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Determination of the Reactivity Ratios, Sequence Distribution and Stereoregularity of Butyl Acrylate–Methyl Methacrylate Copolymers by Means of Proton and Carbon-13 NMR

A. M. Aerdtst† and A. L. German*

Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

G. P. M. van der Velden

DSM Research BV, P.O. Box 18, 6160 MD Geleen, The Netherlands

The 400 MHz proton NMR spectra of butyl acrylate (BA)–methyl methacrylate (MMA) copolymers prepared by free radical polymerization in solution at 323 K were used for the determination of the reactivity ratios. The reactivity ratios r_M and r_B calculated by the error-in-variables method are 2.279 and 0.395, respectively. The methoxy region of the MMA proton signal resonance was found to be sensitive for MMA-centred sequences and a new assignment is proposed. The coisotacticity parameter σ_{BM} was calculated using a non-linear least-squares procedure with relative error estimation based on the new assignment and was found to be 0.39. The carbon-13 NMR spectra of the BA–MMA copolymers, in particular the carbonyl signal resonances, are sensitive for MMA- and BA-centred configurational sequences. The same assignment is used as for the ethyl acrylate–methyl methacrylate copolymer.

KEY WORDS NMR ^1H NMR ^{13}C NMR Butyl acrylate Methyl methacrylate Copolymers

INTRODUCTION

Acrylate and methacrylate copolymers and also multi-(meth)acrylate polymers are extensively used as coating membranes, binder latices, adhesives and sealants, especially owing to the great variety of glass-transition temperatures (T_g). Comparing, e.g., the system ethyl acrylate–methyl methacrylate (EA–MMA) with the system butyl acrylate–methyl methacrylate (BA–MMA), it is well known, that the T_g of the latter system is substantially lower than that of the former, which leads to a more flexible system in the second case.¹ Sometimes, the above-mentioned homo-, co- and multi-polymers contain copolymerized species for more polar comonomers such as acrylic acid (AA) or methacrylic acid (MAA).²

In binder latices, especially the system BA–MMA is used in order to bind the filler materials such as TiO_2 .¹ However, no extensive study is available in which the microstructure was studied using ^1H or ^{13}C NMR spectroscopy. Recently an NMR review was published,³ but little attention has been paid to the above-mentioned systems, although it is well known that ^1H and ^{13}C

NMR are particular effective in the determination of the intramolecular chain structure.

It is still astonishing that, in retrospect, the most complex system was studied first by a combination of ^1H and ^{13}C NMR, i.e. the system MMA–MAA was studied in detail by Klesper *et al.*⁴ in the mid-1970s. Much later this system was re-examined by Llauro *et al.*⁵ via ^{13}C NMR in pyridine- d_5 solvent. The very complex splittings in the carbonyl ^{13}C NMR spectra were interpreted using pentad configurational patterns and compositional triads.

Increasing the chain length of the ester group of the MMA unit, the homopolymer MMA–MMA (PMMA),³ extensively studied by ^{13}C NMR, can be left out and the following system is ethyl methacrylate–methyl methacrylate (EMA–MMA). This system has been studied by ^{13}C NMR by Brar's group.⁶ In this case, the carbonyl pattern was analysed in compositional triads, neglecting any effects of configurational splittings. A related system, i.e. ethyl methacrylate–butyl methacrylate (EMA–BMA),⁷ was studied by the same group and using the same analysis of the observed carbonyl pattern. Apparently, the system propyl methacrylate–methyl methacrylate (PMA–MMA) has not been studied, but the following homologue of the series, methacrylate–methacrylate has been studied again by Brar's group, i.e. BMA–MMA.⁷ Again, emphasis was given to the analysis of the carbonyl pattern observed in the same NMR solvent CDCl_3 at 25°C as used for the previously mentioned systems EMA–MMA and EMA–

* Author to whom correspondence should be addressed.

† Present address: Laboratory of Macromolecular Structural Chemistry, Department of Chemistry, Catholic University of Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium.

Table 1. Overview of co-methacrylates and acrylate-methacrylate and co-acrylate copolymers characterized in terms of compositional triads (sequences) and configuration (tacticity) by means of NMR

System	NMR	Sequences	Tacticity	Ref.
MAA-MMA	^1H , ^{13}C	Yes Yes	No Yes	4, 5
EMA-MMA	^{13}C	Yes	No	6
PMA-MMA	No			—
BMA-MMA	^{13}C	Yes	No ^a	7
2naMA-MMA	^1H	Yes	Yes	8
GMA-MMA	No			—
EMA-BMA	^{13}C	Yes	No ^a	7
MAA-(dma)MA	^{13}C	Yes	No	9
(tnbt)MA-MMA	^{13}C , ^{119}Sn	Yes	No	10
AA-MMA	^{13}C	Yes	No	11
MA-MMA	^1H	Yes	Yes	12, 13
EA-MMA	^{13}C	Yes	Yes	14
PA-MMA	No			—
BA-MMA	^1H , ^{13}C	Yes Yes	Yes Yes	15 This work
HA-MMA	^{13}C	Yes		16
PhA-MMA	^1H	Yes	Yes	17
(i)BA-GMA	^{13}C	Yes	No	18
AA-MA	No			—
EA-MA	No			—
(i)PA-MA	No			—
BA-MA	^{13}C	No effects		19

^a Is not taken into account.

BMA. The splitting was again exclusively interpreted in terms of compositional triads. Still larger homologues have been studied, e.g. the system 2-naphthyl methacrylate-methyl methacrylate.⁸ However, a sequence analysis has not been performed. Apparently, a system such as glycidyl methacrylate-methyl methacrylate (GMA-MMA) has not been examined via sequence analysis using either ^{13}C NMR or ^1H NMR.

Some related systems have been studied via sequence analysis, such as the systems methacrylic acid-(dimethylamino)ethyl methacrylate⁹ and tri-*n*-butyltin methacrylate-methyl methacrylate.¹⁰ The latter system has been studied using ^{13}C and ^{119}Sn NMR. In this case the observed patterns were again interpreted in terms of mixed configurational and compositional triads.

Switching over to the acrylate-methacrylate systems, to our knowledge only one study has been published using both ^1H and ^{13}C NMR, which dealt with a sequence analysis for the parent system acrylic acid-methyl methacrylate (AA-MMA). Brar's group¹¹ considered the carbonyl splittings patterns in the ^{13}C NMR spectra, resolving these exclusively with AA and MMA compositional triads. The first homologue of the acrylate-methacrylate series, i.e. methylacrylate-methyl methacrylate (MA-MMA) was studied in the mid-1970s by Mori *et al.*¹² and recently by Lopez-Gonzalez *et al.*¹³ Both performed a sequence analysis using ^1H NMR. No ^{13}C NMR analysis has been published. The next higher homologue, i.e. EA-MMA, has been extensively studied via ^{13}C NMR by San Roman and Valero.¹⁴ In their study, the coisotacticity parameter,

i.e. $\sigma = 0.41$, was derived from an analysis of the quaternary carbon and/or methyl patterns. This parameter was used subsequently to unravel the complex carbonyl splitting patterns observed for this system. Their system was interpreted in terms of a mixed configurational/compositional triad pattern. However, the analysis of the coisotacticity parameter is not completely clear and certainly not applicable to the current system, i.e. BA-MMA. Similarly to the methacrylate series, the propylacrylate-methyl methacrylate (PA-MMA) system has not been studied by ^{13}C NMR. The next homologue (BA-MMA) has been studied by Brosse *et al.*¹⁵ via ^1H NMR. They showed that the methoxy resonances of the MMA unit are sensitive to different configurational sequences. However, initial experiments on this system at substantially higher fields, performed in our laboratory, have shown considerably more splittings to occur, leading us to a re-examination of this system via both ^1H and ^{13}C NMR. Apparently this system has not been studied by ^{13}C NMR. However, the spectra of this system are expected to show a strong resemblance to the spectra of the system EA-MMA, studied by San Roman and Valero.¹⁴ Attention has also been paid to some larger homologues of this series, i.e. the system heptyl acrylate-methyl methacrylate¹⁶ in a study of reactivity ratios, and phenyl acrylate-methyl methacrylate by San Roman and Madruga¹⁷ in a study of stereochemical configurations.

The systems BA-GMA and i-BA-GMA have also been studied via ^{13}C NMR by Dhal *et al.*¹⁸ Again, attention was mainly paid to an analysis of the splitting patterns of the carbonyl signals, interpreting these as

only split by compositional sequence triad distribution effects.

Considering co-acrylic systems, to our knowledge no systematic studies have been published which deal with the systems AA-MA, EA-MA and i-PA-MA. In a thesis,¹⁹ the system BA-MA was studied by means of ^1H and ^{13}C NMR. However, no sequence-induced splittings were observed in these spectra.

Reviewing the situation, mixed results have been reported for (meth)acrylate-related systems. For methacrylate-related systems effects of splittings induced by a combination of configurational and compositional effects have been well documented for the systems MAA-MMA¹ and EA-MMA¹⁴ in the analysis of the carbonyl patterns in the respective ^{13}C NMR spectra. In all other systems, only sequence-induced splittings have been taken into account, and no splittings have been found to occur in the co-acrylic systems. In Table 1 a summary is given of the systems discussed.

It was the intention in this study to analyse the ^1H and ^{13}C NMR spectra of the commercially important system BA-MMA. The procedure to be followed was to determine the coisotacticity parameter from the methoxy-induced splitting of the MMA unit in the ^1H NMR spectra, taking into account recent results for related systems such as styrene-MMA,²⁰ styrene-MA²¹ and styrene-EMA.²² The necessary reactivity ratios were also measured via a new approach. Subsequently, the ^{13}C NMR spectra of the BA-MMA system were studied, mainly devoted to an analysis of the carbonyl patterns.

EXPERIMENTAL

Copolymer synthesis

The monomers butyl acrylate and methyl methacrylate (Merck) were distilled at reduced pressure under nitrogen. The middle fraction of the distillate was collected and used. The free radical initiator azobisisobutyronitrile (AIBN) (Fluka) was recrystallized once from methanol. The solution-synthesized copolymers were prepared in a 100 ml glass vessel, thermostated at 323 K. The total monomer concentration was 3 mol l⁻¹ in toluene. The total conversion was determined by means of solid weight, and amounted to a maximum of 6 wt%. The initiator concentration was 8 mmol l⁻¹. To isolate and purify the copolymer, the reaction mixture was poured into a tenfold excess of cold hexane. The final product was dried at 328 K in a vacuum oven for at least 72 h at 10⁻⁵ Torr (1 Torr = 133.3 Pa).

NMR

^1H NMR spectra were recorded with a (Bruker AM 400) 400 MHz spectrometer at 393 K, using 1,2,4-trichlorobenzene as a solvent and 1,1,2,2-tetrachloroethane-*d*₂ as locking agent. The spectra were obtained using a spectral width of 6024 Hz, and acquisition time of 2.7 s, a flip angle of 45° and a pulse delay of 5 s after accumulating 240 scans, using a sample con-

centration of 1% (w/v). The digital resolution was 0.368 Hz per point, corresponding to a data length of 32K. The chemical shift is referred to C₆-H-7.35 ppm.

The ^{13}C NMR spectra were recorded at 100 MHz with the same spectrometer at 393 K. The sample concentration was 10% (w/v) in 1,2,4-trichlorobenzene. 1,1,2,2-Tetrachloroethane-*d*₂ was used as locking agent. The spectra were obtained accumulating 12000 scans with a digital resolution of 1.526 Hz per point, corresponding to a spectral width of 25000 Hz and a data length of 32K. The flip angle and the pulse delay were 45° and 4 s, respectively. The chemical shift is referred to C-5-127.8 ppm (of 1,2,4-trichlorobenzene).

In performing quantitative NMR measurements via compositional sequence and tacticity placements, one must take into account differences in spin-lattice relaxation times (*T*₁). No differential *T*₁s were observed and for the carbonyl signals differential NOEs were assumed not to occur. The relative peak areas were measured by planimetry. The inaccuracy in determining the peak areas from the NMR spectra was about 8%.

Calculations

The reactivity ratios were determined by a non-linear least-squares fit calculation. It is known as the error-in-variables (EVM) method,²³ where the errors in both the dependent and independent variables are taken into account.

RESULTS AND DISCUSSION

The ^{13}C NMR spectra lead to a superposition of signals of the MMA and BA system. As is evident from visual inspection of the ^{13}C NMR spectral region between 15 and 60 ppm (see Fig. 1), extensive overlapping signals occur, e.g. between the α -CH₃ main chain group of the MMA unit and the CH₂ adjacent to the CH₃ of the BA unit, therefore excluding any detailed analysis of this region. Such a spectral overlap is not present in the EA-MMA system.¹⁴

A similar overlapping region is seen for resonances belonging to the quaternary carbon of the MMA unit. In this case, however, in our opinion, no differences occur for the EA-MMA and BA-MMA systems (compare, e.g., Fig. 1 in Ref. 14 with Fig. 1 here). Nevertheless, from these quaternary signals the coisotacticity parameter was calculated for the EA-MMA system. We prefer, in our system, to calculate this parameter from the ^1H NMR spectra. The value of this parameter is used in order to assign the various carbonyl signals of the BA-MMA system. As a starting point, the signal assignments of San Roman and Valero¹⁴ are used, because we do not expect large variations on going from the EA-MMA to the BA-MMA system. This observation is corroborated by mutual comparison of the carbonyl patterns observed for both systems (compare Fig. 7 in Ref. 14 and Fig. 2 here).

Figure 1. 100 MHz ^{13}C NMR spectrum of a BA-MMA copolymer with $F_M = 0.69$, showing only region from 70 to 0 ppm.

Figure 2. Expanded 100 MHz ^{13}C NMR spectra of the carbonyl carbon resonance signals of MMA- and BA-centred sequences.

¹H NMR

Copolymer composition. The average copolymer composition (mole fraction of methyl methacrylate F_M) can be readily obtained by using the equation

$$F_M = \frac{2A_1}{2A_1 + 3A_2}, \quad (1)$$

where A_1 and A_2 represent the total peak areas of the proton resonances $-\text{OCH}_3-$ of the MMA unit and of the $-\text{OCH}_2-$ of the BA unit, respectively. This is shown in Fig. 3, where a 400 MHz spectrum of a BA-MMA copolymer ($F_M = 0.36$) is shown. The composition of copolymers as determined by ¹H NMR along with the feed composition is given in Table 2.

Reactivity ratios. The reactivity ratios for the AIBN-initiated system at 323 K were determined according to EVM method.²³ The resulting reactivity ratio estimates were $r_M = 2.279$ and $r_B = 0.395$. The 95% posterior

Figure 3. 400 MHz proton NMR spectrum of a BA-MMA copolymer with $F_M = 0.36$.

Figure 4. 95% posterior probability contour for estimated r_B and r_M values.

probability contour is shown in Fig. 4. In Fig. 5 the experimental and theoretical relationships between the molar feed composition and the copolymer composition are presented.

Assignment of the methoxy proton (MMA). In Fig. 6, some of the expanded 400 MHz proton NMR spectra of BA-MMA copolymers with different feed compositions are shown. Expansions of the methoxy region are shown since in particular this region displays additional

Table 2. Normalized peak areas of the methoxy proton of the MMA-centred triads of BA-MMA copolymers obtained by low conversion batch solution processes^a

f_M	F_M	A	B	C	D	E	
0.036	0.17	0.26	0.13	0.30	0.10	0.21	Exp.
	0.143	0.28	0.14	0.358	0.09	0.132	Calc.
0.125	0.28	0.22	0.19	0.31	0.16	0.12	Exp.
	0.261	0.211	0.226	0.270	0.145	0.147	Calc.
0.184	0.36	0.162	0.40	0.28	0.21	0.11	Exp.
	0.355		0.274	0.208	0.175	0.181	Calc.
0.300	0.53		0.549			0.451	Exp.
	0.507		0.522			0.478	Calc.
0.400	0.595		0.44			0.56	Exp.
	0.613		0.426			0.574	Calc.
0.408	0.629		0.469			0.535	Exp.
	0.620		0.418			0.582	Calc.
0.512	0.69		0.396			0.604	Exp.
	0.711		0.328			0.672	Calc.
0.779	0.854		0.16			0.84	Exp.
	0.890		0.131			0.869	Calc.

^a Predicted relative areas calculated using the ultimate model for low conversion copolymers, and Ref. $r_M = 2.279$ and Ref. $r_B = 0.395$, $\sigma_{BM} = 0.39$ and the appropriate assignment for various initial feed compositions f_M .

Figure 5. Relationship between copolymer feed composition f_M and the average copolymer composition F_M .

splitting due to combined configurational (=tacticity) and compositional sequence effects.¹⁵ Brosse *et al.*¹⁵ published the 100 MHz proton NMR spectra of BA-MMA copolymers and assigned the split methoxy

resonance of the MMA-centred triads as follows:

$$\delta_{3.65 \text{ ppm}} = (1 - \sigma)^2 \text{BMB} + (1 - \sigma_{\text{MM}})(1 - \sigma) \text{MMB}$$

$$\begin{aligned} \delta_{3.60 \text{ ppm}} = & \text{MMM} + [\sigma_{\text{MM}}\sigma + \sigma_{\text{MM}}(1 - \sigma) \\ & + (1 - \sigma_{\text{MM}})\sigma] \text{MMB} \\ & + [\sigma\sigma + 2\sigma(1 - \sigma)] \text{BMB} \end{aligned}$$

where σ is σ_{BM} , the coisotacticity parameter (*meso* configuration between a BA and a MMA unit) and σ_{MM} is the isotacticity (*meso* configuration between two MMA units). An MMM sequence shows no tacticity since in the proton NMR spectrum of PMMA only a single peak signal exists at 3.6 ppm.

However, the improved resolution of the methoxy region in proton NMR spectra recorded at higher magnetic fields (in our case at 400 MHz) leads to a significantly more observable fine structure. This allows us to assign a more accurate assignment of the methoxy protons. As shown in Fig. 6(a) ($F_M = 0.17$), the methoxy resonance signal of the MMA-centred units has been reinterpreted in terms of five major peak signals, each of which is attributed to an individual or two MMA-centred sequences. This has not been observed before because Brosse *et al.*¹⁵ showed the spectra of BA-MMA of $F_M = 0.42$ and of higher fractions of MMA in the copolymer. It has been found (Fig. 6) that no additional splitting can be observed in copolymers with fractions of MMA higher than 0.3.

Figure 6. Expanded 400 MHz proton NMR spectra showing the methoxy region of four different BA-MMA copolymers.

Table 3. Assignment of carbonyl resonances of BA-MMA copolymers according to the work of San Roman and Valero¹⁴ for the EA-MMA system

$$\begin{aligned}
 \text{I} &= (1 - \sigma_{\text{MM}})^2 \text{MMM} \\
 \text{II} &= 2\sigma_{\text{MM}}(1 - \sigma_{\text{MM}})\text{MMM} + \sigma_{\text{BM}}(1 - \sigma_{\text{BM}})\text{BMM} + (1 - \sigma_{\text{BM}})(1 - \sigma_{\text{MM}})\text{BMM} \\
 \text{III} &= \text{MBM} \\
 \text{IV} &= \sigma_{\text{MM}}^2 \text{MMM} + (1 - \sigma_{\text{BM}})\sigma_{\text{MM}} \text{BMM} + [\sigma_{\text{BM}}^2 + 2\sigma_{\text{BM}}(1 - \sigma_{\text{BM}})]\text{BMB} + \sigma_{\text{MM}}\sigma_{\text{BM}}\text{BMM} \\
 \text{V} &= \text{MBB} \\
 \text{VI} &= (1 - \sigma_{\text{MB}})^2 \text{BMB} \\
 \text{VII} &= \text{BBB}
 \end{aligned}$$

The assignment of the peak signals is as follows:

$$\begin{aligned}
 \text{A} &= (1 - \sigma)^2 \text{BMB} \quad (\delta = 3.74 \text{ ppm}) \\
 \text{B} &= (1 - \sigma) \text{MMB} \quad (\delta = 3.72 \text{ ppm}) \\
 \text{C} &= 2\sigma(1 - \sigma) \text{BMB} \quad (\delta = 3.69 \text{ ppm}) \\
 \text{D} &= \sigma \text{MMB} \quad (\sigma = 3.67 \text{ ppm}) \\
 \text{E} &= \sigma^2 \text{BMB} + \text{MMM} \quad (\delta = 3.63 \text{ ppm})
 \end{aligned}$$

where σ is the coisotacticity parameter. No tacticity effects of two adjacent MMA units are assumed to occur. It is very clear in Fig. 6(a) that peaks A, C and E belong to the BMB triad. The MMM triad is resonating at 3.63 ppm, i.e. also peak E. Hence peaks B and D are subsequently assigned to the BMM triads. A BA unit in racemic configuration towards the MMA-centred unit gives more deshielding than a BA unit in *meso* configuration, so the $(1 - \sigma)\text{MMB}$ resonates at lower field than σMMB .¹⁵ It is unclear from where the intensities next to peaks A and E in Fig. 6(a) arise. These are probably artifacts.

The clear peak splitting does not hold over the entire range of BA-MMA copolymers, as can be seen in Fig. 6. In Fig. 6(b) we still can see five peak signals. In Fig. 6(c) only four peak signal areas (A + B, C, D, E) can be observed and at higher fractions of MMA in the copolymer we can distinguish only two peak signals

(A + B + C, D + E). Because of the accuracy the peak assignment at high mole fractions of MMA in the copolymer is combined as follows:

$$\delta_{3.72 \text{ ppm}} = \text{A} + \text{B} + \text{C}$$

$$\delta_{3.63 \text{ ppm}} = \text{D} + \text{E}$$

Coisotacticity parameter. The coisotacticity parameter is calculated using a non-linear least-squares procedure with relative error estimation²⁴ based on the current assignment. A σ of 0.39 ± 0.05 was found, which is in agreement with the coisotacticity parameter of the related EA-MMA system, which amounted 0.41 (measured by ¹³C NMR).¹⁴

Peak areas and sequence distribution. In Table 2, the molar feed composition f_{M} , the average copolymer composition F_{M} , the experimentally observed peak areas and the calculated peak areas are given. The theoretical triads can be calculated by assuming the validity of the ultimate model²⁵ (Alfrey/Mayo kinetics = first-order Markov statistics).²⁶ As can be seen, very good agreement is achieved between experimentally observed and theoretically calculated peak areas. As a result, the new peak assignment and a coisotacticity parameter of 0.39

Table 4. Experimentally observed (NMR) and theoretically calculated peak areas of the carbonyl carbon resonances of BA- and MMA-centred sequences^a

f_{M}	F_{M}	I	II	III	IV	V	VI	VII	
0.063	0.17	0	0	0	0.05	0.27	0.07	0.61	Exp.
	0.143	0.002	0.031	0.018	0.089	0.206	0.048	0.606	Theo.
0.085	0.146	0	0	0	0.05	0.24	0.06	0.65	Exp.
	0.261	0.003	0.034	0.031	0.072	0.263	0.037	0.560	Theo.
0.125	0.28	0.03	0.07	0.06	0.12	0.29	0.06	0.37	Exp.
	0.355	0.010	0.086	0.051	0.125	0.281	0.059	0.388	Theo.
0.184	0.36	0.03	0.09	0.09	0.18	0.31	0.09	0.25	Exp.
	0.507	0.025	0.139	0.084	0.138	0.296	0.058	0.260	Theo.
0.400	0.595	0.12	0.25	0.14	0.15	0.17	0.03	0.04	Exp.
	0.613	0.128	0.296	0.160	0.136	0.189	0.035	0.056	Theo.
0.408	0.629	0.14	0.25	0.15	0.16	0.17	0.06	0.07	Exp.
	0.620	0.139	0.313	0.150	0.141	0.172	0.035	0.049	Theo.
0.512	0.69	0.20	0.31	0.13	0.15	0.11	0.06	0.05	Exp.
	0.711	0.203	0.342	0.163	0.122	0.123	0.022	0.023	Theo.
0.779	0.854	0.45	0.31	0.13	0.06	0.05	0	0	Exp.
	0.890	0.400	0.369	0.118	0.081	0.026	0.004	0.001	Theor

^a Predicted relative areas obtained by using the ultimate model for low conversion copolymers, and $r_{\text{M}} = 2.279$ and $r_{\text{B}} = 0.395$, $\sigma_{\text{MM}} = 0.23$, $\sigma_{\text{BM}} = 0.39$ and the appropriate assignment for various initial feed compositions f_{M} .

can be used for analysing all types of BA-MMA copolymers (low and high conversion solution or emulsion copolymers) in terms of triad sequences.

¹³C NMR

Assignment of the carbonyl carbon (MMA + BA). In Fig. 1 a 100 MHz ¹³C NMR spectrum is shown of a BA-MMA copolymer ($F_M = 0.69$). Owing to the improved resolution at higher magnetic fields, the carbonyl carbon resonance signals between $\delta = 180$ and 174 ppm can be divided into at least seven resonance signal groupings whose intensities change drastically with the composition, as can be seen in Fig. 2. As already mentioned, the pattern of the carbonyl resonance area of the BA-MMA copolymers is very similar to the earlier observed pattern of the carbonyl resonance area of the EA-MMA copolymers (Fig. 7 in Ref. 14). As a result, the same assignment has been applied to the BA-MMA system. The assignment of the carbonyl resonance signals is given in Table 3, not only for reasons of completeness, but also because one configurational sequence (mm MMA) is missing in the original assignment of the carbonyl resonances of San Roman and Valero¹⁴ for the EA-MMA system. It should be noted that the peak signals are assigned in terms of compositional triads and no configurations are taken into account. More fine splittings in the peak signals are observed, probably caused by configurations. These effects are not clear enough to make an accurate assignment.

In Table 4 the experimentally observed peak areas of the carbonyl region are presented, together with the calculated peak areas, obtained from the calculated triads and the isotacticity parameter from the literature, $\sigma_{mm} = 0.23$,²⁷ and the coisotacticity parameter $\sigma_{bm} = 0.39$ from this work. The good agreement between the experimental and calculated values confirms the suggested assignment of the carbonyl resonance signals.

CONCLUSIONS

The proton NMR spectra of statistical BA-MMA copolymers at higher magnetic fields show more fine resonance splitting in the methoxy region, which enables us to make a more accurate assignment. The

methoxy region is sensitive for MMA-centred sequences. There is a satisfactory agreement between experimental and theoretical peak areas over a wide range of copolymer compositions, based on the ultimate copolymerization model and a coisotacticity parameter $\sigma_{BM} = 0.39$. The reactivity ratios measured via proton NMR and calculated by the EVM method, r_M and r_B , are 2.279 and 0.395, respectively.

The ¹³C NMR spectra of the BA-MMA copolymers, in particular the carbonyl resonance signals, were very similar to the ¹³C NMR spectra of the EA-MMA copolymers. The same peak assignment for the carbonyl resonances was applied in terms of both MMA-centred and BA-centred triads, and very good agreement between experimental peak areas and theoretical calculated peak areas was achieved.

ABBREVIATIONS OF COPOLYMERS

AA	Acrylic acid
BA	Butyl acrylate
EA	Ethyl acrylate
HA	Heptyl acrylate
MA	Methyl acrylate
PA	Propyl acrylate
PhA	Phenyl acrylate
BMA	Butyl methacrylate
EMA	Ethyl methacrylate
GMA	Glycidyl methacrylate
MAA	Methacrylic acid
MMA	Methyl methacrylate
PMA	Propyl methacrylate
(2na)MA	2-Naphthyl methacrylate
(dma)MA	Dimethylamino methacrylate
(tnbt)MA	Tri- <i>n</i> -butyltin methacrylate
PMMA	Poly(methyl methacrylate)

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REFERENCES

1. R. Zeelenberg, personal communication, 1994.
2. S. Hvilsted, in *Atlas de Polymer- und Kunststoffanalyse*, Band 2, Teil b/1, p. 223, Carl Hanser Verlag (1988).
3. H. Angad Gaur, *Recl. Trav. Chim. Pays-Bas*, **110**, 553 (1991).
4. E. Klesper, A. Johnsen, W. Gronski, F. W. Wehrli and W. Felix, *Makromol. Chem.* **176**, 1071 (1975), and references cited therein; A. Johnsen, E. Klesper and T. Wirthlin, *Makromol. Chem.* **177**, 2397 (1976).
5. M. F. Llauro, R. Spitz and C. Pichot, *J. Macromol. Sci. Chem.*, **A19**, 881 (1983).
6. A. S. Brar and A. K. Saini, *J. Appl. Polym. Sci.*, **32**, 4607 (1986); A. S. Brar, G. S. Kapur and S. K. Dubey, *Eur. Polym. J.* **24**, 807 (1988).
7. G. S. Kapur and A. S. Brar, *Indian J. Chem.*, **30A**, 493 (1991).
8. C. I. Simionescu, A. Natansohn and V. Percec, *Colloid. Polym. Sci.* **259**, 697 (1981).
9. L. Merle and Y. Merle, *Macromolecules* **15**, 360 (1982).
10. W. F. Manders, J. M. Bellama, R. B. Johanneses, E. J. Parks and F. E. Brinckman, *J. Polym. Sci., Part A*, **25**, 3469 (1987).
11. A. S. Brar, E. Arunan and G. S. Kapur, *Polym. J.* **21**, 689 (1989).
12. Y. Mori, A. Ueda, H. Tanzawa, K. Matsuzaki and H. Kobayashi, *Makromol. Chem.* **176**, 699 (1975).
13. M. M. C. Lopez-Gonzalez, M. Fernandez-Garcia, J. M. Barrales-Rienda, E. L. Madruga and C. Arias, *Polymer* **34**, 3123 (1993).

14. J. San Roman and M. Valero, *Polymer* **31**, 1216 (1990).
15. J. C. Brosse, J. M. Gauthier and J. C. Lenain, *Makromol. Chem.* **184**, 1379 (1983).
16. Y. E. Shapiro, N. A. Budanov, Z. V. Orlova and S. I. Kuchanov, *Vysokomol. Soedin. Ser. B* **31**, 123 (1989).
17. J. San Roman and E. L. Madruga, *Eur. Polym. J.* **18**, 481 (1982).
18. P. K. Dhal, G. N. Babu and R. K. Nanda, *Macromolecules* **17**, 1131 (1984).
19. G. H. J. van Doremaele, PhD Thesis Eindhoven University of Technology, 1990, Chapt. 4.
20. A. M. Aerdt, J. W. de Haan, A. L. German and G. P. M. van der Velden, *Macromolecules* **24**, 1473 (1991); A. M. Aerdt, J. W. de Haan and A. L. German, *Macromolecules* **26**, 1965 (1993).
21. G. H. J. Van Doremaele, A. L. German, N. K. de Vries and G. P. M. van der Velden, *Macromolecules* **23**, 4206 (1990).
22. J. C. J. F. Tacx, G. P. M. van der Velden and A. L. German, *J. Polym. Sci., Polym. Chem. Ed.* **26**, 1439 (1988).
23. M. Dube, R. Amin Samayei, A. Penlidis, K. F. O'Driscoll and P. M. Reilly, *J. Polym. Sci. Polym. Chem. Ed.* **29**, 703 (1991).
24. A. M. van Herk, *J. Chem. Educ.* in press.
25. I. A. Maxwell, A. M. Aerdt and A. L. German, *Macromolecules* **26**, 1956 (1993).
26. J. L. Koenig, *Chemical Microstructure of Polymer Chains*. Wiley, New York, (1980).
27. Y. Inoue, A. Nishioka and R. Chujo, *Makromol. Chem.* **156**, 207 (1972).