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Effects of the Sequence Distribution of Poly(acrylonitrile−butadiene) Copolymers on the Surface Chemical Composition As Determined by XPS and Dynamic Contact Angle Measurements

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Introduction. Poly(acrylonitrile−butadiene) rubbers (NBRs) are used for various purposes because of their oil-resistant characteristics. Methods have already been established to determine average molecular weights, molecular-weight distribution, acrylonitrile content, and microstructures of NBRs. However, the oil-resistant characteristic, which is one of the most important properties of NBRs, is known to be dependent not only on the acrylonitrile content but also on the surface morphology and surface composition. Therefore, it is necessary to study the surface structure and properties of NBRs.

X-ray photoelectron spectroscopy (XPS) has been widely used to study the surface of copolymers and polymer blends, and it can provide a quantitative measure of the surface chemical composition.[1−3] In addition, angle-resolved XPS analyses can provide information on the homogeneity of the composition and structure in the topmost 15−70 Å of a polymer surface.[4,5]

The surface segregation in copolymers is governed by several factors. The thermodynamic driving force for minimizing the total free energy of the system results in preferential surface segregation of the lower surface energy constituent of the polymer. However, a number of other factors, such as the relative length of the blocks, their sequence length distribution and the concentration of the constiuents may also play an important role in determining the surface composition of copolymers. Briggs and co-workers[6,7] have done extensive work in characterization of segmented poly(ether urethanes) by surface analysis techniques. Their results show that there may be a very small amount of, or no, hard segment present at the uppermost surface.

A detailed characterization of a series of acrylonitrile-*co*-methyl methacrylate statistical copolymers and "blocky" copolymers (average polyacrylonitrile sequence lengths >100) by XPS has been performed by Kulmer et al.[8] Their results indicate that the surface composition of the statistical copolymers is same as the bulk. However, the surface of the "blocky" copolymers shows an excess of poly(methyl methacrylate). Another study of copolymer surfaces by XPS also shows that the surface composition of a series of dimethylsiloxane−urea−urethane segmented copolymers depends on the lengths of the segments.[9] The surface concentration of the poly(dimethylsiloxane) (PDMS) increases with the length of this segment. The topmost surface of the copolymers is nearly 100% PDMS when the segmental molecular weight reaches 27 000.

Table 1. Characterization of NBRs

polymers	bulk composition (wt %)[a]		
	1, 2-(vinyl) BD	1,4 (cis and trans) BD	AN
PB	93.20	6.80	0.00
NBR-23	7.31	69.76	22.93
NBR-29	0.00	70.92	29.08
NBR-30	6.44	63.61	29.96
NBR-35	12.70	52.56	34.74
NBR-40	0.00	60.53	39.47

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

Table 2. Peak Intensities of Olefinic Carbons in ^{13}C NMR Spectra of NBRs

sequence[a] triad and tetrad	intensity (%)[b]				
	NBR-23	NBR-29	NBR-30	NBR-35	NBR-40
ABB	9.85	14.88	11.95	15.57	17.27
ABA/BAB	25.71	37.81	31.76	36.30	52.17
BBBB	2.33	0.00	0.00	0.00	0.00
BBBA	4.77	5.03	5.04	4.01	0.00
BBB	38.05	26.69	31.08	18.10	8.95
VV/VB	8.39	0.00	7.23	8.63	0.00
ABBA	7.08	8.88	7.96	9.10	6.69
AAB	3.82	6.71	4.97	7.21	12.84
AAA	0.00	0.00	0.00	1.09	2.09

[a] A = acrylonitrile unit; B = 1,4-butadiene unit; V = 1,2-butadiene. [b] Relative intensities were calculated from those of olefinic peaks.

In this paper, the effects of the sequence distribution of NBRs, determined by ^{13}C NMR, on the surface chemical composition, determined by XPS and dynamic contact angle (DCA) measurements, were studied.

Experiment. All polymer materials used were obtained from Scientific Polymer Products, Inc. and a full listing is presented in Table 1. NBRs were dissolved in tetrahydrofuran (THF) and precipitated in methanol and then washed with *n*-hexane twice to remove the additives. The purified NBRs were then vacuum-dried at 40 °C and stored in a dessicator. The bulk compositions were determined by ^{1}H-NMR and the sequence distribution was determined by ^{13}C-NMR.[10−13] The sequence distribution of NBRs is shown in Table 2. Polybutadiene and polyacrylonitrile (PAN) were used as received. All polymers were dissolved in either THF or *N*,*N*-dimethylforamide (DMF). Solutions of approximately 3 wt % polymer were prepared. The XPS samples were prepared by spin-casting the polymer solutions onto silicon wafers.

^{13}C-NMR measurements were performed using a JEOL JNM EX-400 NMR spectrometer operating at 100.40 MHz. The samples were dissolved in chloroform-d_1. Solutions of approximately 5 wt % polymer were prepared. A pulse width and pulse delay of 5.1 and 13.3 μs, respectively, were used. For each spectrum, 2000 scans were made and 32 768 data points were acquired over acquisition time of 1088 s. ^{1}H-NMR measurements were carried out at 399.65 MHz.

Dynamic contact angle measurements were made using a Cahn DCA-322 analyzer operating at 25 °C and with the stage moving at a speed of 50.4 μm/s. Solutions of approximately 3 wt % polymer were prepared. Ultraclean glass slides of 18 mm × 18 mm were slowly dipped into the polymer solutions, coating both sides uniformly. These samples were air-dried for about 0.5 h, followed by further drying under vacuum at room temperature for 24 h.

XPS spectra were recorded on a PHI 5600 multitechnique system in the fixed analyzer transmission mode

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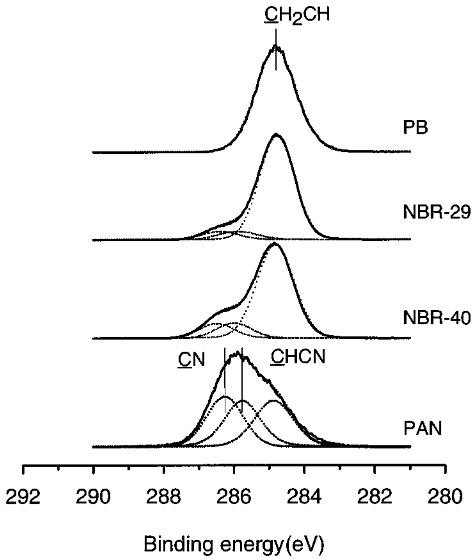

Figure 1. XPS spectra of PAN, PB, and NBR copolymers.

using a monochromatic Al Kα X-ray source. The pass energies were 23.5 and 188 eV for the measurements of the core-level spectra and survey scans, respectively. Charge neutralization was achieved by using a low-energy electron flood gun. Binding energies were referenced to the C_{1s} peak of the aliphatic carbon (set at 284.8 eV). All measurements except angle-resolved measurements were performed at an emission angle of 45° (the angle between the exit photoelectrons and the surface normal). For angle-resolved measurements, the emission angle varied from 75 to 25°, corresponding to sampling depths of approximately 30−70 Å, respectively (the attenuation length is assumed to be 22 Å[14]). A linear-background method removed the XPS background, and curve-fitting used an iterative least-squares fitting routine.

Results and Discussion. XPS analyses of the homopolymers (PAN and PB) were used to determine the surface chemical composition of the pure materials and also to determine the binding energy of various functional groups and full width at half-maximum (FWHM) of the peaks in the C_{1s} high-resolution spectra. The XPS survey spectra of the homopolymers show that only peaks corresponding to the elements expected from the bulk are present, ensuring sample purity.

Figure 1 shows the high-resolution spectra for PB, NBR-29, NBR-40, and PAN. There are few XPS studies on PAN.[8,15−18] The most recent one indicates that the C_{1s} peak comprises of three peaks which correspond to CH_2, CH−CN, and C≡N groups.[18] Our curve fitting of the PAN and NBR C_{1s} spectra reveals that the peaks at 284.8, 286.0 ± 0.2, and 286.4 ± 0.2 eV are identified as the CH_2, CH−CN, and C≡N groups, respectively. The ratio of the peak areas of the functional groups, CH_2:CH−CN:C≡N, is approximately equal to the expected values of 1:1:1 for PAN. These results are similar to those reported.[18] The concentrations of the AN group of the NBR copolymers were determined by using the C_{1s}/N_{1s} peak-area ratios obtained from the spectra for PAN and NBRs. The surface concentration of the AN group in the NBR is calculated by the following equation:

$$\frac{[A(C_{1s})/A(N_{1s})]_{NBR}}{[A(C_{1s})/A(N_{1s})]_{PAN}} = \frac{4(1-w)/54}{3w/53} + 1 \qquad (1)$$

$A(C_{1s})$ and $A(N_{1s})$ are the areas for C_{1s} and N_{1s} peaks, respectively, and w is the weight fraction of the AN group. The two ratios—$[A(C_{1s})/A(N_{1s})]_{NBR}$ and $[A(C_{1s})/A(N_{1s})]_{PAN}$—are determined from the NBR and PAN spectra, respectively.

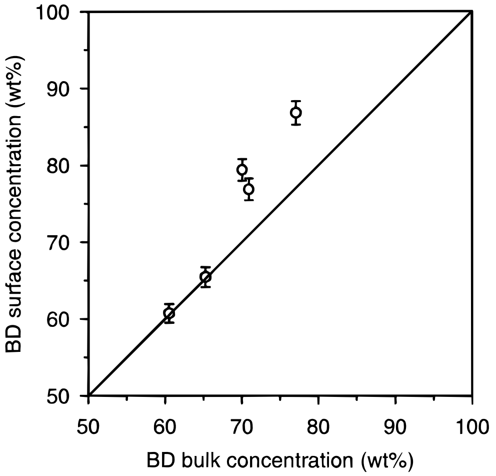

Figure 2. surface concentration (wt %) vs the BD bulk concentration (wt %).

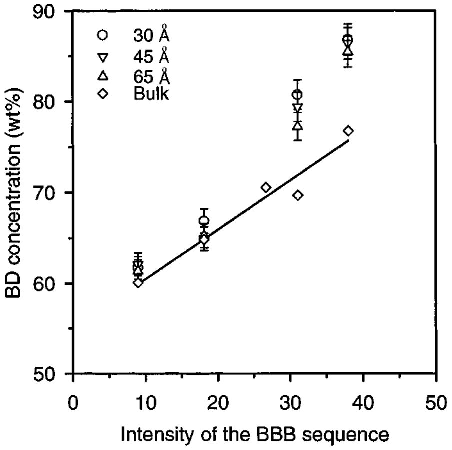

Figure 3. BD surface concentration (wt %) as a function of the relative intensity of bulk triad (BBB) sequence of NBRs at different sampling depths.

Table 3. XPS Results Showing the Surface Composition for NBR Copolymers

samples	bulk fraction AN (wt %)	surface fraction AN (wt %)
NBR-23	22.93	14.87
NBR-29	29.08	23.15
NBR-30	29.96	20.51
NBR-35	34.74	34.56
NBR-40	39.47	39.29

The bulk composition determined by ^{1}H-NMR and the surface composition of the NBRs determined by XPS are summarized in Table 3. Figure 2 shows the relationship between the BD surface concentration and the BD bulk concentration. The surface compositions of NBR-35 and NBR-40 are very close to their bulk compositions.

To investigate the possible relationship between the surface chemical composition and the molecular structure of the copolymers, XPS and ^{13}C NMR results are compared. One of the major differences between the copolymers showing BD surface segregation (NBR-23, NBR-29, and NBR-30) and the copolymers showing no surface segregation of the BD group (NBR-35 and NBR-40) is the triad sequence (BBB), as indicated by the

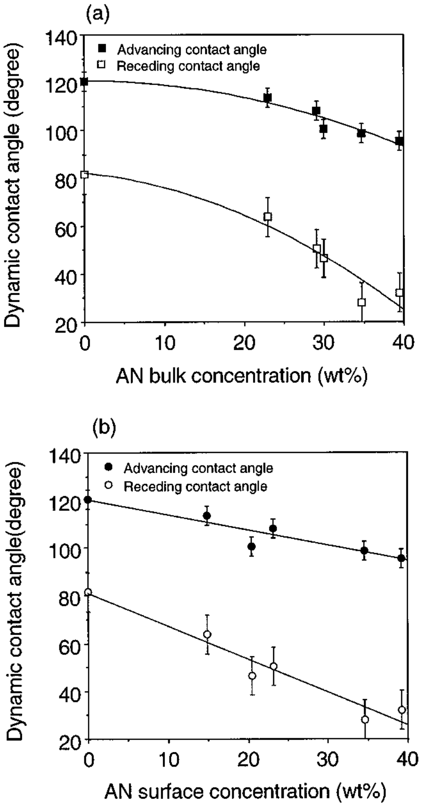

Figure 4. (a) Dynamic contact angle of PB and NBR copolymers as a function of the AN bulk concentration. (b) Dynamic contact angle of PB and NBR copolymers as a function of the AN surface concentration.

results shown in Tables 2 and 3. Surface segregation of the BD group occurs in copolymers with a high intensity of the triad sequence (BBB). However, the intensity of the other triad sequence ABB does not have any major effect on the surface segregation of the BD group. This is indicated by the fact that the intensity of ABB is much higher (17.27%) for NBR-40 than for NBR-23 (9.85%) yet there is no detectable surface segregation of the BD group for NBR-40. A plot of the BD surface composition at different sampling depths versus the intensity of the triad (BBB) sequence in the bulk is presented in Figure 3. For NBR copolymers (NBR-35 and NBR-40) with a low BBB intensity, the surface chemical compositions are homogeneous (no surface segregation of the BD groups, the lower surface energy component of the copolymer) over the sampling depths of the XPS experiment (30−70 Å), as shown in Figure 3. The BD surface concentration increases with the intensity of the BBB sequence. Maximum BD surface segregation is observed for the copolymer with the highest BBB intensity. From these results, it is clear that the sequence distribution and its intensity play an important role in determining the surface properties of copolymers. These results further suggest that a minimum length of the BD segment (BBB) and its intensity above a certain value are needed for the surface segregation of the BD groups to occur. The effect of annealing and solvent on the surface composition of the copolymers will be discussed in a forthcoming paper.[19]

The solid surface tension of the homopolymer (PB) and copolymer (NBRs) was determined by dynamic contact angle measurements. The dynamic contact angles of the homopolymer and the copolymers are shown in Figure 4. Although the dynamic contact angles (θ_{Adv} and θ_{Rec}) are not exact measurements of the surface free energy,[5] a comparison of the relative values can provide an empirical measure of the surface tensions. Figure 4a shows that both advancing and receding dynamic contact angles decrease as the AN content increases, indicating that the AN group is the higher surface energy component of the copolymers. In addition, surface segregation of the BD segments in NBR-23, NBR-29, and NBR-30 also increases the dynamic contact angle values. Figure 4b shows the plot of advancing and receding contact angles as a function of AN surface concentration, indicating a linear relationship between the contact angle and the AN surface concentration.

Conclusions. The results of XPS and ^{13}C NMR analyses suggest that surface segregation of the lower surface energy segment (BD) of the NBR copolymers occurs only when the BD segment length is at least equal to the length of the BBB segment and the BBB intensity is above a certain value.

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References and Notes

(1) McGrath, J. E.; Dwight, D. W.; Riffle, J. S.; Davidson, T. F.; Webster, D. C.; Vishwanathan, R. *Polym. Prepr., ACS Div. Polym. Chem.* **1979**, *20* (2), 528.
(2) Green, P. F.; Christensen, T. M.; Russell, T. P.; Jerome, R. *Macromolecules* **1989**, *22*, 2189.
(3) Lhoest, J. B.; Bertrand, P.; Weng, L. T.; Dewez, J. L. *Macromolecules* **1995**, *28*, 4631.
(4) Bhatia, Q. S.; Burrel, M. C. *Polymer* **1991**, *32*, 1948.
(5) Chan, C. M. *Polymer Surface Modification and Characterization*; Hanser: New York, 1994.
(6) Hearn, M. J.; Ratner, B. D.; Briggs, D. *Macromolecules* **1988**, *21*, 2950.
(7) Hearn, M. J.; Briggs, D.; Yoon, S. C.; Ratner, B. D. *Surf. Interface Anal.* **1987**, *10*, 384.
(8) Kulmer, P. L.; Matteson, H. L.; Gardella, J. A., Jr. *Langmuir* **1991**, *7*, 2479.
(9) Chen, X; Gardella, J. A., Jr.; Ho, T.; Wynne, K. J. *Macromolecules* **1995**, *28*, 1635.
(10) Kondo, A.; Ohtani, H.; Kosugi, Y.; Tsuge, S.; Kubo, Y.; Asada, N.; Inaki, H.; Yoshioka, A. *Macromolecules* **1988**, *21*, 2918.
(11) Suzuki, T; Takegami, Y.; Furukawa, J.; Kobayashi, E.; Arai, Y. *Polym. J.* **1973**, *4*, 657.
(12) Segre, A. L.; Delfini, M.; Conti, F.; Boicelli, A. *Polymer* **1975**, *16*, 338.
(13) Bajaj, P.; Padmanaban, M.; Gandhi, R. P. *Polymer* **1985**, *26*, 391.
(14) Clark, D. T.; Thomas, H. R. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2843.
(15) Dwight, D. W.; McGrath, J. L.; Wightman, J. P. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **1978**, *34*, 35.
(16) Hiraoka, H; Lee, W. Y. *Macromolecules* **1978**, *11*, 622.
(17) Barry, A. O.; Riedle, B.; Adnot, A.; Kaliaguine, S. C. *J. Electron Spectrosc. Relat. Phenom.* **1991**, *57*, 47.
(18) Beamson, G.; Briggs, D. *High Resolution XPS of Organic Polymers: The Scienta ESCA 300 Database*; John Wiley and Sons: Chichester, England, New York, 1992; p 184.
(19) Li, L.; Chan, C.-M.; Weng, L. T. Manuscript in preparation.

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