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Determination of triad sequence distribution of copolymers of maleic anhydride and its derivates with donor monomers by ^{13}C n.m.r. spectroscopy

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Abstract

Several alternating and semi-alternating copolymers were analysed by quaternary ^{13}C n.m.r. spectroscopy. The aromatic ‘next to polymer chain’ carbon (C7) of donor monomer (1) units is sensitive to the unit 1-centred triad sequence distribution. The acceptor monomer is referred to as 0. The chemical shifts of the non-alternating (111), semi-alternating (011 + 110) and alternating (010) triad sub-peaks were assigned in ppm in Table 1. © 1998 Elsevier Science Ltd. All rights reserved.

Table 1

Copolymer of monomer with monomer 1	111	011	(+)	110	010 Triad sequence
Maleic anhydride with styrene	147.5	145			
		146		141.5	
				140.5	136.5
Maleic anhydride with *trans*-stilbene				138	132
Maleic anhydride with α-methylstyrene	152	148			
		148 (145.5)		142.5	139
Maleic anhydride with allylbenzene	Not sensitive to triad sequence distribution and appears at 142–139 ppm				
Citraconic anhydride with styrene	147.5	145			
		147		143.5	137.5
Bromomaleic anhydride with styrene	147.5	145	141.5	140	136.5
Dichloromaleic anhydride with styrene	147.5	145	141.5	138	133
Maleimide with styrene	147.5	145		140.5	136.5

Keywords: Triad sequence distribution; Quatenary aromatic ‘next to polymer chain’ carbon; ^{13}C n.m.r. spectroscopy

1. Introduction

There are two possibilities on the origin of chemical shift splitting in styrene-containing polymers; they are stereochemical configurations and copolymer sequences. In the homopolymer of styrene, the carbon which has the special ‘status’ of a quaternary carbon and the special ‘position’ as a ‘next to polymer chain’ aromatic carbon in poly(styrene) was reported to split into three distinct groups, which were assigned to isotactic (mm), heterotactic (mr) and syndiotactic (rr) by Inoue et al. [1] and mentioned by Bovey [2]. For the styrene-containing copolymers, the effect of copolymer sequences besides that of stereochemical configurations are considered. The ‘next to polymer chain’ aromatic quaternary carbon of the copolymer of maleic anhydride (MA or 0) and styrene (ST or 1) was also indicated for ST(1)-centred triad sequence distribution [3,4]. This carbon was further used for determination of the triad sequence distribution in copolymers of ST(1) and citraconic (α-methyl maleic) anhydride (CA or 0) [5,6]. The triad sequence distribution of the copolymer of styrene (ST or 1) and sulfur dioxide (SO_2 or 0) was also reported

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in the ^{13}C n.m.r. spectrum of this quaternary aromatic carbon of ST(1) units [7]. In copolymers of ST(1) and acrylonitrile (ACN or 0), the spectra of the quaternary 'next to polymer chain' aromatic carbon of ST(1) units and nitrile carbon of ACN(0) units were assigned the chemical shifts for the three ST(1) centred triad sub-peaks and the three ACN(0)-centred triad sub-peaks, respectively, by Sandner et al. [8]. The chemical shift assignments were confirmed by Pichot and Pham [9]. The spectra of those aromatic and nitrile quaternary 'next to polymer chain' carbons were further used for quantitative determination of the triad sequence distribution by Hill et al. [10,11]. Barron et al. [12] were successful in assigning the chemical shifts for the three ST(1)-centred triads (111, 011 + 110, 010) observed by the chain methylene carbon of the ST(1) units in MA(0)-ST(1) copolymers as a consequence of the subtracted DEPT ^{13}C n.m.r. sub-spectra of the methylene (-CH$_2$-) carbon. The quantitative determination of ST(1)-centred triad sequence distribution following this method [12] was further elaborated by Brown and Fujimori [13], and Ha et al. [14]. Similar determination of *p*-substituted styrene (1) centred triad distribution was reported by Brown et al. for copolymers of maleic anhydride (MA or 0) with *p*-chlorostyrene [15,16], and copolymers of MA (0) with *p*-methoxystyrene [15,17].

This study reports a qualitative determination of the aromatic donor (1) unit-centred triad sequence distribution observed by the quaternary aromatic 'next to polymer chain' carbon in the copolymers of maleic anhydride (MA or 0) with styrene (ST or 1), MA with *trans*-stilbene (STI or 1), MA with α-methylstyrene (MST or 1), and in the copolymers of ST(1) with citraconic anhydride (CA or 0), ST with bromomaleic anhydride (BMA or 0), ST with dichloromaleic anhydride (DCMA or 0) and ST with maleimide (MI or 0).

2. Experimental

N,N′-azobisisobutyronitrile (AIBN, Riedel de Haen) was recrystallised from dried methanol. Maleic anhydride (MA, Ajax) was recrystallised from dried benzene. Citraconic anhydride (CA, Fluka), assay 99%; bromomaleic anhydride (BMA, Aldrich), 97%; dichloromaleic anhydride (DCMA, Aldrich), 99% and maleimide (MI, Aldrich), 99% were used as supplied. Styrene (ST, Ajax) 99.5%; *trans*-stilbene (STI, Fluka); α-methylstyrene (MST, Aldrich) and allylbenzene (AB) with purities of $>$ 97% were used as supplied. Solvents were distilled and dried using regular methods.

All copolymerisations were carried out in the regular way at 50°C or at 60°C in solvents. Required amounts of the comonomers, AIBN and solvent were filled in an ampoule. The ampoule was sealed under vacuum after repeated freeze–degas–thaw procedures. The copolymerisation was carried out in an oil thermostat. The ampoule was shaken well throughout the reaction. The conversion was kept less than 10% in general, and less than 5% when the monomer mole fraction of acceptor monomer (f_0) in the feed was smaller than 0.2 or larger than 0.8. The copolymers prepared in CCl$_4$, CHCl$_3$ or methyl ethyl ketone (MEK) were precipitated and reprecipitated from acetone solution in petroleum spirit. The copolymers prepared in N,N-dimethylformamide (DMF) were precipitated and reprecipitated in dried diethyl ether. All copolymers were then dried in a desiccator under vacuum at room temperature for about 20 h.

Apart from MA-STI copolymer and poly(ST), which were solved in CDCl$_3$, and MI-ST copolymer, which was solved in DMSO-d$_6$, all other copolymers were solved in acetone-d$_6$ with a concentration of 0.08–0.23 w/w (g copolymer/g deuterated solvent) in precision NMR tubes. A Brucker AC-300 NMR spectrometer was used for running ^{13}C n.m.r. experiments at 75.46 MHz with a broad band ^{1}H dual 5 mm probe, over 15–20 h periods at 308 K (35°C). The ^{1}H decoupler- and ^{13}C-$\pi/2$ pulse time were set at 9.9 and 4.2 μs, respectively. The recycle delay (T_1) was set to 4, 2 and 5 s for ^{13}C, DEPT ^{13}C and quaternary ^{13}C n.m.r. acquisitions, respectively. The J modulation time (Δ) was set to 0.0035 s, equivalent to $J = 142.86$ Hz ($\Delta = 0.5/J$ for the optimum polarisation and/or sensitivity) for the DEPT experiments, and 0.00345 s ($J = 144.93$ Hz) for the quaternary experiments. The DEPT FID-acquired spectra were exponential fourier transformed and generated by linear combination for the DEPT sub-spectra [18].

3. Results and discussion

Maleic anhydride (MA or 0) is a strong electron acceptor and does not homopolymerise under ordinary conditions [19], but copolymerises with styrene (ST or 1) to form the alternating MA(0)-ST(1) copolymers. This evidence serves us in the assignments of n.m.r. peaks; the (010) peak is much more intense than the other two peaks. The quaternary aromatic 'next to polymer chain' carbon (C7) [3] and the methylene (-CH$_2$-) 'polymer chain' carbon (C1) [12] of ST(1) units were reported to be sensitive to the ST(1)-centred triad sequence distribution observed by the ^{13}C n.m.r. spectra. Fig. 1 shows a typical ^{13}C n.m.r. spectrum of an alternating MA-ST copolymer where the peaks were assigned the chemical shifts according to Butler et al. [20]. Because MA and ST alternate strongly, the non-alternating (111 or ST-ST-ST) sequences are shown only when the MA mole fraction in feed is very small ($f_0 = 0.01$–0.05) (Fig. 1). When $f_0 = 0.90$, the fully alternating copolymer was formed, i.e. only the resonance of the alternating (010) triad sub-peak appears in the spectra of C7 and C1. The resonance of C7 carbon appears in a shorter range [$147.5 - 136.5 = 11$(ppm)] than the range for C1 carbon [$47 - 33 = 14$(ppm)]. In the spectra of C7 carbon, the non-alternating (111) and semi-alternating (011 + 110) triad sub-peaks overlap by around 1 ppm at the most when the

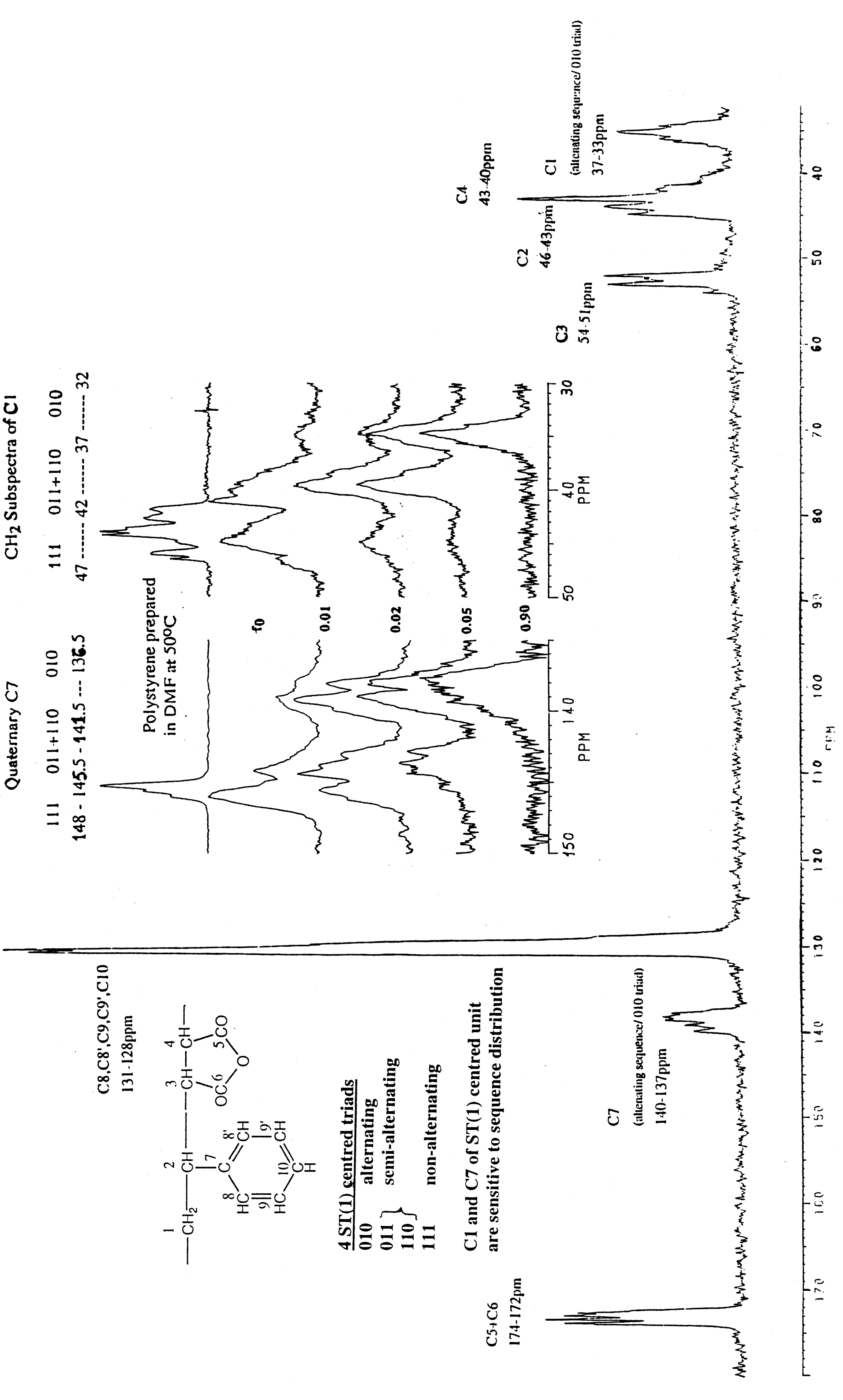

Fig. 1. Typical ^{13}C n.m.r. spectrum of an alternating MA(0)-ST(1) copolymer perpared with [MA + ST] = 4.000 mol/l, [AIBN] = 0.0305 mol/l in DMF at 50°C and the MA mole fraction in feed $f_0 = 0.5$. The quaternary aromatic 'next to polymer chain' carbon C7 and the methylene (-CH$_2$) 'polymer chain carbon' C1 of styrene (ST or 1) units are sensitive to the ST(1)-centred triad sequence distribution.

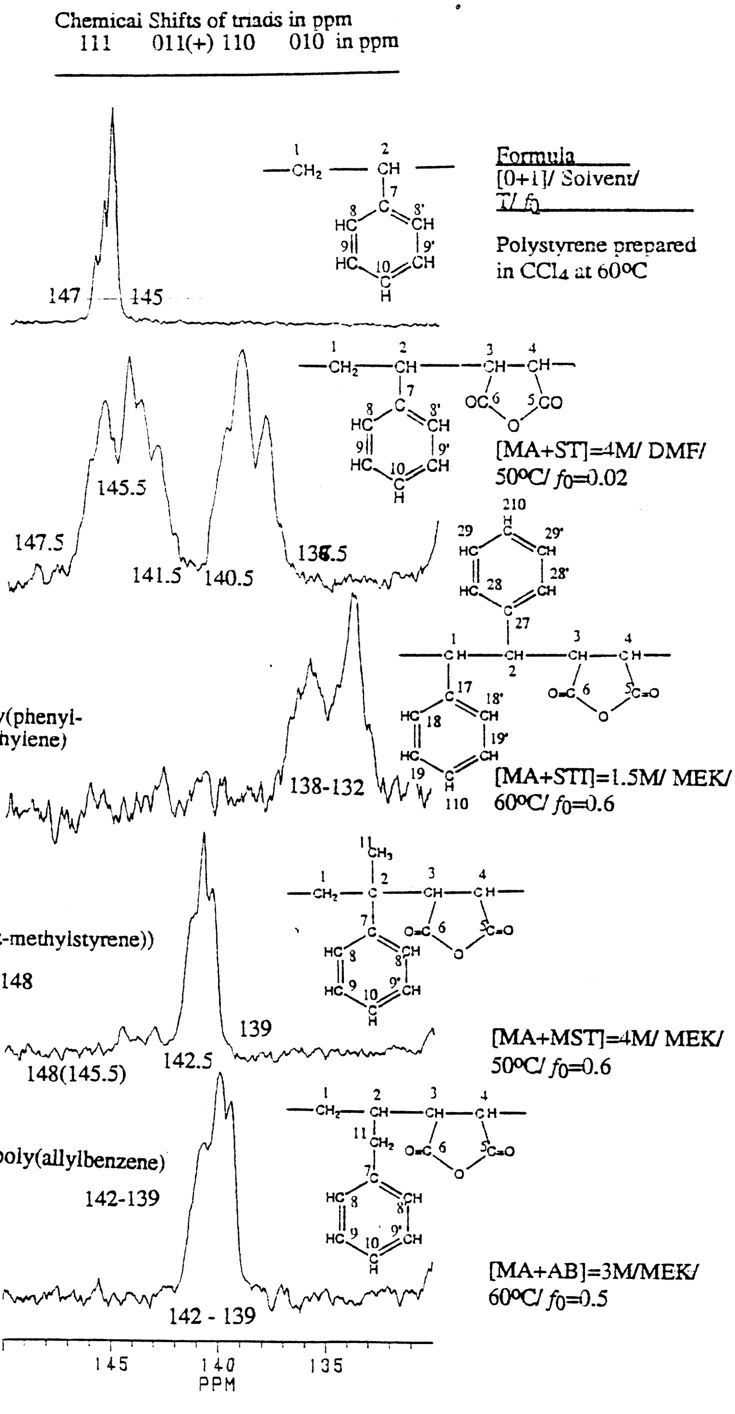

Fig. 2. Quaternary ^{13}C n.m.r. spectra of the aromatic ‘next to polymer chain’ carbon C7 of aromatic donor (1) units in MA(0)-ST(1), MA(0)-STI(1), MA(0)-MST(1) and MA(0)-AB(1) copolymers.

MA mole fraction in the feed is very small ($f_0 = 0.01–0.02$); while they quite clearly separated in the C1 spectra. The qualitative determination or the chemical shift assignments for the three ST(1)-centred triad sub-peaks in the spectra of C7 carbon is confirmed by the consistence of the appearances of the three triad sub-peaks from both spectra of C1 and C7.

Fig. 2 shows the quaternary ^{13}C n.m.r. spectra of the aromatic quaternary C7 carbon of the aromatic donor (1) units in the MA(0)- ST(1) copolymer, the MA(0)-*trans*-stilbene (STI or 1) copolymer, the MA(0)-α-methylstyrene (MST or 1) copolymer and the MA(0)- allylbenzene (AB or 1) copolymer. The spectrum of the C7 carbon of poly(styrene) is also shown to compare the chemical shift of the non-alternating (111) ST triad. In the MA-ST copolymer, the sub-peak of the alternating (010) triad appears separately upfield at 140.5–136.5 ppm, while the non-alternating (111 or ST sequence) triad and the semi-alternating (011 + 110)

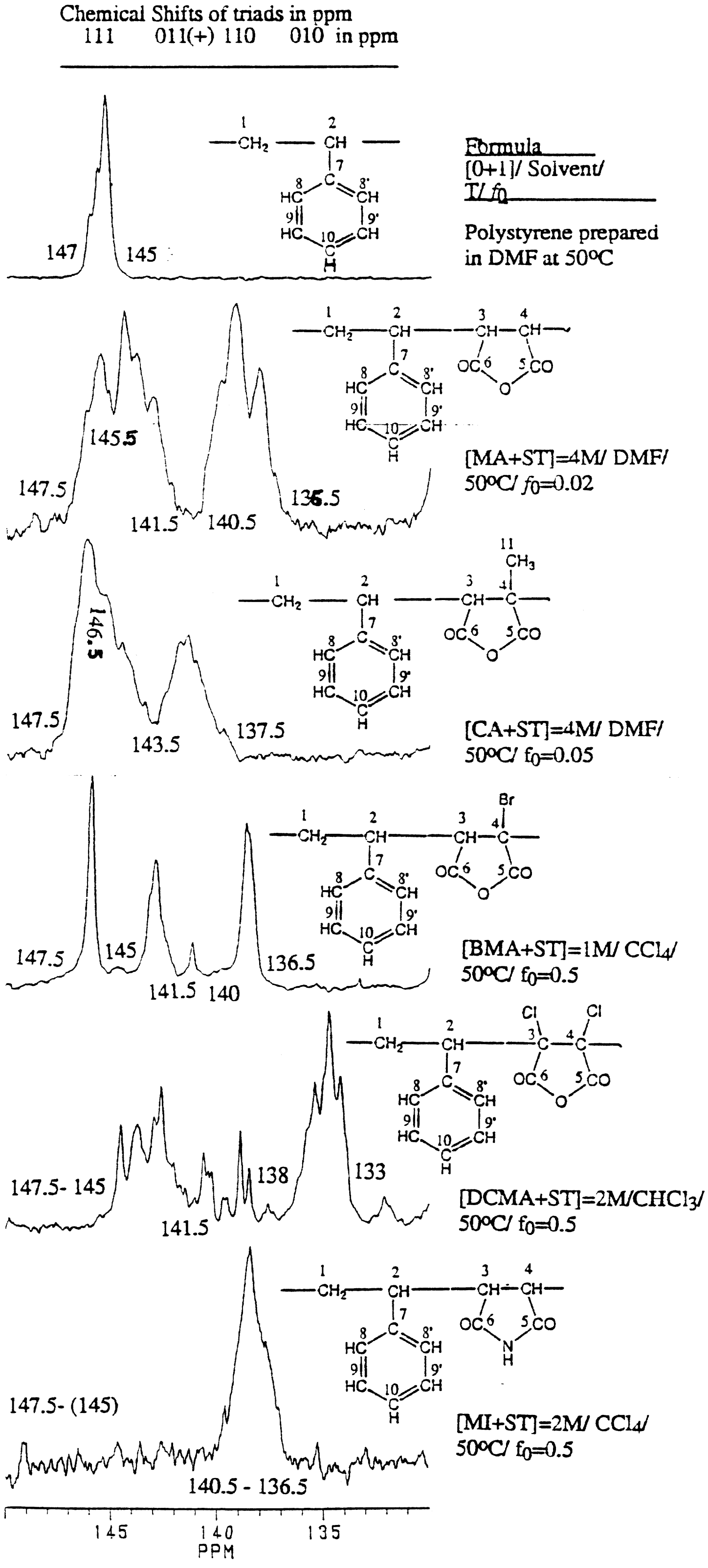

Fig. 3. Quaternary ^{13}C n.m.r. spectra of the aromatic ‘next to polymer chain’ carbon C7 of ST(1) units in MA(0)-ST(1), CA(0)-ST(1), BMA(0)-ST(1), DCMA(0)-ST(1) and MI(0)-ST(1) copolymers.

triads overlap each other by around 1 ppm in the range 146–145 ppm.

The MA-STI copolymer, which is completely alternating [21,22], gives only the sub-peak for the alternating (010) triad at 138–132 ppm, which splits at 135 ppm due to *trans/cis* linkage configurations at the cyclic MA units. The poly(phenylmethylene) or non-alternating (111) triad would be expected to resonate downfield at around 160–145 ppm.

The peak of the alternating (010) triads of MA(0)-MST(1) copolymer appears at 142.5–139 ppm, while the C7 resonance of poly(α-methylstyrene) appears at around 152–148 ppm [23], and that of the semi-alternating (011 + 110) triad would be expected at around (148)145.5–142.5 ppm.

The resonance of the C7 of poly(allylbenzene) [23] and that of the MA-AB copolymer appear in a similar chemical shift area of 142–139 ppm. This means that the triad sub-peaks appear overlapping each other because of the quaternary carbon C7 of allylbenzene (AB or 1) units in the poly(allylbenzene), and that in the MA-AB copolymer is not the 'next to polymer chain' carbon as in the other three copolymers mentioned above.

Fig. 3 shows the spectra of the C7 aromatic quaternary 'next to polymer chain' carbon of the ST(1) units in the MA(0)-ST(1) copolymer, the CA(0)-ST(1) copolymer, BMA(0)-ST(1) copolymer, DCMA(0)-ST(1) copolymer and MI(0)-ST(1) copolymer. The chemical shifts for their triad sub-peaks are also indicated in the figure.

Citraconic (α-methylmaleic) anhydride (CA) can be considered as a weaker electron acceptor monomer unit compared to maleic anhydride (MA) due to its bulky CH_3 group. Since the deshielding effect on the resonance of the C7 carbon by the CA units is less than that by the MA unit, the C7 peak of CA-ST copolymer shrinks downfield, resulting in a large overlap between the triad sub-peaks. The extent of the overlap is estimated to be up to 2 ppm at 147–145 ppm between the non-alternating (111) triad sub-peak and the semi-alternating (011 + 110) triad sub-peak.

Because of the high negativities of halogens, halogen derivates of MA can be considered as stronger electron acceptor monomer units when compared to MA. The existence of the α-bromine atom in the bromomaleic anhydride (BMA) units sharpens the triad sub-peaks of C7 carbon so that the four sub-peaks corresponding to the four kinds of triads, 111, 011, 110 and 010, are clearly observed.

The two chlorine atoms of dichloromaleic anhydride (DCMA) units may strengthen the deshielding effect on the resonance of C7 carbon so that the C7 spectrum of DCMA-ST copolymer spreads more upfield, as compared to the spectrum of the C7 carbon in the MA-ST copolymers. The four triad (111, 011, 110 and 010) sub-peaks appear in multiplets which may correspond to the conformation of the copolymer chain.

The spectrum of the C7 carbon of the maleimide-styrene (MI-ST) copolymers seems to appear in a very similar manner as for the spectrum of the C7 carbon of the MA-ST copolymers, in which the alternating (010) triad sub-peak appears at around 140.5–136.5 ppm.

In general, by comparing the chemical shifts of the homopolymer, poly(styrene) in this case, which has only non-alternating (111) triads, and the chemical shifts of the carbon at a similar position in the copolymer, a clear assignment for triad sub-peaks could be made.

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