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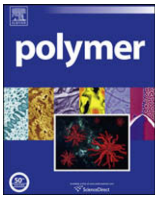

Multivariate analysis of ^{13}C NMR spectra of methacrylate copolymers and homopolymer blends

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ABSTRACT

^{13}C NMR spectra of copolymers of methyl methacrylate and *tert*-butyl methacrylate with various chemical compositions, the homopolymers of the two methacrylates, and blends of the homopolymers with various blend ratios were subjected to principal component analysis. The first and second principal components correlated chemical composition and the randomness of comonomer sequence, respectively. Chemical composition of the copolymers was determined with high accuracy and precision by the partial least-squares regression without assignment of individual resonance peaks.

1. Introduction

Many industrial polymers have been developed to give electronic, optical and composite materials. A large part of those polymers are copolymers made up of several different kinds of monomer. Detailed analysis of their molecular structures including chemical composition, comonomer sequence, stereoregularity and the distribution of these properties within the polymer, is essential for further improvement of the polymer materials.

NMR spectroscopy is the method of choice for the characterization of the copolymers mentioned above. However, resonances arising from each group in copolymers often exhibit overlapped splitting due to comonomer sequences and configurational sequences, and thus assignment of the individual peaks is troublesome [1,2]. Increasing the number of monomer components in copolymers makes the resonances broader and more complicated.

Multivariate analysis is recognized as a powerful tool in the transformation of complex information into a set of useful information. Principal component analysis (PCA) and partial least-squares regression (PLSR), developed by Kowalski [3,4] and Wold [5], have been successfully applied to the discrimination of ethylene-vinyl acetate copolymers with different compositions and the prediction of the content of vinyl acetate in the copolymers by Raman [6] or near-infrared [7] spectroscopy. PCA was also utilized to analyze the FTIR and DSC data of various types of polyethylenes, to classify chain-branching types, chain-branching content as well as its distribution [8]. In the field of NMR spectroscopy, metabolic profiling based on multivariate analysis has recently been attracting much attention [9–14]. General reviews on the multivariate and chemometric treatments of NMR spectroscopic data have also published [15,16]. However, there is no report on the multivariate analysis of NMR spectra of synthetic polymers to the best of our knowledge.

Here, we report an approach to obtain quantitative information from NMR spectra of copolymers without assigning the resonance peaks. As a preliminary investigation of this approach, ^{13}C NMR spectra of seven copolymers of methyl methacrylate (MMA) and *tert*-butyl methacrylate (TBMA) with various chemical compositions, homopolymers of the two methacrylates (PMMA and PTBMA), and nine blends of the homopolymers with various blend ratios were subjected to PCA and PLSR.

2. Experimental

2.1. Materials

Polymer samples were prepared as follows: a mixture of monomer (20 wt%) and 2,2′-azobisisobutyronitrile (AIBN) (0.5 or 20 mol% of the monomer mixture) were dissolved in ethyl lactate. Polymerization was carried out at 80 °C under a nitrogen atmosphere. After 4 h, the polymerization mixture was cooled to room temperature and poured into a large volume of methanol/water

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mixture (3/7 to 1/1 vol/vol). The polymer precipitated and was collected by filtration and dried over night at 60 °C *in vacuo*. Table 1 summarizes the feed ratio and chemical composition (mol% in TBMA units), M_n, M_w/M_n and the yield of the polymer samples used in the present work. Table 2 shows the chemical compositions of the blends of PMMA and PTBMA (H-0 and H-100 in Table 1) as determined by ^{1}H NMR.

2.2. Measurements and procedures

The homopolymers, copolymers and homopolymer blends were dissolved in chloroform-*d* (8% wt/vol). ^{1}H and ^{13}C NMR spectra were measured at 55 °C on a JEOL ECX400 spectrometer equipped with a 10 mm multinuclear probe (^{1}H: 45° pulse (8.5 μs), pulse repetition = 8.90 s, 16 scans; ^{13}C: 45° pulse (7.5 μs), pulse repetition = 2.73 s, 10,000 scans, with ^{1}H broadband decoupling). A line-broadening factor of 3.0 Hz was applied before Fourier transform of the ^{13}C NMR data. The ^{13}C NMR chemical shift of chloroform-*d* was set to 77.0 ppm as an internal standard. Chemical composition was determined from integral intensities of ^{1}H NMR signals due to the ester groups of MMA and TBMA units.

Bucket integration of the spectral regions 44–48 ppm (the backbone quaternary carbons) and 175–179 ppm (the carbonyl carbons) at an interval of 0.25 ppm was performed with JEOL Alice2 ver.5 for metabolome ver.1.6 software. Sum of integral intensities in each spectral region was normalized to 100. Average integral intensity was subtracted from each integral intensity. A data set thus obtained consists of 32 mean-centered bucket integral values. PCA and PLSR of the data sets were conducted using Pattern Recognition Systems Sirius ver.7.0 software.

Table 2
TBMA unit compositions of the blends of PMMA and PTBMA.

Code	TBMA (mol%)[a]
B-90	86.9
B-80	80.4
B-70	69.9
B-61	61.1
B-51	50.7
B-42	41.8
B-32	31.6
B-22	22.1
B-13	12.8

[a] Determined by ^{1}H NMR.

3. Results and discussion

Fig. 1 shows ^{13}C NMR spectra of the carbonyl and the backbone quaternary carbons of PMMA, PTBMA, a homopolymer blend and a copolymer. The spectra of the homopolymers show splitting due to configurational triads or pentads (Fig. 1a and d). The spectrum of the copolymer (Fig. 1b) is more complicated and somewhat broader than that of the homopolymer blend (Fig. 1c) though the copolymer and the homopolymer blend have similar chemical compositions (41.8 and 43.1 mol% in TBMA units, respectively). These two spectra clearly indicate that the spectral pattern of the copolymer includes information about comonomer sequences. Although the resonances arising from the α-methyl, methylene and ester groups of the polymers can also be sensitive to the chemical composition and comonomer sequence, the resonances from the carbonyl and quaternary carbons were selected and taken into account in the present study for simplicity.

Fig. 2 shows the PCA score plots for the data sets of the 18 polymer samples. The variances for the first (PC1) and second principal components (PC2) were 85.2% and 13.7%, respectively, and their total amounted to 98.9%, indicating that the spectral information of the data sets was explained well with these two parameters. The plots for the homopolymers (◆), and their blends (◇) show a linear relationship between PC1 and PC2, whereas those for copolymers (■) showed an inverted parabolic relationship regardless of the molecular weights of the samples. Differences between the PC2 scores for the homopolymer blends and the copolymers had a maximum at equimolar chemical composition. The PC2 scores should reflect randomness of comonomer sequences, as the stereoregularity of the copolymers is not expected to vary greatly with the feed monomer ratio in this copolymerization [17,18].

Table 1
Preparation of PMMA, PTBMA and poly(MMA-*co*-TBMA)s.

Code	TBMA (mol%)[c]		M_n[d] (10^{-3})	M_w/M_n[d]	Yield (%)
	Feed	Copolymer			
H-100[a]	100	100	9.18	2.39	86
H-83[a]	80.0	82.7	8.47	2.54	87
H-65[a]	60.0	64.5	8.47	2.51	85
H-43[a]	40.0	43.1	8.50	2.47	85
H-24[a]	20.0	24.0	8.33	2.46	83
H-0[a]	0	0	9.22	2.22	83
M-78[b]	75.0	78.0	4.60	1.69	55
M-54[b]	50.0	53.8	5.70	1.56	45
M-29[b]	25.0	29.2	6.34	1.39	35

[a] Conditions: $[\mathrm{AIBN}]_0 = 0.5$ mol% of monomer.
[b] Conditions: $[\mathrm{AIBN}]_0 = 20$ mol% of monomer.
[c] Determined by ^{1}H NMR.
[d] Determined by SEC in THF calibrated with standard PMMA samples.

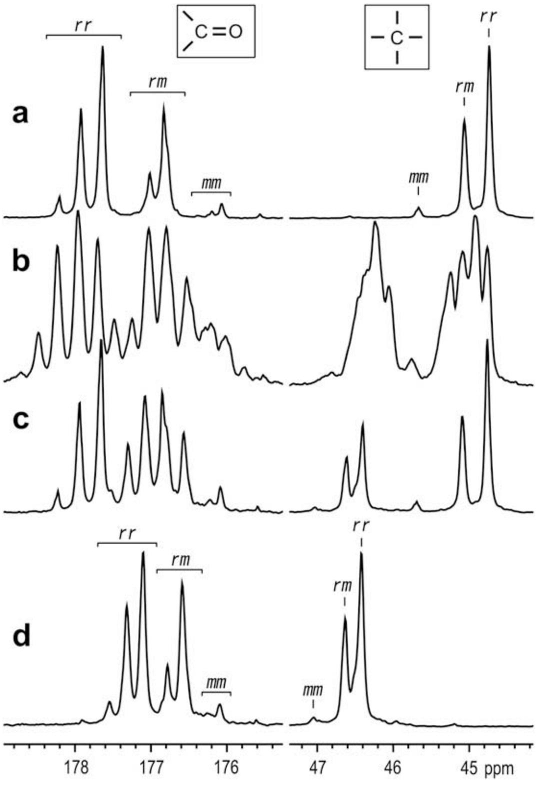

Fig. 1. ^{13}C NMR spectra due to the carbonyl and backbone quaternary carbons of a) PMMA [H-0], b) poly(MMA-*co*-TBMA) [H-43], c) homopolymer blend [B-42], and d) PTBMA [H-100] (in chloroform-*d* at 55 °C and 100 MHz).

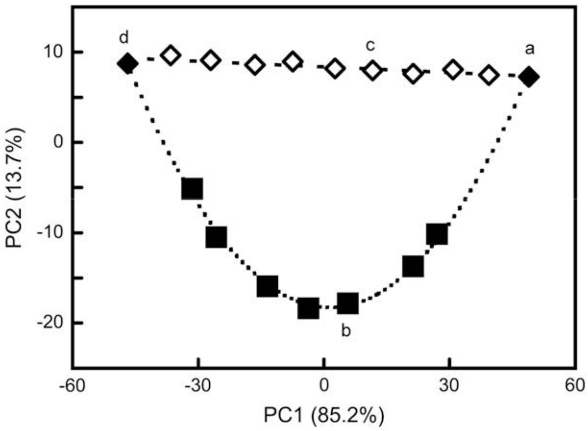

Fig. 2. Principal component score plots for the carbonyl and backbone quaternary ^{13}C NMR signals of homopolymers (◆), homopolymer blends (◇) and copolymers (■). See Fig. 1 for the abbreviations a–d.

The PC1 scores for all polymer samples increased linearly with decreasing TBMA unit composition. The relationship between the PC1 score (y) and the chemical composition in mol% of TBMA units (x) was derived as the following equation with a correlation coefficient (R^2) of 0.997:

$$y = -0.975x + 50.7$$

The close correlation between the chemical composition and the PC1 scores for *all* polymer samples suggests that the chemical composition of a given copolymer could be determined by multivariate analysis of the NMR spectra of the copolymer and the homopolymer blends. PLSR was performed using the bucket-integral data sets for the homopolymer blends and the chemical composition data shown in Table 2 as a training (reference) set. The first latent variable was found to explain 99.9% of the spectral information. The chemical compositions of the seven copolymers determined by the PLSR (z) agreed with those determined by ^{1}H NMR within ± 3.4% and with an R^2 of 0.998. The relationship between x and z was derived as follows:

$$z = -0.998x + 0.751$$

The results of our preliminary investigation suggest that the multivariate analysis of NMR spectra should be useful for the quantitative characterization of a wide range of copolymers including terpolymers, tetrapolymers as well as for complex polymer mixtures in addition to the examples shown here. The NMR spectra of several relevant homopolymers, copolymers and/or their blends are all that is required, for use as training data sets, to carry out the multivariate analysis of the NMR spectrum of a given polymer sample. In principle, no assignment of resonance peaks is required. Further investigation is now under way to extend the possibility of this method to the determination of comonomer sequence distributions, stereoregularity and irregular structures in polymers.

References

[1] Brar AS, Kapur GS. Polym J 1988;20:811–7.
[2] Nishiura T, Kitayama T, Hatada K. Int J Polymer Anal Char 2000;5:401–13.
[3] Kowalski BR, Bender CF. J Am Chem Soc 1972;94:5632–9.
[4] Kowalski BR, Bender CF. J Am Chem Soc 1973;95:686–93.
[5] Wold S. Technometrics 1974;16:1–11.
[6] Shimoyama M, Maeda H, Matsukawa K, Inoue H, Ninomiya T, Ozaki Y. Vib Spectrosc 1997;14:253–9.
[7] Shimoyama M, Hayano S, Matsukawa K, Inoue H, Ninomiya T, Ozaki Y. J Polym Sci B Polym Phys 1998;36:1529–37.
[8] Hughes J, Shanks R, Cerezo F. J Therm Anal Calorim 2004;76:1069–78.
[9] Krishnan P, Kruger NJ, Ratcliffe RG. J Exp Bot 2005;56:255–65.
[10] Holmes E, Tang H, Wang Y, Seger C. Planta Med 2006;72:771–85.
[11] Viant MR, Ludwig C, Gunther UL. Metabolomics, metabonomics and metabolite profiling. In: Griffiths WJ, editor. Cambridge: Royal Society of Chemistry; 2008. p. 44–70 [chapter 2].
[12] Coen M, Holmes E, Lindon JC, Nicholson JK. Chem Res Toxicol 2008;21:9–27.
[13] Tarachiwin L, Ute K, Kobayashi A, Fukusaki E. J Agric Food Chem 2007;55:9330–6.
[14] Tarachiwin L, Katoh A, Ute K, Fukusaki E. J Pham Biomed Anal 2008;48:42–8.
[15] Brekke T, Kvalheim OM. Signal treatment and signal analysis in NMR. In: Rutledge DN, editor. Elsevier; 1996. p. 422–51 [chapter 20].
[16] Alam TM, Alam MK. Ann Rep NMR Spectrosc 2005;54:41–80.
[17] Yuki H, Okamoto Y, Shimada Y, Ohta K, Hatada K. J Polym Sci Polym Chem 1979;17:1215–25.
[18] Hill DJT, O'Donnell JH, Pomery PJ, Whittaker MR. Polym Gels and Networks 1995;3:85–97.