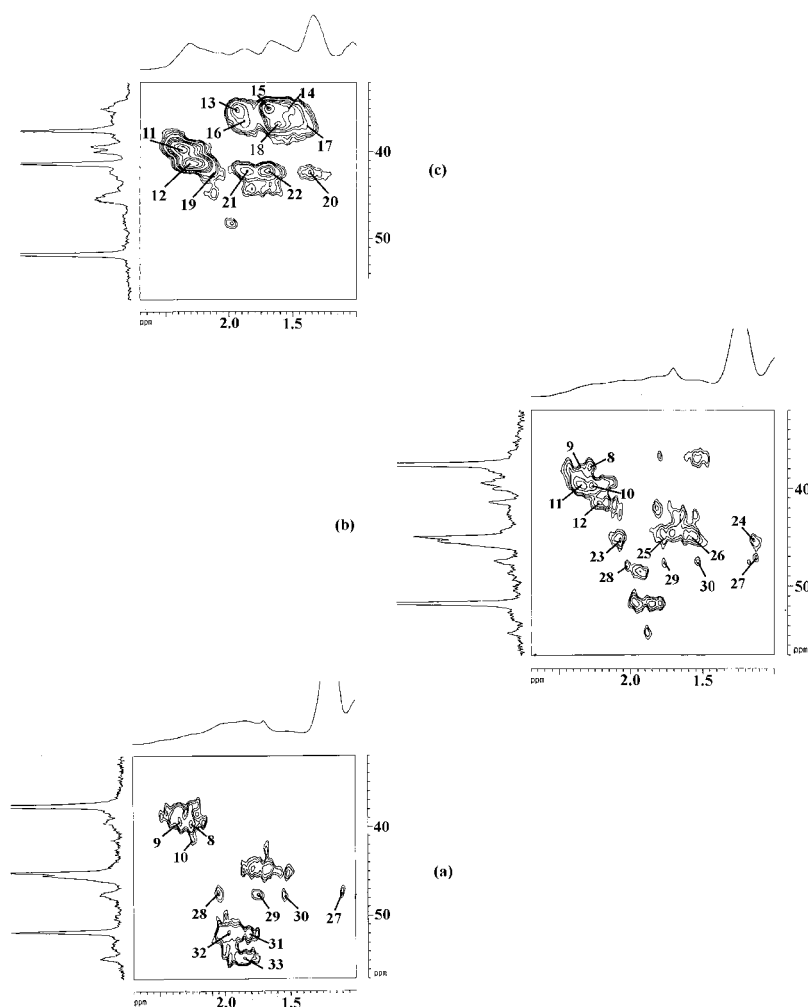
Figure 8 shows the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of backbone methylene region of various compositions of E/A copolymers with PE and PMA homopolymers. This region stretches from 35.0 to 55.0 ppm in the E/A copolymers. The methylene region can be divided into three envelopes extending from 35.0–36.70, 42.10–47.80, and 52.10–4.80 ppm, which was tentatively assigned to AA, AE + EA, and EE dyads, respectively. This region shows both configurational and compositional sensitivity and can be further assigned to higher tetrad sequences.

### AA dyad region: 2D HSQC and 2D TOCSY NMR studies

This region corresponds to AA dyad, which can be further assigned up to tetrad level. Figures 6 and 7



**Figure 5** DEPT-90 NMR spectra showing the methine carbon resonance patterns of PMA and E/A copolymers with increasing  $F_E$  in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .



**Figure 6** 2D HSQC NMR spectra of E/A copolymers showing the methine and backbone methylene region in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ : (a)  $F_E = 0.86$ , (b)  $F_E = 0.55$ , and (c)  $F_E = 0.26$ .

show 2D HSQC and 2D TOCSY spectra for various compositions of E/A copolymers. The crosspeaks 13 and 14 centered at  $35.0/1.95$  and  $35.0/1.50$  ppm [Fig. 6(c)] in 2D HSQC NMR spectra were assigned to AAmAA ( $H_a$ ) and AAmAA ( $H_b$ ) tetrads, respectively. This gives rise to a crosscorrelation peak II centered at  $1.50/1.95$  ppm in 2D TOCSY NMR spectrum arising due to the geminal couplings between the two nonequivalent protons  $H_a$  and  $H_b$  of  $m$  dyad [Fig. 7(c)], whereas the tetrad AArAA gives rise to a

single crosspeak 15 centered at  $35.0/1.70$  ppm in 2D HSQC NMR spectrum [Fig. 6(c)]. Similarly, increasing E content in E/A copolymer gives rise to crosspeaks 16 and 17 centered at  $36.70/1.90$  and  $39.70/1.40$  ppm corresponding to AAmAE ( $H_a$ ) and AAmAE ( $H_b$ ) tetrad, respectively, in 2D HSQC NMR spectra [Fig. 6(c)], which are absent in Figure 6(a,b). The geminal coupling between nonequivalent  $H_a$  and  $H_b$  protons of AAmAE tetrad results in a crosscorrelation peak I centered at  $1.40/1.90$  ppm in 2D

**TABLE IV**  
Spectral Assignments of Methine Carbon Resonances  $^{13}\text{C}\{^1\text{H}\}$  NMR and 2D HSQC Spectra

Peak	Peak assignments	Peak position ( $^{13}\text{C}\{^1\text{H}\}$ NMR; ppm)	Peak position (2D HSQC; $^{13}\text{C}/^1\text{H}$ ; ppm)
8	EEAEE	39.10	39.10/2.32
9	AEAEE	39.40	39.40/2.35
10	EAAEE	40.01	40.01/2.27
11	EAAEA	40.41	40.41/2.34
12	AAA	41.30	41.30/2.27

**TABLE V**  
**Theoretical and Experimental A-Centered Triad Fractions**  
**Determined from Methine Carbon Resonance Patterns**

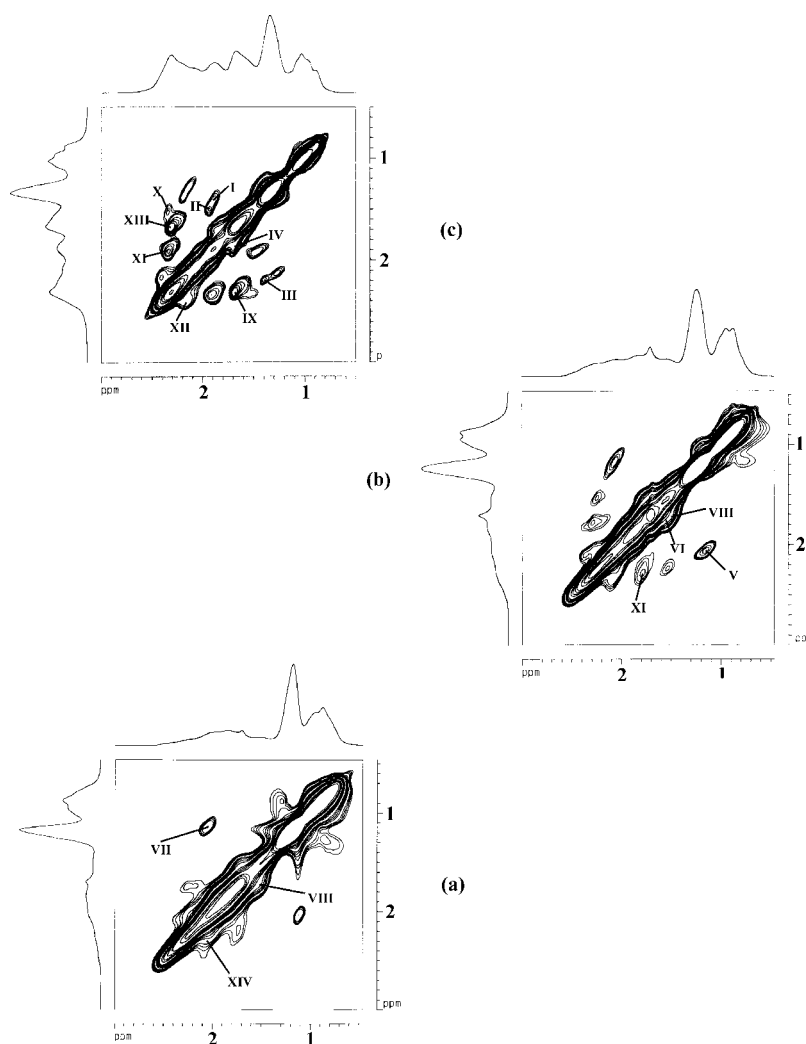
$F_E$	Triad fraction					
	Calculated			Experimental		
	AAA	EAA + AAE	EAE	AAA	EAA + AAE	EAE
0.14	0.02	0.25	0.73	0.03	0.25	0.75
0.45	0.14	0.48	0.35	0.14	0.47	0.33
0.63	0.38	0.47	0.15	0.39	0.47	0.17
0.74	0.53	0.39	0.07	0.53	0.40	0.08

TOCSY NMR spectrum [Fig. 7(c)]. The tetrad AArAE gives a single crosspeak 18 centered at 36.70/1.60 ppm in 2D HSQC NMR spectrum [Fig. 6(c)].

Coupling between methylene protons of AmA ( $H_b$ ) dyad and the methine proton of AAE triad resulted in crosspeak X centered at 1.49/2.35 ppm in 2D TOCSY NMR spectrum [Fig. 7(c)]

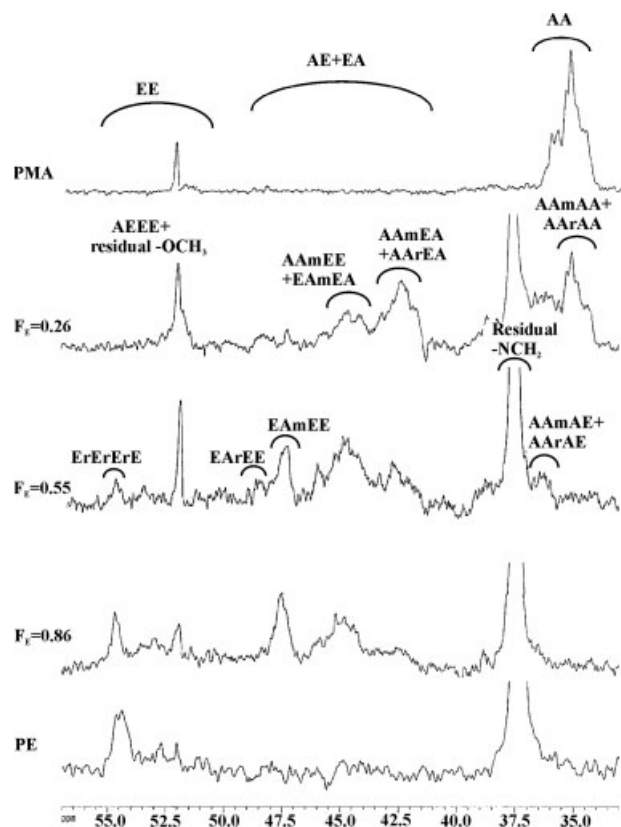
#### AE/EA dyad region: 2D HSQC and 2D TOCSY NMR studies

This region corresponds to AE/EA dyad, which can also be further assigned to tetrad level. The meso and racemic protons for AE/EA dyads are under different chemical environments because of which each of them shows two crosspeaks in 2D HSQC NMR spectra and a single crosscorrelation peak in 2D TOCSY NMR spectra. The crosspeaks 19 and 20 centered at 42.10/2.14 and 42.1/1.37 ppm were assigned to AAmEA ( $H_a$ ) and AAmEA ( $H_b$ ) tetrads, respectively, in 2D HSQC NMR spectrum [Fig. 6(c)]. The geminal coupling between the nonequivalent protons  $H_a$  and  $H_b$  of this tetrad results in a cross-correlation peak III centered at 1.38/2.14 ppm in 2D TOCSY NMR spectrum [Fig. 7(c)]. The nonequivalent racemic protons of AArEA tetrad also result in two crosspeaks 21 and 22 centered at 42.10/1.86 and 42.10/1.70 ppm in 2D HSQC NMR spectrum [Fig. 6(c)]. The geminal couplings between the non-



**Figure 7** 2D TOCSY NMR spectra of E/A copolymers in  $CDCl_3$  at  $25^\circ C$ : (a)  $F_E = 0.86$ , (b)  $F_E = 0.55$ , and (c)  $F_E = 0.26$ .





**Figure 8** Expanded backbone methylene carbon resonance patterns of PE, PMA, and E/A copolymers with decreasing  $F_E$  in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .

equivalent protons of this tetrad result in a crosscorrelation peak IV centered at 1.70/1.86 ppm in 2D TOCSY NMR spectrum [Fig. 7(c)].

The increase in E content in the E/A copolymer gives rise to crosspeaks 23 and 24 centered at 45.30/2.06 and 45.30/1.15 ppm, which correspond to AAmEE/EAmEA ( $H_a$ ) and AAmEE/EAmEA ( $H_b$ ) tetrad, respectively [Fig. 6(b)]. A single crosscorrelation peak V centered at 2.07/1.15 ppm arises because of the geminal couplings between the nonequivalent protons of AAmEE/EAmEA tetrads [Fig. 7(b)].

The racemic protons  $H_a$  and  $H_b$  of AArEE/EArEA tetrads being under different chemical environment gives two crosspeaks 25 and 26 centered at 45.10/1.76 and 45.10/1.55 ppm, respectively, in 2D HSQC NMR spectrum [Fig. 6(b)]. The geminal couplings between these protons give a crosscorrelation peak VI centered at 1.76/1.55 ppm in 2D TOCSY NMR spectrum [Fig. 7(b)].

Further increase in E content results in crosspeaks 27 and 28 centered at 47.50/1.15 and 47.50/2.05 ppm corresponding to EAmEE ( $H_a$ ) and EAmEE ( $H_b$ ) tetrads, respectively [Fig. 6(b,c)]. The geminal coupling of the nonequivalent protons of this tetrad results in a single cross-correlation peak VII centered at 1.15/2.05 ppm in 2D TOCSY NMR spectrum [Fig. 7(a)].

Also the racemic protons being under different chemical environment gives rise to crosspeaks 29 and 30 centered at 47.80/1.75 and 47.80/1.55 ppm corresponding to EArEE ( $H_a$ ) and EArEE ( $H_b$ ) tetrads, respectively. The geminal coupling between the  $H_a$  and  $H_b$  protons of EArEE tetrad gives rise to crosscorrelation peak VIII at 1.75/1.55 ppm [Fig. 7(a,b)] in the 2D TOCSY spectra.

The 1,3 bond order couplings between methine proton of A unit with methylene proton of E and A unit were further studied by 2D TOCSY NMR studies (Fig. 7). The crosscorrelation peaks IX and XI centered at 1.70/2.32 and 1.87/2.33 ppm were assigned to 1,3 bond order couplings between methine proton of EAEEA pentad with methylene proton of AArEA ( $H_b$ ) and AArEA ( $H_a$ ) tetrads, respectively. The crosscorrelation peaks XII and XIII centered at 2.15/2.3 and 2.06/2.33 ppm can be attributed to the 1,3 bond order couplings between AEAEE and AAE methine proton with EAmEE ( $H_a$ ) and AmE ( $H_a$ ) methylene proton, respectively.

#### EE dyad region: 2D HSQC and 2D TOCSY NMR studies

The increase in E content in E/A copolymers results in crosspeaks 31 and 32 centered at 52.10/1.84 and 52.10/1.99 ppm, which correspond to AEEE tetrads. The crosspeak 33 was assigned to ErErErE tetrad where the protons are under similar chemical environments and as they are equivalent, they do not

**TABLE VI**  
Spectral Assignments of Backbone Methylene Carbon Resonances in 2D HSQC Spectra

Peak	Peak assignment	Peak position 2D HSQC; $^{13}\text{C}/^1\text{H}$ ; ppm
13	AAmAA( $H_a$ )	35.0/1.95
14	AAmAA( $H_b$ )	35.0/1.50
15	AArAA	35.0/1.70
16	AAmAE ( $H_a$ )	36.70/1.90
17	AAmAE ( $H_b$ )	36.70/1.40
18	AArAE	36.70/1.60
19	AAmEA ( $H_a$ )	42.10/2.14
20	AAmEA ( $H_b$ )	42.10/1.37
21	AArEA ( $H_a$ )	42.10/1.86
22	AArEA ( $H_b$ )	42.10/1.70
23	AAmEE/EAmEA ( $H_a$ )	45.30/2.06
24	AAmEE/EAmEA ( $H_b$ )	45.30/1.15
25	AArEE/EArEA ( $H_a$ )	45.10/1.76
26	AArEE/EArEA ( $H_b$ )	45.10/1.55
27	EAmEE ( $H_a$ )	47.50/1.15
28	EAmEE ( $H_b$ )	47.50/2.05
29	EArEE ( $H_a$ )	47.80/1.75
30	EArEE ( $H_b$ )	47.80/1.55
31	AEEE	52.10/1.84
32	AEEE	52.10/1.99
33	ErErErE	54.80/1.80

TABLE VII  
Cross-Correlation Peak Assignments in 2D TOCSY Spectra for Couplings between Geminal and Vicinal Protons of E/A Copolymers

Peak	Coupled protons		Cross-correlation peak position ( $^1\text{H}/^1\text{H}$ ; ppm)
	Proton I	Proton II	
I	AAmAE ( $\text{H}_a$ )	AAmAE ( $\text{H}_b$ )	1.40/1.90
II	AAmAA ( $\text{H}_a$ )	AAmAA ( $\text{H}_b$ )	1.50/1.95
III	AAmEA ( $\text{H}_a$ )	AAmEA ( $\text{H}_b$ )	1.39/2.14
IV	AArEA ( $\text{H}_a$ )	AArEA ( $\text{H}_b$ )	1.70/1.86
V	EAmEA/AAmEE ( $\text{H}_a$ )	EAmEA/AAmEE ( $\text{H}_b$ )	2.07/1.15
VI	EArEA/AArEE ( $\text{H}_a$ )	EArEA/AArEE ( $\text{H}_b$ )	1.55/1.76
VII	EAmEE ( $\text{H}_a$ )	EAmEE ( $\text{H}_b$ )	1.15/2.05
VIII	EArEE ( $\text{H}_a$ )	EArEE ( $\text{H}_b$ )	1.75/1.55
IX	AArEA ( $\text{H}_b$ )	EAAEA	1.70/2.32
X	AmA ( $\text{H}_b$ )	AAE	1.49/2.35
XI	AArEA ( $\text{H}_a$ )	EAAEA	1.87/2.33
XII	EAmEE ( $\text{H}_a$ )	AEAAA	2.15/2.30
XIII	AmE ( $\text{H}_a$ )	AAE	2.06/2.33

show any cross-correlation peak in 2D TOCSY NMR spectra.

On the basis of these studies, the complete spectral assignment of the  $^1\text{H}$  NMR spectrum was done as shown in Figure 1.

Tables VI and VII lists the various peak assignment done using 2D HSQC and 2D TOCSY NMR spectra for three different compositions of E/A copolymers.

Table VIII lists and compares the experimental and calculated dyad fractions for the methylene carbon resonance patterns for different compositions of E/A copolymers by taking reactivity ratios as  $r_A = 0.69$  and  $r_E = 1.16$ .

### Spectral analysis of the carbonyl region

HMBC NMR studies can be used to study long-range couplings between carbonyl carbon with  $\alpha\text{-CH}_3$  and  $\beta\text{-methylene}$  protons. Figure 10 shows expanded  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the carbonyl region for various compositions of E/A copolymers and also the homopolymers.

Only E-centered triads are observed when carbonyl carbon couples with  $\alpha\text{-CH}_3$  proton. Figure 9 shows

the 2D HMBC spectra of E/A copolymers at different compositions. The crosspeaks 34 (175.80/1.15 ppm) and 35 (175.90/1.04 ppm) were assigned to the couplings between carbonyl carbon of AEA triad with

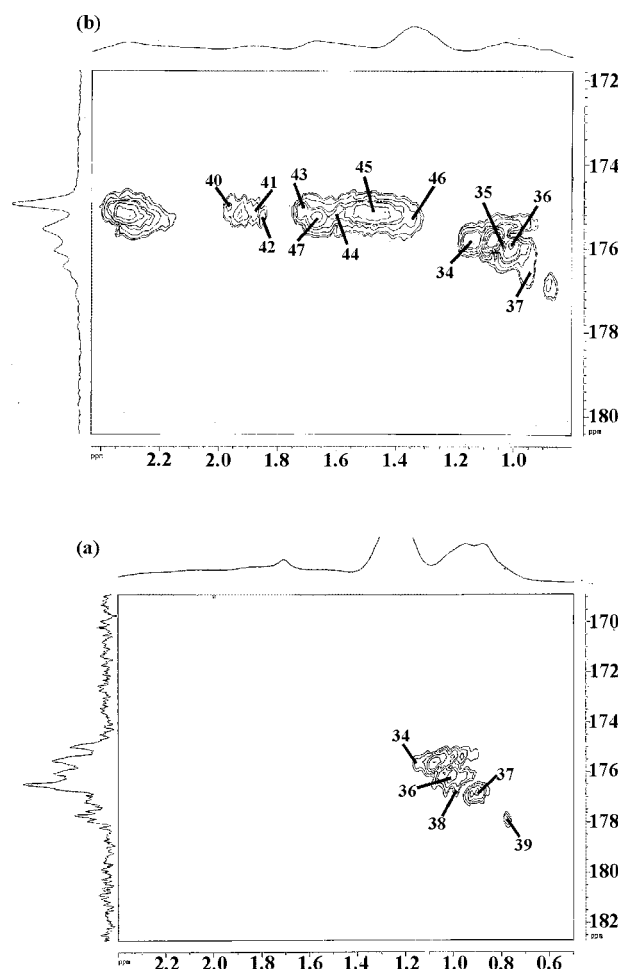
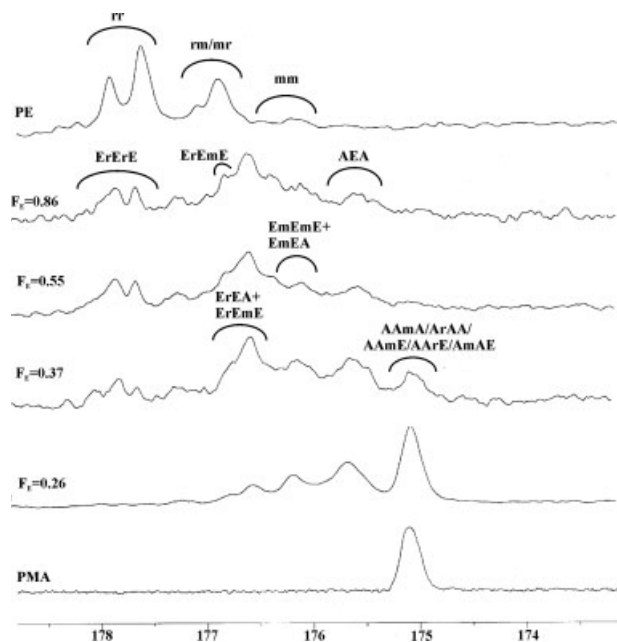


Figure 9 2D HMBC NMR spectra of E/A copolymers in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ : (a)  $F_E = 0.55$  and (b)  $F_E = 0.26$ .

TABLE VIII  
Experimental and Calculated Dyad Fractions Determined from Methylene Carbon Resonance Patterns

$F_E$	Dyad fractions					
	Calculated			Observed		
	EE	EA + AE	AA	EE	EA + AE	AA
0.86	0.69	0.29	0.02	0.67	0.30	0.02
0.55	0.31	0.52	0.18	0.30	0.52	0.18
0.37	0.12	0.49	0.39	0.15	0.47	0.40
0.26	0.06	0.40	0.54	0.08	0.40	0.54



**Figure 10** Expanded carbonyl region of PMA, PE, and E/A copolymers with increasing  $F_E$  in  $\text{CDCl}_3$  at 25°C.

$\alpha$ -CH<sub>3</sub> proton of AEA triad, respectively. The crosspeaks 36 (176.0/1.03 ppm), 37 (176.56/0.96 ppm), 38 (176.62/0.99 ppm), and 39 (177.80/0.78 ppm) were assigned to couplings between carbonyl carbon with  $\alpha$ -methyl proton of AEmE, ErEA, ErEmE, and ErErE triads, respectively. The couplings between carbonyl carbon and  $\beta$ -methylene protons give rise to A-centered triads. Crosspeaks 40 (175.15/1.95 ppm), 41 (175.21/1.89 ppm), 42 (175.30/1.86 ppm), and 43 (175.11/1.70 ppm) were assigned to carbonyl carbon couplings of AAmA, AmAE, AArE, and ArAA triads with  $\beta$ -methylene protons of AAmAA

(H<sub>a</sub>), AAmAE, AArEA (H<sub>a</sub>), and AArAA tetrads, respectively.

The crosspeaks 44 (175.22/1.60 ppm), 45 (175.20/1.50 ppm), 46 (175.39/1.37 ppm), and 47 (175.30/1.69 ppm) were assigned to the couplings between carbonyl carbon of AArA, AmAA, AAmE, and AArE triads with  $\beta$ -methylene of AArAE, AAmAA (H<sub>b</sub>), AAmEA, and AArMA (H<sub>a</sub>) tetrads, respectively.

Figure 10 shows the carbonyl carbon region for the E/A copolymers, which was completely assigned on the basis of assignments done in 2D HMBC NMR studies. Table IX lists the various carbon resonances of carbonyl region done on the basis of  $^{13}\text{C}\{^1\text{H}\}$  and 2D HMBC NMR studies.

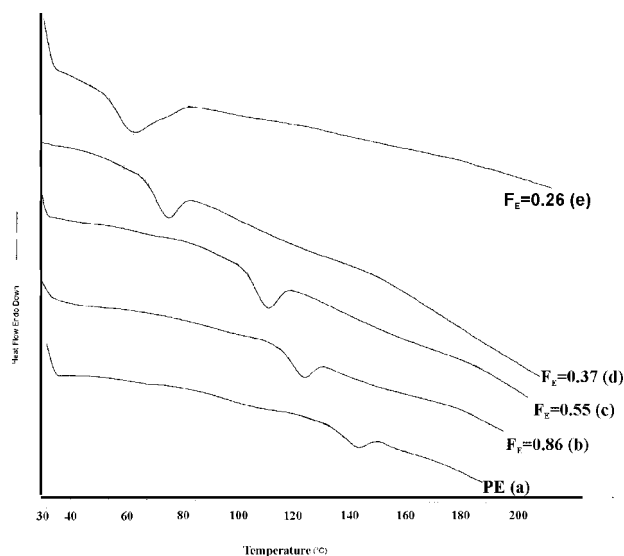
### Thermal studies

Figure 11 shows the DSC curves for various compositions of E/A copolymers and PE. The glass transition temperatures ( $T_g$ ) of these polymers<sup>46</sup> were determined using DSC. The  $T_g$  values lie in the range of 62–123°C, whereas that of PE was found to be 141°C (Table I). With decreasing E content, the  $T_g$  of the E/A copolymers decreases. This decrease can be explained on the basis of flexibility provided to the polymeric chain with decreasing E content. Carbazole moiety provides rigidity to the polymeric chain and as the flexible groups such as A gets incorporated in the main chain, its flexibility increases preventing its close packing, which in turn results in lowering of  $T_g$  due to the increase of free volume in the polymeric chain.

As more of A unit gets incorporated in the main chain, further decrease in  $T_g$  is observed as a result of greater separation of the bulky carbazole side groups. This lowering of  $T_g$  is beneficial as it results

**TABLE IX**  
Spectral Assignments of Carbonyl Carbon Resonance in 2D HMBC Spectra

Peak	Coupled carbonyl carbon with $\alpha$ -CH <sub>3</sub> and methylene		Peak position (2D HMBC; $^{13}\text{C}/^1\text{H}$ ; ppm)
	Carbon peak assignment	Proton peak assignment	
34	CO of AEA	$\alpha$ -CH <sub>3</sub> of AEA	175.80/1.15
35	CO of AEA	$\alpha$ -CH <sub>3</sub> of AEA	175.90/1.04
36	CO of AEmE	$\alpha$ -CH <sub>3</sub> of AEmE	176.0/1.03
37	CO of ErEA	$\alpha$ -CH <sub>3</sub> of ErEA	176.56/0.96
38	CO of ErEmE	$\alpha$ -CH <sub>3</sub> of ErEmE	176.62/0.99
39	CO of ErErE	$\alpha$ -CH <sub>3</sub> of ErErE	177.80/0.78
40	CO of AAmA	CH <sub>2</sub> of AAmAA (H <sub>a</sub> )	175.15/1.95
41	CO of AmAE	CH <sub>2</sub> of AAmAE	175.21/1.89
42	CO of AArE	CH <sub>2</sub> of AArEA (H <sub>a</sub> )	175.30/1.86
43	CO of ArAA	CH <sub>2</sub> of AArAA	175.11/1.70
44	CO of AArA/ArAE	CH <sub>2</sub> of AArAE	175.22/1.60
45	CO of AmAA	CH <sub>2</sub> of AAmAA (H <sub>b</sub> )	175.20/1.50
46	CO of AAmE	CH <sub>2</sub> of AAmEA	175.39/1.37
47	CO of AArE	CH <sub>2</sub> of AArEA (H <sub>a</sub> )	175.30/1.69



**Figure 11** DSC curves of (a) PE (b)  $F_E = 0.86$ , (c)  $F_E = 0.55$ , (d)  $F_E = 0.37$ , and (e)  $F_E = 0.26$ .

in orientation enhancement effect,<sup>18</sup> which in turn is beneficial to the photorefractive effect.<sup>47</sup>

## CONCLUSIONS

The reactivity ratios for different compositions of E/A copolymers obtained by KT and RREVM methods are  $r_E = 1.16 \pm 0.02$ ,  $r_A = 0.69 \pm 0.01$  and  $r_E = 1.18$ ,  $r_A = 0.68$ , respectively. The microstructure of E/A copolymers were analyzed by 1D ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , DEPT-45, 90, 135) and 2D (HSQC, TOCSY, HMBC) NMR spectroscopy. The complex and overlapped  $\beta$ -methylene and methine region has been resolved using 2D HSQC and 2D TOCSY NMR studies. Complete spectral assignments for carbonyl region were performed using 2D HMBC studies.  $T_g$  for different compositions of E/A copolymers was determined using DSC, showing a decrease in  $T_g$  with decreasing E content due to increasing flexibility of the polymeric chain.

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