Macromolecules **1992,** *25,* 5287–5290

Blends of Poly(styrene-*stat*-acrylonitrile) and Poly(butadiene-*stat*-acrylonitrile): A Guide to the Butadiene–Acrylonitrile Segmental Interaction

J. M. G. Cowie,* John H. Harris, and Iain J. McEwen

Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, U.K.

Received October 15, 1991; Revised Manuscript Received June 3, 1992

ABSTRACT: A range of butadiene–acrylonitrile and of styrene–acrylonitrile statistical copolymers have been synthesized and blended to establish a value for the segmental interaction energy density between butadiene and acrylonitrile. Two series of blends were examined. In the first series, "internal" blends from butadiene–acrylonitrile copolymers of different composition were found to be miscible only when the compositions differed by less than about 4 vol %. In contrast, blends of butadiene–acrylonitrile copolymers with styrene–acrylonitrile copolymers formed a fairly extensive miscibility region which was analyzed by considering this to form part of a conic section in composition space. A value for the butadiene–acrylonitrile segmental interaction energy density $B_{\text{B-AN}}$ of 33–37 J cm^{-3} appropriately describes the phase behavior in this system.

Introduction

Butadiene–acrylonitrile copolymers (BAN), or nitrile rubbers, were first developed commercially in Germany from 1934 onward, and grades containing from 20% to 45% acrylonitrile are now commonly available.[1] More recently introduced nitrile rubbers contain reactive functions, while hydrogenation produces materials with enhanced heat stability.[2] A further important modification can be obtained by blending these nitrile rubbers with other polymers. Since the majority of blending work has been undertaken within an industrial context, most reports center on the physical properties and commercial uses rather than on the search for miscible regions within BAN blend systems which might produce other mixtures with useful properties. The exception to this is the BAN–poly(vinyl chloride) system which became the first commercial polymer blend available following its introduction[1,3] in the 1940s.

In a previous communication[4] we have reported in some detail the miscibility limits of BAN with chlorinated polyethylenes. BAN has also been described as miscible with other polymers,[5] namely, cellulose acetate–butyrate, poly(chloroprene), styrene–butadiene rubbers, and poly(styrene-*stat*-acrylonitrile) (SAN). A more recent paper[6] has reported upper and lower critical solution phase boundaries in a cast film of BAN (40% AN) with SAN (26% AN), and the viscoelastic behavior of BAN (34% AN) with SAN (also 34% AN) shows this composition combination also to be at least partially miscible.[7] Other researchers have examined the suitability of SAN–BAN blends as potential new thermoplastic elastomers.[8]

In this paper we establish the composition limits of miscibility for BAN + SAN blends and analyze the segmental interactions in this system. As described previously,[9-11] the blend segmental interaction energy density B_{blend} is used as the criterion of miscibility, and a mixture is miscible in all proportions when $B_{\text{blend}} < B_{\text{crit}}$, where B_{crit} is defined in terms of polymer molar volumes $V_{1,2}$ by

$$B_{\text{crit}} = 0.5RT(V_1^{-0.5} + V_2^{-0.5})^2 \quad (1)$$

B_{blend} depends only on copolymer composition[12] and is expressed in terms of segmental interaction parameters B_{ij}. For the general case of two statistical copolymers comprising four different segments, $A_xB_{1-x} + C_yD_{1-y}$

$$B_{\text{blend}} = xyB_{AC} + (1-x)yB_{BC} + x(1-y)B_{AD} + (1-x)(1-y)B_{BD} - x(1-x)B_{AB} - y(1-y)B_{CD} \quad (2)$$

where x and y are volume fraction compositions.

The negative terms in eq 2 have engendered the phrase "intramolecular repulsion effect", applied when discussing the enhanced miscibility exhibited in many copolymer blends. Krause[13] has pointed out that B_{ij} parameters are a measure of the relative strengths of *attractive* forces. Equation 2 is then more correctly interpreted as expressing a global interaction minimum at a specific blend composition. The so-called intramolecular repulsion is simply an artifact of the algebraic form of eq 2 which is, in actuality, a rearrangement of the equation of an ellipse

$$ax^2 + by^2 + cxy + dx + ey + f = 0 \quad (3)$$

where the following interrelations hold:

$$B_{CD} = (b/a)B_{AB} \quad (4)$$

$$B_{AC} = ((a + b + c + d + e + f)/a)B_{AB} + B_{\text{blend}} \quad (5)$$

$$B_{AD} = ((a + d + f)/a)B_{AB} + B_{\text{blend}} \quad (6)$$

$$B_{BC} = ((b + e + f)/a)B_{AB} + B_{\text{blend}} \quad (7)$$

$$B_{BD} = (f/a)B_{AB} + B_{\text{blend}} \quad (8)$$

The form of eqs 4–8 accounts for the need to normalize the equation of an ellipse by using one previously determined B_{ij} to obtain the appropriate set of B_{ij} values as discussed previously.[4,16] An experimental phase boundary in x–y composition space is, or is part of, an ellipse. The coefficients a–f which describe the ellipse can be evaluated, and given the value of B_{AB}, all the remaining B_{ij} values may be calculated from eqs 4–8 since, at the phase boundary, $B_{\text{blend}} = B_{\text{crit}}$.

Experimental Section

The monomers acrylonitrile (AN), butadiene (B), and styrene (S) were obtained from Aldrich. Prior to each copolymerization the butadiene was vacuum distilled into a calibrated cold trap before being introduced into the polymerization vessel. Both the styrene and acrylonitrile were washed with dilute aqueous hydroxide and water until neutral to litmus and dried finally over anhydrous magnesium sulfate. Acrylonitrile was distilled under an atmosphere of nitrogen, and styrene under a reduced pressure of nitrogen, prior to their use.

0024-9297/92/2225-5287$03.00/0

Table I
Characteristics of BAN Samples Used in Phase Studies

designation	AN (vol %)	$10^{-3}M_n$[g] (g mol^{-1})	M_w/M_n	T_g (K)	1,4-trans (%)
BAN18[a]	13.0	22.5	1.6	223	79
BAN24[b]	18.6	109	6.5	231	81
BAN29[c]	23.6	68.7	5.2	246	86
BAN33[c]	27.0	65.7	4.3	250	87
BAN37[c]	30.9	85.6	5.2	251	87
BAN40[c]	33.5	74.8	4.1	258	88
BAN47[d]	39.7	59.0	11	268	86
BAN50[e]	43.0	54.9	3.7	271	87
BAN57[f]	49.6	39.8	2.9	287	87
BAN62[f]	55.5	65.8	1.5	296	82
BAN67[f]	60.3	(64.5)	(1.6)	312	86
BAN70[f]	64.0	(68.1)	(1.5)	319	85

[a] Bayer. [b] Emulsion polymerization. [c] BP. [d] Aldrich. [e] Polysar. [f] Bulk polymerization. [g] Values in parentheses are in poly(ethylene oxide) equivalents.

Table II
Characteristics of SAN Samples Used in Phase Studies

designation	AN (vol %)	$10^{-3}M_n$ (g mol^{-1})	M_w/M_n	T_g (K)
PS[a]		52	1.1	375
SAN6[b]	5.4	124	2.2	381
SAN13	11.9	175	1.8	377
SAN16	14.4	187	1.8	387
SAN19	17.5	198	1.8	376
SAN22	20.3			386
SAN24	21.8	157	2.3	388
SAN30	27.5	190	2.0	390
SAN34	31.3	138		388
SAN40	37.3	215	1.9	390
SAN46	42.8	142		389
SAN67	64.5	200		391

[a] Polysciences. [b] Dow experimental sample.

Table III
Glass Transition Data for BAN–BAN Blends

BAN–BAN pairing	T_g (K)	T_a[a] (K)	t_a[a] (h)	T_{peak} (K)	vol fractn difference
29–47	247, 267				0.16_1
33–47	248, 267				0.12_7
37–40	252	244	3	262	0.02_6
37–47	251, 268				0.08_8
37–50	251, 270				0.12_1
40–47	258, 268				0.06_2
47–50	268	258	64	277	0.03_3
50–57	270, 284				0.06_6
57–62	287, 298				0.05_9
62–67	298, 313				0.04_8
62–70	295, 319				0.08_5
67–70	317	301	8	327	0.03_7

[a] Aging temperature and aging time.

SAN copolymers and BAN copolymers were synthesized by bulk polymerization at 333 K using α,α'-azobis[isobutyronitrile] as initiator. A further BAN sample was prepared at 323 K using aqueous emulsion polymerization with sodium lauryl sulfate as surfactant and potassium persulfate as initiator. All copolymerizations were carried out under vacuum and conversions restricted to less than 10% to limit composition drift. Products were isolated by precipitation into an excess of methanol. Two further reprecipitations from dichloromethane solution into methanol were carried out prior to drying for 48 h under vacuum, followed by elemental analysis to determine average composition. Commercial samples were also twice reprecipitated and dried before elemental analysis.

Molar masses were measured by the Polymer Supply and Characterisation Centre of RAPRA Technology using gel permeation chromatography (GPC). For most samples tetrahydrofuran was used as solvent with narrow distribution polystyrene samples as calibration standards. Two of the BAN samples were insoluble in tetrahydrofuran, and these were run in dimethylformamide solution. In this case poly(ethylene oxide) standards were used for calibration. Since GPC-derived molar masses are nonabsolute and may introduce an error in the value of B_{crit} (eq 1), three samples were run using a "Viscotek" viscosity detector in line with the normal refractive index detector. The calibration factor using this technique is the viscometric hydrodynamic volume which allows for the difference in eluting times between structurally different polymers. Although strictly not an absolute method, as long as the polymer behaves normally in solution (i.e., a random coil configuration), it allows for differences in solvated size and gives actual molar masses. Tables I and II show that the M_n values are, at most, 15% different from the polystyrene calibration.

The microstructure of the butadiene component of BAN copolymers was examined using a Perkin-Elmer FTIR 1720X infrared spectrometer to determine the absorbances at 970 cm^{-1} (1,4-trans addition) and at 920 cm^{-1} (1,2 addition). The amount of 1,4-cis addition was not determined (the band is broad, 720–770 cm^{-1}, and relatively weak), but this omission is not regarded as serious for our present purpose since the majority of the butadiene in BAN copolymers occurs in 1,4-trans units.[14]

Blends of SAN with BAN and of BAN with BAN were prepared either by dropwise reprecipitation of methylene dichloride solutions containing 50 wt % of each component into methanol or by casting from methyl ethyl ketone (MEK) directly onto glass slides. Both the coprecipitated and the cast blends were examined after drying in vacuum as described below.

Glass transition (T_g) values were obtained using a Perkin-Elmer DSC-2 scanning at 20 K min^{-1}. For blends the criterion of miscibility was normally taken as the appearance of a single reproducible T_g. In cases where the T_g values of the blend components were too close to enable this to be used, the aging technique of Bosma, ten Brinke, and Ellis was employed,[15] and the criterion for a single-phase blend was then the appearance of a single enthalpy relaxation peak.

The phase separation of the miscible cast blends was studied using annealing cycles in the DSC-2. Blends were held for 10 min at successively higher temperatures (in 10 K increments) above the blend T_g, and after each annealing period the blend was quenched and then scanned in the normal way over the required temperature range. A lower critical solution temperature (lcst) was adjudged to be near the annealing temperature which led to evidence of double T_g behavior on rescanning. The characterization data for the BAN and the SAN copolymer samples used for blending studies are displayed in Tables I and II.

Results and Discussion

The most direct manner by which an estimate of the butadiene–acrylonitrile interaction $B_{B\text{-}AN}$ may be obtained is to examine "internal" blends of B_xAN_{1-x} + B_yAN_{1-y}, i.e., binary mixtures of BAN copolymers of different compositions. Equation 2 then simplifies in this case to

$$B_{blend} = (x - y)^2 B_{B\text{-}AN} \tag{9}$$

which has solutions when $B_{blend} = B_{crit}$ of

$$y = x \pm (B_{crit}/B_{B\text{-}AN})^{0.5} \tag{10}$$

$(B_{crit}/B_{B\text{-}AN})^{0.5}$ is thus the composition difference at which blends of BAN copolymers will no longer be miscible.

The results for a series of internal blends of BAN are shown in Table III where it is immediately apparent that single-phase behavior occurs only when compositions are extremely close indeed. For the miscible pairings shown, the occurrence of a single glass transition was confirmed by the presence of only one enthalpy relaxation peak after appropriate aging of the blend.[15]

According to the data in Table III, the condition $0.037 \leq (B_{crit}/B_{B\text{-}AN})^{0.5} \leq 0.048$ holds where one of the two equalities defines the possible limiting composition at which phase separation occurs. The molar volumes of the copolymer blends forming these limits were calculated

Table IV
Coefficients of Best-Fit Ellipses to SAN + BAN One-Phase Areas in Figures 1 and 2 and Resulting Segmental Interaction Parameters

	coefficients				B_{ij} (J cm^{-3})		
	Figure 1	Figure 2	i–j^a	i–j^b	Figure 1	Figure 2	interaction
a	1.000	1.000	A–B	S–AN	22.8	22.8[c]	intra
b	1.584	1.591	C–D	B–AN	36.1	36.3	intra
c	−2.340	−2.372	A–C	S–B	2.8	2.6	inter
d	−0.052	−0.035	B–D	AN–AN	0	0	
e	−0.070	−0.073	B–C	B–AN	34.5	34.7	inter
f	−0.003	−0.003	A–D	S–AN	21.6	22.0	inter

[a] In A_xB_{1-x} + C_yD_{1-y} from eqs 4–8. [b] In S_xAN_{1-x} + B_yAN_{1-y}. [c] Input value for eqs 4–8 with B_{crit} = 0.062 J cm^{-3} calculated from the six copolymer pairs located close to the phase boundary.

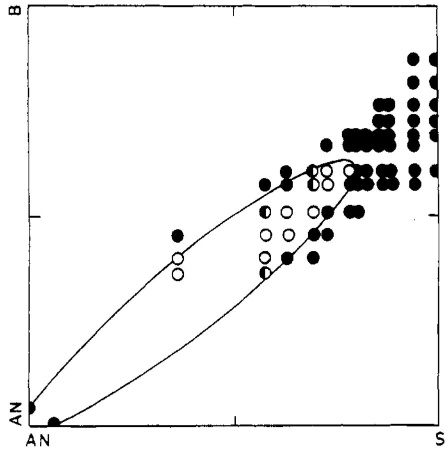

Figure 1. Phase behavior of SAN + BAN copolymer blends prepared by coprecipitation: ○, miscible blend; ●, immiscible blend. The points on the AN–S and the AN–B axes are the calculated internal miscibility limits for these respective systems. The best-fit ellipse shown has the coefficients listed in Table IV.

from their compositions and respective polystyrene-equivalent molar masses using a group additivity scheme[17] to estimate repeat unit molar volumes. Equation 1 then gives B_{crit} = 0.081 J cm^{-3} as appropriate for both the limiting pairs of BAN blends (BAN67–BAN70 and BAN62–BAN67). $B_{B\text{-}AN}$ is then readily calculated to lie in the range 35–59 J cm^{-3}.

Despite the close definition of the critical composition range within which the phase boundary occurs, given in Table III, the extreme sensitivity of eq 10 at small values leads to a somewhat unsatisfactory spread in the estimate of $B_{B\text{-}AN}$. (It is instructive to note that a 15% difference between polystyrene-equivalent and viscosity-derived M_n values evaluates to an uncertainty in $B_{B\text{-}AN}$ of only 1/100 of this, emphasizing the relative importance of composition changes to molar mass changes.) One can conclude, however, and with some confidence, that the butadiene–acrylonitrile segmental interaction is large, and comparable with that reported for styrene–acrylonitrile[11,16] $B_{S\text{-}AN}$. Blends of SAN with BAN therefore exemplify a system where there are no direct favorable segmental interactions which would promote miscibility, and this system is examined next.

For the blend S_xAN_{1-x} + B_yAN_{1-y} there are only three segmental interaction parameters to consider. The appropriate form of the equation of an ellipse describing the phase behavior in such a system can be shown to be

$$ax^2 + by^2 + cxy - f = 0 \qquad (11)$$

The experimental phase behavior is shown in Figure 1 where the copolymer samples available quite clearly define an area of miscibility lying close to the diagonal with its limit at about 0.75 volume fraction styrene in SAN. For the molar masses used, styrene is immiscible in BAN copolymers of any composition. Two further points may be included in this diagram, one at $y \simeq 0.04$ from the internal limit of miscibility in the B_xAN_{1-x} + B_yAN_{1-y} system, and a second at $x \simeq 0.06$ (via eq 10 with $B_{S\text{-}AN}$ = 22.8 J cm^{-3})[16] corresponding to the internal miscibility of SAN copolymers.

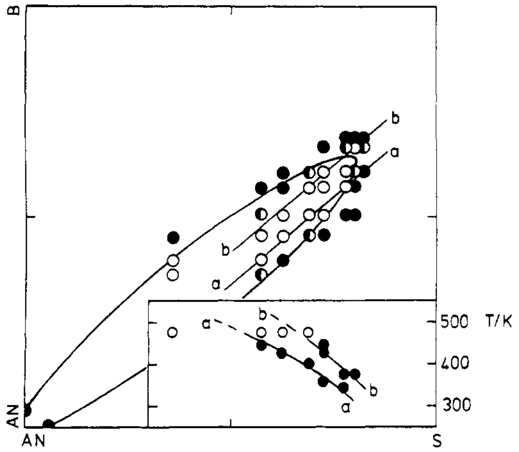

Figure 2. Phase behavior of SAN + BAN copolymer blends prepared by casting from MEK: ○, miscible blend; ●, immiscible blend; ◐, partially miscible blend. The points on the AN–S and the AN–B axes are the calculated internal miscibility limits for these respective systems. The best-fit ellipse shown has the coefficients listed in Table II. The inset shows the lcst behavior for the miscible-as-cast blends: ○, lcst above 475 K; ●, lcst values adjacent to the loci a–a and b–b marked within the ellipse.

Now eq 11 describes an ellipse centered on the origin; contrarily, however, the experimental one-phase area is closer to being cigar-shaped and so not centered on the origin. The phase boundary shown in Figure 1 was selected by overlaying a series of computer-generated ellipses until a reasonable best fit was obtained, with the resulting coefficients *a*–*f* as shown in Table IV. Since both *e* and *d* are nonzero, a full set of six nonidentical interactions are required to satisfy this condition, and these may be evaluated from relations 4–8 using B_{AB} = $B_{S\text{-}AN}$, with the added restriction that B_{BD} = $B_{AN\text{-}AN}$ = 0. Using an average B_{crit} of 0.062 J cm^{-3} for this system, the calculated B_{ij} values are collected in Table IV where they are identified with the segmental interactions in the SAN–BAN system.

Miscible blends obtained by casting did not prove totally suitable for optical detection of demixing, but were readily observed to develop two-phase behavior on high-temperature annealing as described in the Experimental Section. The phase diagram for blends cast from methyl ethyl ketone is shown as Figure 2 along with the lsct values for the miscible-as-cast compositions. Blends heated to above 473 K discolored slightly and no longer exhibited reproducible behavior; thus, any lcst behavior above this temperature could not be reliably recorded. The phase behavior shown in Figure 2 is only slightly different from that of the precipitated blends in that the one-phase area extends marginally to copolymers of higher styrene and butadiene contents. The best-fit elliptical boundary is consequently little changed from that in Figure 1, as are the resulting B_{ij} values also shown in Table IV. Indeed, since the best-fit ellipses are a matter of some subjectivity, the differences between Figures 1 and 2 are approximately the same as the "experimental error" obtained by examining a number of equally acceptable fits to the data.

The behavior of B_{blend} along both the major and the minor axes of the ellipse is quadratic. One could expect lcst values to reflect this (in an inverse sense) by being at a maximum at the ellipse center and becoming lower near the phase boundary (where $B_{\mathrm{blend}} = B_{\mathrm{crit}}$). The lcst data in Figure 2 are limited, but are sufficient to show this trend for samples progressively located closer toward the "tip" of the phase boundary. Similar behavior transverse to the major axis of the ellipse is not obvious from the data, but would probably be difficult to detect experimentally over such a narrow composition span.

Within the confines of the present mean field theory, the nonidentity of B_{CD} with B_{BC} and of B_{AB} with B_{AD} (which otherwise would lead to eq 11 and an origin-centered semielliptical phase boundary), resulting from the chosen fits to the data, implies a differentiation of both the S–AN and the B–AN *intra*molecular and *inter*molecular contacts. Other researchers in this area have suggested that such a refinement may be justified,[17,18] and indeed we have had to employ this distinction previously to define phase behavior adequately in earlier systems.[10] It could be argued of course that the apparent nonidentity of intra- and intermolecular contact interactions is an illusion masking the effects of other variables such as copolymer composition and molecular weight distributions. Examination of Table I shows that the commercial BAN samples used in this study have broad molecular weight distributions, and data obtained using these may be less reliable than those from the narrower distribution blends. The interaction possibly will vary also with butadiene microstructure; however, Table I shows that this effect should at least be minimal for this series of samples. A compositional dependence of B_{ij} or, equivalently, the change in sequence distribution with copolymer composition could equally well account for deviations from simple "conic section" behavior. The effect on the phase behavior of a change in the local environment was proposed some time ago[19] and has been demonstrated more recently.[20] Such may be so, but the introduction of further variables to quantify these detracts from the simplicity of the present approach. In light of these remarks the the intra- and intersegmental interaction densities are averaged so that a value of $B_{\mathrm{B-AN}}$ = 33–37 J cm^{-3} best characterizes this interaction.

The above value corresponds to the lower limit found from the internal miscibility study, and implies that internal phase separation actually occurs close to the upper composition difference of 0.048 volume fraction. We have previously published an estimate for this interaction in terms of the Flory χ-parameter,[4] which transforms to $B_{\mathrm{B-AN}} \simeq 38$ J cm^{-3} with a $V_{\mathrm{ref}} \simeq 70$ cm^3 mol^{-1} based on the average segment molar volumes involved. The remaining interaction parameter in Table IV, between styrene and butadiene, $B_{\mathrm{S-B}} \simeq 2.7$ J cm^{-3}, agrees satisfactorily with the value given by Roe and Zin of 2.4 J cm^{-3} obtained from cloud point measurements involving polystyrene and styrene–butadiene copolymers,[21] and this too gives further weight to the analysis of the phase boundary presented here.

Acknowledgment. We thank the SERC for the award of a studentship to support J.H.H.

References and Notes

(1) Hofmann, W. Rubber Review for 1963. *Rubber Chem. Technol.* **1964**, *37*, Part 2.
(2) Bertram, H. H. In *Developments in Rubber Technology-2*; Whelan, A., Lee, K. S., Eds.; Applied Science Publications: London, 1981.
(3) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic Press: New York, 1979.
(4) Cowie, J. M. G.; Elexpuru, E. M.; Harris, J. H.; McEwen, I. J. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 691.
(5) Krause, S. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978.
(6) Ougizawa, T.; Inoue, T. *Polym. J.* **1986**, *18*, 521.
(7) Takayanagi, M.; Harina, H.; Iwata, Y. *Mem. Fac. Eng., Kyushu Univ.* **1963**, *23*, 1.
(8) Koran, A. Y.; Patel, R. *Rubber Chem. Technol.* **1981**, *54*, 892.
(9) Cowie, J. M. G.; McEwen, I. J.; Reid, V. M. C. *Polymer* **1990**, *31*, 486.
(10) Cowie, J. M. G.; McEwen, I. J.; Reid, V. M. C. *Polymer* **1990**, *31*, 905.
(11) Cowie, J. M. G.; Lath, D. *Makromol. Chem., Makromol. Symp.* **1988**, *16*, 103.
(12) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(13) Krause, S. *Macromolecules* **1991**, *24*, 2108.
(14) Anachkov, M. P.; Stefanova, R. V.; Rakovsky, S. K. *Br. Polym. J.* **1989**, *21*, 429.
(15) Bosma, M.; ten Brinke, G.; Ellis, T. S. *Macromolecules* **1988**, *21*, 1465.
(16) Cowie, J. M. G.; Elexpuru, E. M.; McEwen, I. J. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 407.
(17) Cantow, H.-J.; Schulz, O. *Polym. Bull.* **1986**, *15*, 539.
(18) van Hunsel, J.; Balazs, A. C.; Koningsveld, R.; MacKnight, W. J. *Macromolecules* **1988**, *21*, 1528.
(19) Koningsveld, R.; Kleintjens, L. A.; Market, G. *Macromolecules* **1977**, *10*, 1105.
(20) Galvin, M. E. *Macromolecules* **1991**, *24*, 6354.
(21) Roe, R. J.; Zin, W. C. *Macromolecules* **1980**, *13*, 1221.

Registry No. SAN (copolymer), 9003-54-7; BAN (copolymer), 9003-18-3.