Polymer Bulletin 29, 689–696 (1992)

Polymer Bulletin

A GPC method to determine the composition of two component copolymers

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Summary

The overall composition of random and block copolymers comprising two kinds of repeat units can be determined as a function of molecular weight by a new dual (e.g., UV and RI) detector GPC technique, if one of the repeat units can be specifically "seen" by one of the detectors. The method is demonstrated by the use of random copolymers of styrene (St) and isobutylene (IB) as the UV "visible" and "invisible" components, respectively. Novel triblock copolymers comprising two polyacenaphtylene (PAc) outer-segments and a polyisobutylene (PIB) mid-segment are also analyzed.

Introduction

The most common contemporary method to determine the molecular weight of polymers is the GPC technique. This technique, particularly by the use of modern dual detectors (i.e., refractive index and UV absorption detectors) provides not only molecular weights but compositional information also.
This communication describes a simple new method for the determination of the overall composition of two component copolymers (blocks, random, alternating etc.) as a function of molecular weights by using commercially available dual detector (RI and UV) GPC instrumentation. This method is being used in our laboratories for the analysis of two-component copolymer systems, one of which is UV visible (e.g, St) the other invisible (e.g., IB). A similar method which employs RI and UV traces for the analysis of PIBs containing an aromatic initiator residue has been described and is being used extensively (1,2). The UV and RI detector signals were used to estimate the distribution of functionality in functionalized ethene-propene-norbornene terpolymers (3). The degree of functionality was measured separately.

Theoretical

The signals of the RI and UV detectors of the GPC equipment must be strictly proportional to the concentration of the macromolecules analyzed and as a consequence,

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the area under the GPC traces must be strictly proportional to the total amount of the macromolecules in the sample. If a dilute solution of two or more different macromolecules passes through the detectors, the response of the detectors will be additive in respect to the individual constituents. Specifically, if a solution of homopolymers *1* and *2* passes through a dual (i.e., RI and UV) detector GPC instrument, the following equations are valid:

$$U = a_1c_1 + a_2c_2 \quad [1]$$

$$R = b_1c_1 + b_2c_2 \quad [2]$$

$$rA_U = a_1m_1 + a_2m_2 = r\int Udt \quad [3]$$

$$rA_R = b_1m_1 + b_2m_2 = r\int Rdt \quad [4]$$

where U and R, respectively, are the magnitudes of the signals of the UV and RI-detectors, (both baseline corrected); c is the concentration (g/100cm^3 or mol monomer units/L); A is the area under the GPC traces calculated by integration according to time; a and b, respectively, are the specific UV and RI responses; m is the total amount of the homopolymer (g or mol monomer units) which passes through the detector during time t; and r is the volumetric rate of the flowing eluent. Eq. 3 was derived from Eq. 1 in the following manner: Since

$$m=r\int cdt \quad \text{and} \quad U=ac;$$

combination of these equations yields

$$m=r\int(U/a)dt \quad \text{and} \quad r\int Udt=am.$$

Similarly Eq. 4 was derived from 2. After rearrangement one gets for the fractions of component *1*:

$$c_1/(c_1+c_2) = (b_2U-a_2R)/[(a_1-a_2)R-(b_1-b_2)U] \quad [5]$$

$$m_1/(m_1+m_2) = (b_2A_U-a_2A_R)/[(a_1-a_2)A_R-(b_1-b_2)A_U] \quad [6]$$

Eq. 5 gives the composition of the mixture at time t, and Eq. 6 gives the average composition of the whole sample.

The values of a and b can be determined by calibration and are valid only for a given GPC system; these quantities must be checked from time to time.

The detectors must be in series. The time lag between the detectors can be readily determined by the use of an internal standard.

These equations were developed for two individual homopolymers. We assume that the additivity remains valid even if the two homopolymers are linked to each other, i.e., they form a block copolymer. It is further assumed that this additivity is valid for both the RI and UV responses for random etc. copolymers, provided the repeat units in the two homopolymers or in the copolymers (random, alternating, tapered, etc.) are linked by σ bonds.

If the first component is UV inactive (e.g., PIB) so that $a_1=0$, Eqs 5 and 6 can be rearranged to yield:

$$c_1/(c_1+c_2) = (Ub_2/a_2-R)/[(b_2/a_2-b_1/a_2)U-R] \quad [7]$$

$$m_1/(m_1+m_2) = (A_Ub_2/a_2-A_R)/[(b_2/a_2-b_1/a_2)A_U-A_R] \quad [8]$$

a_2, b_1, and b_2/a_2 can be obtained by the use of calibration curves (see Figures 1, 3, and 4). b_2 could be determined in this manner but the relative error is somewhat lower if the b_2/a_2 ratio is determined directly from the relationship between A_U and A_R (see Figure 4).

Error Analysis

Errors arise from the error of the calibration constants (a_2, b_1, and b_2/a_2) and from the uncertainty in the UV and RI readings. For simplicity, the errors of the results given by

Eqs 7 and 8 will be calculated. We used the general error proliferation rule (2).
Let ΔU denote the uncertainty in the UV readings (~30 arbitrary units) and ΔR that in the RI reading (~1.5 arbitrary units). Δu and Δr characterize the background noise of the instrument and were found to be constant for months. Their values were estimated from constant base lines. The error of the corrected U_i value in all equations is:

$$\Delta U_i=\Delta U[(t_i-t_a)^2+(t_i-t_b)^2+(t_a-t_b)^2]^{1/2}/(t_a-t_b) \quad [9]$$

where t_a and t_b are the (abscissa) values of the points on the UV trace used to determine the equation of the base line under the peak. t_b is located before or at the beginning of the peak, t_a is after or at the end of the peak, and t_i is the (abscissa) value (e.g. retention time) of the i^{th} individual point on the chromatogram. Eq. 9 shows that the farther t_a and t_b are from each other, the smaller the error of the corrected UV reading.
The integrals were calculated with Simpson's rule (4), i.e.:

$$A_U=h(U_1+4U_2+2U_3+4U_4+...+2U_{n-2}+4U_{n-1}+U_n)/3 \quad [10]$$

where *1*, *2*, *3*, ... are the indexes of the individual readings (i.e., the actual values of *i*), *n* is their total number, and *h* is the time interval between readings (in our case h=5 s). The error of the integral is:

$$\Delta A_U = h[(\Delta U_1)^2+16(\Delta U_2)^2+4(\Delta U_3)^2+16(\Delta U_4)^2+ ... \\ ...+4(\Delta U_{n-2})^2+16(\Delta U_{n-1})^2+(\Delta U_n)^2]^{1/2}/3 \quad [11]$$

The error of the formula is negligible relative to the error of the measurement.
The errors ΔR_i and ΔA_R can be estimated similarly.
Using the error proliferation rule (2), one obtains for the error of the composition at an individual point of the chromatogram (given by Eq. 7):

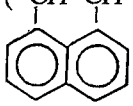
$$\left(\Delta\frac{c_1}{c_1+c_2}\right)_i^2 = b_i^2\,\frac{R_i^2(\Delta U_i)^2 + U_i^2(\Delta R_i)^2 + U_i^4[\Delta(b_2/a_2)]^2}{a_2^2[(b_2/a_2 - b_1/a_2)U_i - R_i]^4} + \\ + U_i^2\,\frac{(U_ib_2/a_2 - R_i)^2[(\Delta b_1)^2 + (\Delta a_2)^2b_1^2/a_2^2]}{a_2^2[(b_2/a_2 - b_1/a_2)U_i - R_i]^4} \quad [12]$$

The error of $[c_2/(c_1+c_2)]_i$ is the same as that of $[c_1/(c_1+c_2)]_i$, because $[c_2/(c_1+c_2)]_i = 1 - [c_1/(c_1+c_2)]_i$. The error of the overall composition can be estimated by using Eq. 12 by substituting U_i by A_U, R_i by A_R, ΔU_i by ΔA_U, and ΔR_i by ΔA_R.

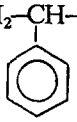
Experimental

A Waters HP GPC assembly was used. The eluent was THF pumped at 1mL/min. The concentration of the samples was 0.2 - 0.4 %(w/v). Sulfur was the internal standard. The columns were loaded with 100 µL samples. The first detector was a Waters Model 440 UV Absorbance Detector set at 365 nm at the sensitivity range of 0.02. The second one was a Waters 410 Differential Refractometer, with its scale factor set at 20. The time lag between the detectors was 15 s. The detectors were connected to two Nelson Analytical Model 960 intelligent interfaces. The interfaces were controlled from an Epson Equity III+ computer using the Model 2600 Chromatography Software Version 4.0.
The software provided the areas under the GPC-traces as the integral of the detector signal as a function of time (i.e. A_U and A_R in Eqs 3 and 4). The interfaces collected the data with 0.2 Hz frequency (every 5th s). The retention time of the internal standard was about 57 min.

The software stored all introductory information (e.g. origin of the sample, calibration file, etc.) in the files with extension .hdr, and the raw data (i.e. detector readings) were stored under the same file names but with extension .pts. To calculate the compositions according to Eqs 5 and 6, the data were used and stored in the .pts extension files.
We have investigated three homopolymers: i.e., polyisobutylene (PIB), polyacenaphtylene (PAc), and polystyrene (PSt). The calibration was done with the homopolymers.
The preparation of PIB, $-(-CH_2-C(CH_3)_2-)_n-$ has been described (5), M_n=28,000, M_w/M_n=1.12; The preparation of PAc, $-(-CH-CH-)_n-$



is given in (6), M_n=1,700; M_w/M_n=2.16; PSt, $-(-CH_2-CH-)_n-$,



(Polyscience) M_n=7,900; M_w/M_n=1.11 was used for calibration purposes.
Two copolymers were also investigated: A random copolymer of IB and St (P(IB-co-St)) (7) and a PAc-PIB-PAc triblock (6). In all equations IB has the index *1* and, since PIB is UV inactive, a_1=0.

Results and Discussion

1. The P(IB-*co*-St) System

The calibration curve to determine b_2 is shown in Figure 1.

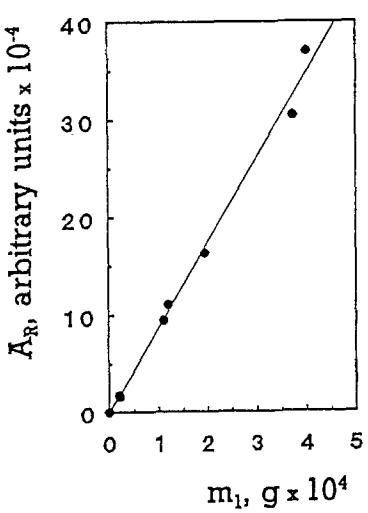


Figure 1: The area under the RI trace (A_R) as a function of PIB (m_1) passed through the RI detector; m_2=0 and r=1mL/min in Eq.4

As shown by the data in Figure 1, the relationship between the areas under the RI traces and the number of IB units that passed through the detector is linear starting from the origin. The slope gives:
$b_1 = (8.59\pm0.57)\times10^8$ arbitrary units/g.
An identical calibration was done to determine the proportionality between the area under the UV trace of the PSt sample and the number of St units that passed through the UV detector. This correlation was also linear starting from the origin, and the slope gave:
$a_2 = (9.72\pm0.10)\times10^9$ arbitrary units/g.
The areas under the UV traces and the corresponding areas under the and RI traces yielded b_2/a_2 as determined in the case of PAc (see Section below).

For PSt: $b_2/a_2 = (1.640\pm0.016)x10^{-2}$

Using these constants, the composition as a function of MW of a random P(IB-co-St) copolymer was calculated (see Figure 2). Figure 2 shows the UV and RI traces and the IB content (calculated by Eq. 7) and the associated error (dotted line calculated by Eq. 12). Evidently, the lower the molecular weight of the copolymer the higher its IB content. In the absence of this method laborious fractionation and fraction analysis were necessary to determine the relationship between copolymer composition and molecular weight.

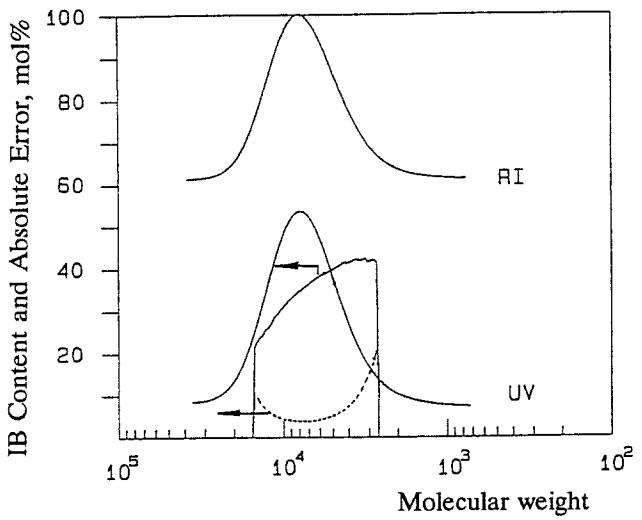


Figure 2. The composition of a random P(IB-co-St) copolymer (solid line) and its error (broken line) as functions of the molecular weight (PIB calibration)

The overall composition of this random P(IB-co-St) was calculated by Eq. 8. According to this method, it contained 35.0±2.0 mol% IB and 65.0±2.0 mol% St. The composition obtained by ^{1}H NMR spectroscopy was 36 mol% IB and 64 mol% St. Furthermore, the synthesis charge contained 36 mol% IB and 64 mol% St and both monomers were completely consumed. These independent data are in very good agreement and substantiate the accuracy of the new method.

A large number of other random P(IB-co-St) copolymers were tested by this methodology, and the compositions calculated by GPC were always in good agreement with those obtained by ^{1}H NMR spectroscopy (5).

Thus, evidently, the assumption in regard to UV and RI additivity is valid in the case of random P(IB-co-St) copolymers.

2. The PAc-PIB-PAc System

The value of b_1 was the same as used for PIB (see above). Figure 3 shows the areas under the UV traces (i.e. the A_U values) as a function of the number of Ac units that passed through the detector. The slope of the rectilinear plot gives

a_2 = (8.85±0.19)x10^{11} arbitrary units/g.

The A_R values in Figure 3 were plotted against A_U, the corresponding areas under the UV traces. Thus Figure 4 shows the A_R versus A_U relationship, and the slope of the linear plot yields

b_2/a_2 = (1.988±0.035)x10^{-3}

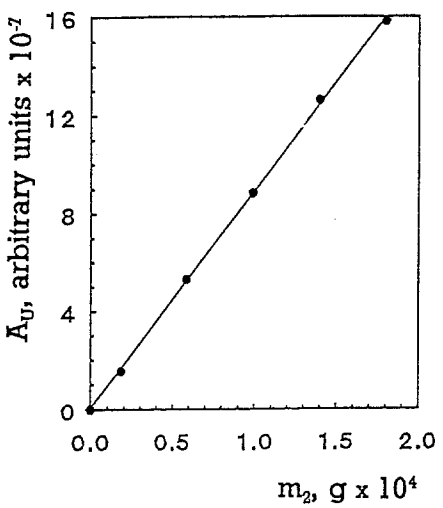


Figure 3. The area under the UV trace (A_U) as a function of PAc (m_2) passed through the UV detector; m_1=0 and r=1mL/min in Eq.4

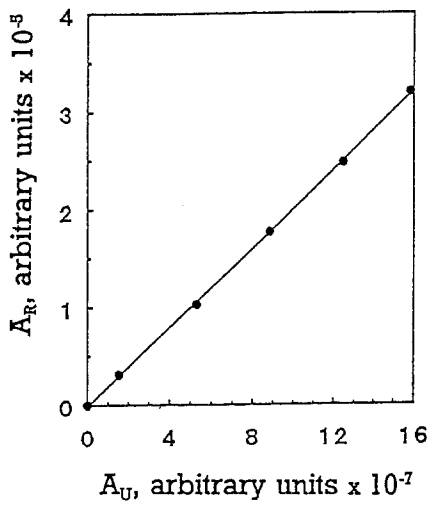


Figure 4. The area under the RI trace as a function of the area under the UV trace in the case of PAc; $b_2/a_2=A_R/A_U$ if m_1=0 in Eqs 3 and 4

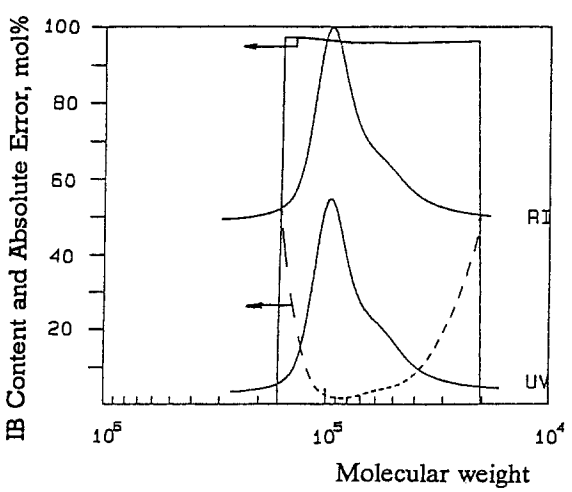


Figure 5. The composition of a PAc-PIB-PAc triblock (solid line) and its error (broken line) as functions of molecular weight (PIB calibration)

Figure 5 shows the UV and RI traces, and the composition, as the function of the molecular weight of a representative PAc-PIB-PAc triblock. The absolute error of the composition is indicated by the broken line. (The shoulders visible in the RI and UV traces at M_n ~6000 arise from the PIB used for the synthesis of the PAc-PIB-PAc; the discussion of the synthesis details, however, falls outside the scope of this communication.) According to Eqs 8 and 12 the product contains 96.15±0.59 mol% IB and 3.85±0.59 mol% Ac. The composition determined by ^{1}H NMR spectroscopy gave 96 mol% IB and 4 mol% Ac. Thus, the results obtained by two independent analytical methods are in very good agreement.

The molecular weight of the fraction corresponding to the peak can be calculated by assuming that the peak shifts only after blocking. The peak MW of the PIB fraction was 78,000 before blocking and the peak indicates 90.8 wt.% IB in the triblock. According these data the MW of the triblock fraction at the peak is 85,900.

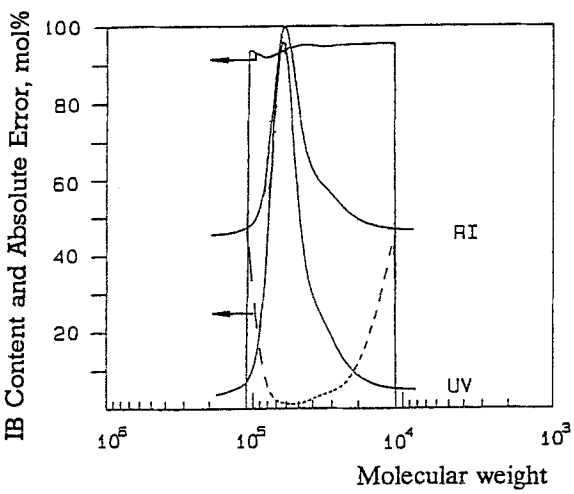


Figure 6. The composition of a PAc-PIB-PAc triblock (solid line) and its error (broken line) as functions of molecular weight (PIB calibration)

Figure 6 shows the composition of another representative PAc-PIB-PAc triblock as a function of MW. The average IB content is 96.00±0.62 mol% and that of Ac is 4.00±0.62 mol%. ^{1}H NMR spectroscopy gave 94 mol% IB and 6 mol% Ac. The composition at the peak is 90.23 wt.% IB and 9.77 wt.% Ac. The MW of the PIB at the peak was 74,800 before blocking. Thus the MW of the triblock fraction at the peak is 82,900.

Limitations of the Method

A limitation of this methodology is that, just as NMR or IR spectroscopy, it does not distinguish between homopolymer contaminants and true copolymer. The method will give reliable overall composition/MW information only if it is independently ascertained that the material is homogenous (i.e., it is a block copolymer, or a random copolymer, etc.)

and is not a mixture of diverse species. This information can be obtained, for example, by preliminary GPC studies, when the GPC traces show a reasonably narrow distribution. In case GPC shows bi- or multimodality, the material must be fractionated prior to analysis.
A complication may arise if one (or both) of the components contains a bulky side group which interact with each other differently in the homopolymer than in the (random, alternating, tapered) copolymer. Suitable calibration may remove this complication (see the case of Ac, above).

Acknowledgement

Drs. I. Majoros and A. Nagy kindly provided the random isobutylene-styrene copolymer. This work was supported by the National Science Foundation Grant 89-20826 and INT-89-05410.

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Accepted October 12, 1992 K