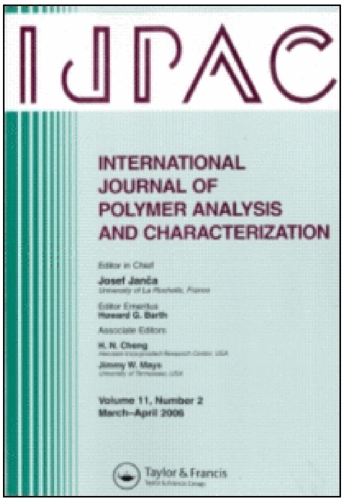

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Microstructure Analysis of Acrylate-Methacrylate Copolymers by ^{13}C NMR Spectroscopy

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Abstract: The carbonyl signal in the ^{13}C NMR spectra of copolymers of methyl methacrylate and several acrylates (methyl to butyl) has been investigated to obtain detailed information on distribution of sequences in the macromolecular chain up to configurational-compositional pentads. Complementary information on distribution of even sequences can be derived from the signal of β-CH_2 carbons of the main chain. Incremental calculation of the chemical shifts of the individual sequences can be performed for both carbonyl and methylene signal and permit for spectral simulation and verification of the signal attribution to the respective sequences.

Keywords: Acrylate-methacrylate copolymers; ^{13}C NMR spectroscopy; Polymer microstructure

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INTRODUCTION

Nuclear magnetic resonance spectroscopy of liquids is practically the only analytical technique providing deep insight into details of the chemical structure of the macromolecular chains of synthetic polymers. In the case of acrylic polymers, the carbonyl signal in the ^{13}C nuclear magnetic resonance (NMR) spectra has been found to be very sensitive to configurational differences in the macromolecular chain. For copolymers composed of similar monomers, say both methacrylates or both acrylates, the carbonyl region becomes very crowded and usually too complicated to perform detailed analysis of their microstructure since carbonyl signals of both commoners occupy practically the same position; hence, they are very difficult to analyze.[1] However, the carbonyl signals of acrylic and methacrylic homopolymers occupy slightly different positions, acrylic at about 174–175 ppm, while that of methacrylic units is at about 176–178 ppm. As a result, in the ^{13}C NMR spectra of acrylate-methacrylate copolymer systems, the carbonyl signal is spread over about a 4 ppm zone and offers quite good resolution to distinguish individual lines up to configurational-compositional pentads.

Detailed analysis of sequence distribution can be performed if we can assign individual lines in the spectrum to respective sequences. Attribution of the lines of pure composition can be performed based on comparison with respective homopolymers; however, the majority of the lines cannot be assigned in this way. We have developed our own method of incremental calculation permitting determination of line positions for each configurational-compositional sequence.[2] For the low-conversion samples of copolymers, Bernoulli/Markov statistics can provide data on line intensities, therefore, spectra simulation may confirm correct attribution and provide detailed spectral data for the individual copolymers. The data collected in this way may be extended to characterize high-conversion samples of industrial importance.

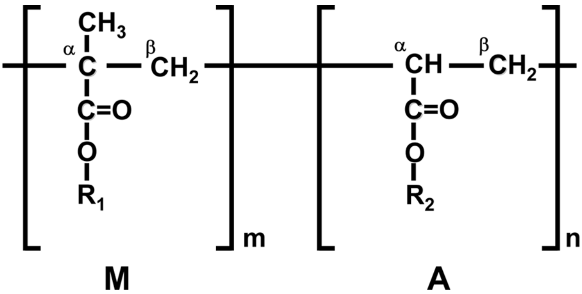
EXPERIMENTAL SECTION

A series of equimolar acrylate-methacrylate copolymers was synthesized by free radical polymerization. The comonomers, taken in respective weight ratio, were poured into butan-2-one to obtain 40 wt.% mixture. The mixture was heated up to 78°C and azobisisobutyronitrile (AIBN) was added as radical initiator (0.5 wt.% with respect to the solution). After polymerization for about 0.5 h, the reaction mixtures were diluted with acetone and poured into a large volume of a water-methanol mixture to precipitate the copolymers. They were washed with methanol and vacuum dried to constant weight.[3] The following copolymers were obtained in this manner: poly(methyl methacrylate-*co*-methyl acrylate), PMMA/MA; poly(methyl methacrylate-*co*-ethyl acrylate), PMMA/EA; poly(methyl methacrylate-*co*-n-propyl acrylate), PMMA/nPA; poly(methyl methacrylate-*co*-n-butyl acrylate), PMMA/nBA; and poly(methyl methacrylate-*co*-tert-butyl acrylate), PMMA/tBA. The composition F_M (molar fraction of methyl methacrylate) values of the copolymers were calculated from their ^{1}H NMR spectra by integration of characteristic, well-separated peaks.[4] Respective homopolymers, i.e., poly(methyl methacrylate), PMMA; poly(methyl acrylate), PMA; poly(ethyl acrylate), PEA; poly(n-propyl acrylate), PnPA; poly(n-butyl acrylate), PnBA; and poly(tert-butyl acrylate), PtBA, were obtained in an analogous manner.

The NMR spectra were recorded with a Bruker AM 400 spectrometer at 40°C, using 10 wt.% solutions in $CDCl_3$ and benzene-d_6. The 400 MHz ^{1}H NMR spectra were obtained for a sample concentration of 10% (w/v), applying pulse delay of 5 s and 240 scans. To record the 100 MHz ^{13}C NMR spectrum a gated decoupling sequence was applied to avoid the nuclear Overhauser effect, and a good signal-to-noise ratio was achieved after about 10,000 scans. The spectra were obtained with a 4 s delay (D1). Simulation of the NMR spectra were performed using our own software, written in the Matlab environment (Math Works, Inc.).

RESULTS AND DISCUSSION

Microstructure of a series of equimolar acrylate-methacrylate copolymers of the chemical structure in Scheme 1 has been investigated.



Scheme 1. Chemical structure of acrylate-methacrylate copolymers. M, A are methacrylate and acrylate repeating units, respectively, R_1 = Me, R_2 = Me, Et, n-Pr, n-Bu, t-Bu.

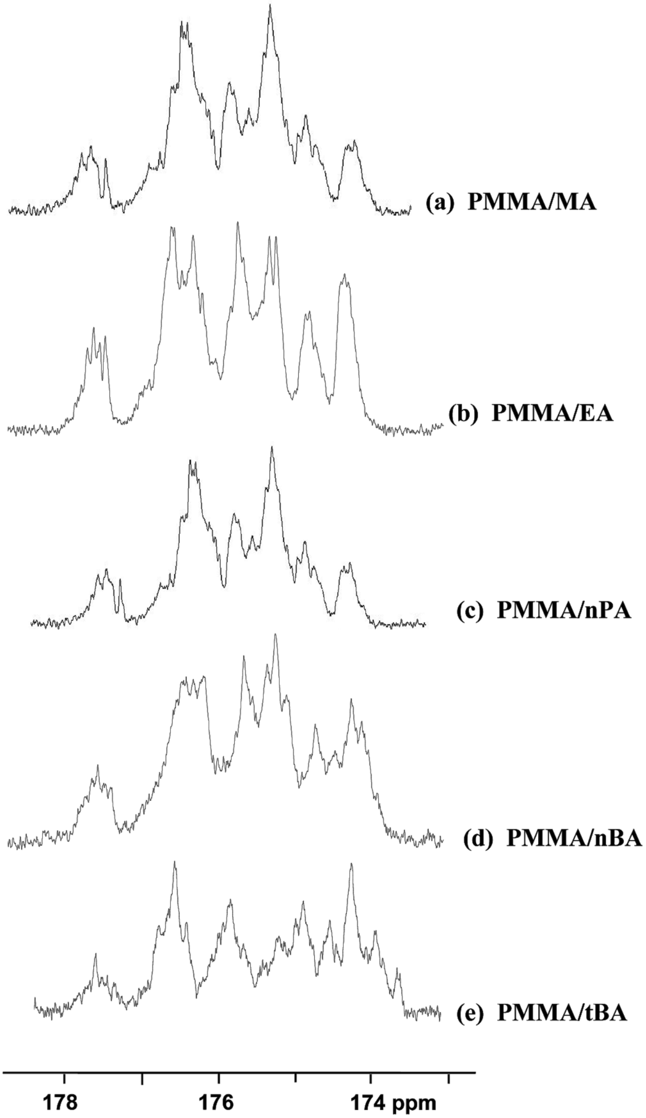


Figure 1. 100 MHz ^{13}C NMR spectra of carbonyl signal of various equimolar acrylate-methacrylate copolymers in $CDCl_3$: PMMA/MA (a), PMMA/EA (b), PMMA/nPA (c), PMMA/nBA (d), and PMMA/tBA (e).

It can be seen that only two carbons, i.e., carbonyl and β-CH_2 carbon, from the main chain are always present in all acrylic structures, hence, only these two signals can provide complete microstructural information. Moreover, these two signals supply complementary information on distribution of even and odd sequences, respectively. The α-carbon is either quaternary in methacrylate units or tertiary in acrylate ones, therefore, it gives rise to signals in different regions. Remaining signals, if sensitive to microstructural effects, have to be regarded as a secondary source of information on sequence distribution.

If we consider a series of copolymers obtained from methyl methacrylate as one comonomer and various alkyl acrylates as the second one, we can observe that for different systems, the characterization of their microstructure based on the carbonyl signal can be performed at the level of pentad length. This signal in the 100 MHz ^{13}C

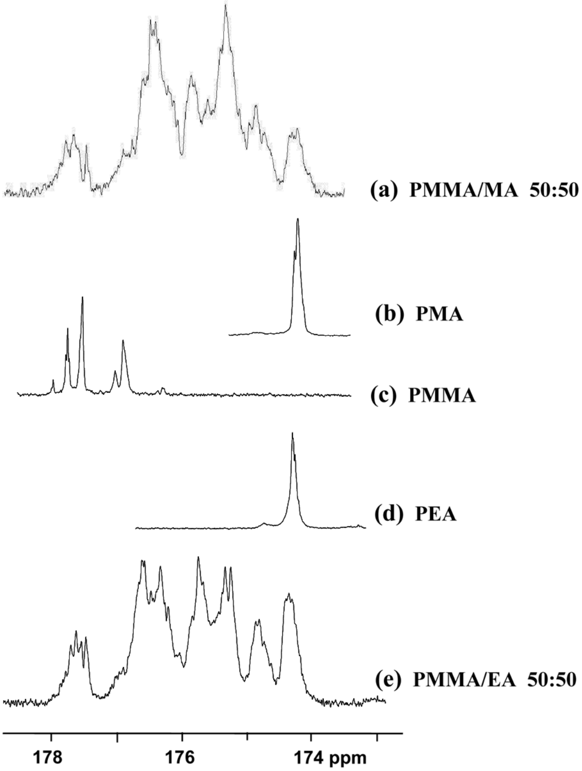


Figure 2. Carbonyl signal of PMMA/MA and PMMA/EA copolymers and their respective homopolymers in $CDCl_3$: PMMA/MA 50:50 (a), PMA (b), PMMA (c), PEA (d), and PMMA/EA 50:50 (e).

NMR spectra of different copolymers exhibits a generally comparable outline for all the copolymers studied (Figure 1). A similar separation into six main bands, due to triad effect, is well visible for all the samples and further splitting due to pentads is well distinguished.

However, different monomers offer different sensitivities to configurational effects. Usually, the signals of methyl methacrylate centered sequences are very sensitive to configurational effects, while those of acrylic units exhibit different properties. For the 100 MHz ^{13}C NMR spectra of methyl methacrylate-methyl acrylate copolymer, PMMA/MA, recorded in deuterated chloroform the carbonyl signal of methyl acrylate repeating units is not at all sensitive to configurational effects (Figures 2(a)–(b)). For the methyl methacrylate-ethyl acrylate system it is possible to observe only traces of configurational splittings in the

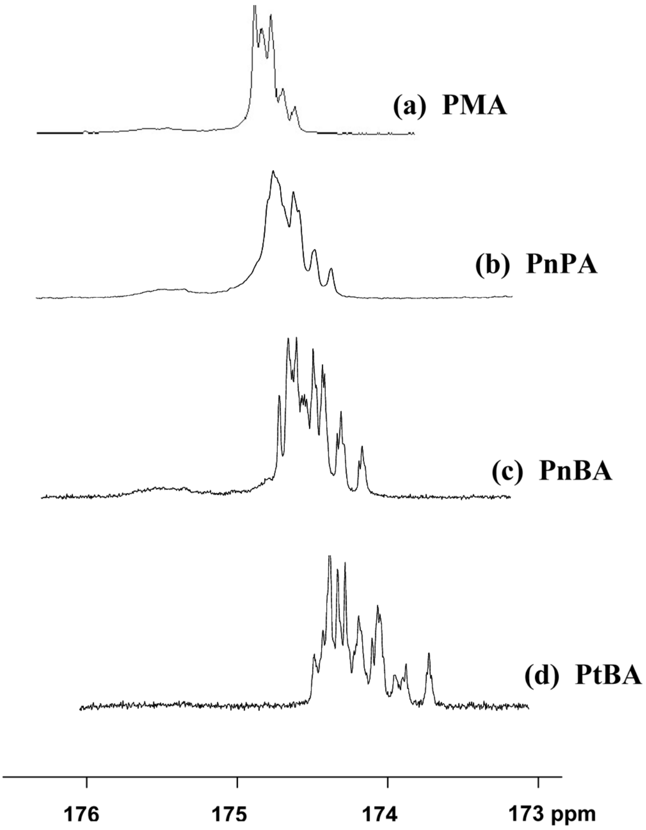


Figure 3. Carbonyl signal of acrylate homopolymers recorded in C_6D_6: PMA (a), PnPA (b), PnBA (c), and PtBA (d).

acrylate signals (Figures 2(c)–(e)), while the spectra of both methyl methacrylate-propyl acrylate and methyl methacrylate-butyl acrylate copolymers exhibit sensitivity of both comonomers to configurational effects.[3]

Moreover, significant differences in sensitivity on configurational effects are visible in the spectra recorded in other solvents, notably benzene. When we compare the carbonyl signals of different acrylate homopolymers recorded in C_6D_6 (Figure 3) it can be seen that in this case even for a polymer with the smallest alkyl substituent, i.e., poly(methyl acrylate), the signal is already split due to configurational effects.

Correct line assignment can be verified based on simulation of NMR spectra. To simulate an NMR signal consisting of several lines one has to know three parameters of the individual lines: intensity, position, and line width (assuming Lorentzian or Gaussian line shape). In the case of a polymer signal split due to the presence of different sequences, the intensities of the lines can be obtained assuming Bernoullian or Markov statistics. For low-conversion acrylic polymers (up to about 10%) usually

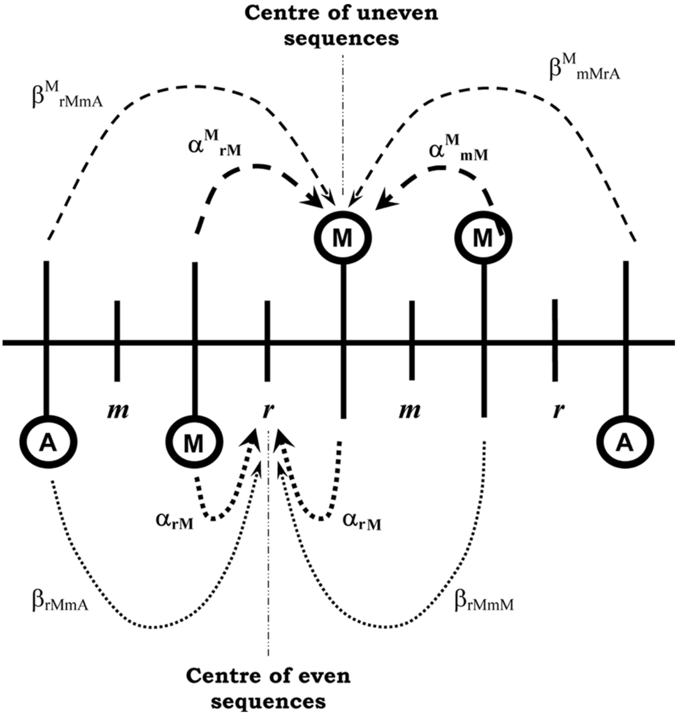


Figure 4. Influences of neighboring units in even and uneven sequences.

first-order Markov statistics is applicable. The line widths can be estimated from the well-resolved lines in the experimental spectrum. However, the positions of the lines have to be established separately. We have developed our own method of determination of chemical shifts of individual sequences.[2,4] This semi-empirical method is based on incremental calculation of the chemical shift of a sequence as a sum of influences of neighboring units. The effect of the closest units is described by α-increments, while that of the next one by β-increments (Figure 4).

Such an approach has been positively applied both to carbonyl and β-CH_2 carbon signals. It has to be noted that in the case of carbonyl signals we obtain the information on distribution of uneven sequences, i.e., triads, pentads, etc. On the other hand, the methylene signal provides information on distribution of even sequences, i.e., diads, tetrads, etc. Moreover, the β-CH_2 carbon signals occupy a relatively large region from about 30 up to even 60 ppm, but they are usually superimposed with the signals of other carbons, like α-C, OMe, and other carbons from alkyl substituents. Analysis of β-CH_2 signals requires, therefore, edition of a spectrum (like the DEPT technique) to record separately the methylene signal.

CONCLUSION

The 100 MHz ^{13}C NMR spectra of the investigated methacrylate-acrylate copolymers offer good resolution of their carbonyl signals and can provide detailed information on distribution of sequences up to configurational-compositional pentads. The presence of bulky alkyl substituent in the acrylate comonomer increases the sensitivity of these units to configurational differences, and therefore for this type of copolymer, configurational effect has to be taken into account for both comonomers. The signal of methylene carbons in the main chain, the β-CH_2 carbons, can supply complementary information on distribution of even configurational-compositional sequences. The spectral parameters obtained for the low-conversion samples may be utilized to determine sequence distribution of analogous industrial samples usually obtained at high conversion.

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