

# Rapid FTIR Method for Quantification of Styrene-Butadiene Type Copolymers in Bitumen

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**ABSTRACT:** The mid-IR molar absorptivity for polystyrene (PS) and polybutadiene (PB) blocks were obtained for five styrene-butadiene-styrene (SBS) and SB copolymers, including linear, branched, and star copolymers, and their blends with bitumen. The average absorptivity for PS and PB blocks was 277 and 69 L mol<sup>-1</sup> cm<sup>-1</sup> and it was little affected by the S/B ratio or the copolymer architecture. In the presence of bitumen, Beer's law was obeyed but the respective PS and PB absorptivity was 242 and 68 L mol<sup>-1</sup> cm<sup>-1</sup>, possibly because of weak interactions between the copolymer and bitumen. The absorptivity values were used to calculate the concentration of SB-type copolymers in blends with bitumen with an accuracy of 10% or better. The method can be used to probe the stability of bitumen-copolymer blends in storage at 165°C, to determine the copolymer concentration in commercial polymer modified bitumen (PMB), and to assess the resistance of PMB to weathering. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1034–1041, 2001

**Key words:** bitumen; blends; polymer; styrene copolymer; butadiene copolymer; IR spectroscopy; quantification; stability; sealants

## INTRODUCTION

Polymer modified bitumen (PMB) is used in many construction applications, the most important being roofing and roadways. In PMB, the polymer is an elastomer or a thermoplastic that allows for greater performance than that possible with bitumen alone.<sup>1</sup> In this respect, styrene-butadiene (SB) and SB-styrene (SBS) block elastomers are commonly used to improve the low temperature cracking resistance of bitumen. The low glass-transition temperature of the butadiene block at about -95°C ensures that an SBS or SB modified bitumen remains elastic during winter.

The performance of modified bitumen is partly governed by its SB or SBS content. Under the

right conditions, this polymer content can be measured accurately. If raw materials are available, calibration standards can be prepared and the polymer can be quantified by IR spectroscopy.<sup>2</sup> If the SBS or SB modified bitumen (SB-MB) is freshly prepared and no crosslinks exist between the bitumen and polymer, the polymer can be extracted with a suitable solvent.<sup>3</sup> These methods lack flexibility, however, because raw materials are most often unavailable. Consequently, the polymer content in SB-MBs from different sources is difficult to obtain, and for the same reasons, it is difficult to assess the resistance of SBS or SB to the aging that SB-MB may incur during field installation<sup>4</sup> or natural weathering.<sup>5</sup>

We present an FTIR method that can be used when SB-MB is aged or when control samples are unavailable. The method can substitute for the previously cited FTIR<sup>2</sup> and extraction methods.<sup>3</sup> It relies on the average molar absorptivities for po-

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**Table I** Copolymer Characteristics

Type	Label	Source and Name	$M_n$	$M_w/M_n$	S/B Ratio			
					Expected		Measured <sup>a</sup>	
					Styrene	Butadiene	Styrene	Butadiene
Linear SBS	L1	Enichem, SOL T166	124,000	1.04	30	70	30	70 (11)
	L2	Shell, Kraton D1101	166,000	1.09	31	69	33	67 (9)
Branched SB	B1	Enichem, SOL T6302	173,000	1.06	30	70	30	70 (12)
	B2	Shell, Kraton D4240E	ND	ND	44	56	48	52 (10)
Star SB	S1	Enichem, SOL T6205	264,000	1.14	25	75	24	76 (11)

ND, not determined.

<sup>a</sup> Measured by NMR according to Günther.<sup>6</sup> The numbers in parentheses are the percent content of terminal alkene in the PB segment.

lybutadiene (PB) and polystyrene (PS) blocks in SB-type copolymers. It is demonstrated that these absorptivities can be used to quantify SB-type copolymers in SB-MB because the copolymer structure has little effect on the molar absorptivity and because bitumen does not prevent the use of Beer's law, despite some interactions with the copolymer. The usefulness of the method is shown by quantifying SBS in seven SB-MBs from different sources, by assessing SB-MB stability during storage at 165°C, and by measuring SBS degradation in a weathered SB-MB sample.

## EXPERIMENTAL

### Materials

The PS (catalog #18138-2) and PB (catalog #18242-7) were purchased from Aldrich. SB-MBs were prepared in the laboratory and obtained from commercial sources. The laboratory samples were prepared from five SB copolymers and two bitumens. The copolymers were supplied by Enichem and Shell (Table I<sup>6</sup>). Bitumens A and B had respective saturates, aromatics, resins, and asphaltene compositions of 2, 35, 40, 23 and 11, 16, 57, 16 wt % as measured with an Iatroscan<sup>7</sup> after elutions in heptane, toluene, and tetrahydrofuran. Bituminous crack sealants were used as commercial SB-MB sources.

### Blends

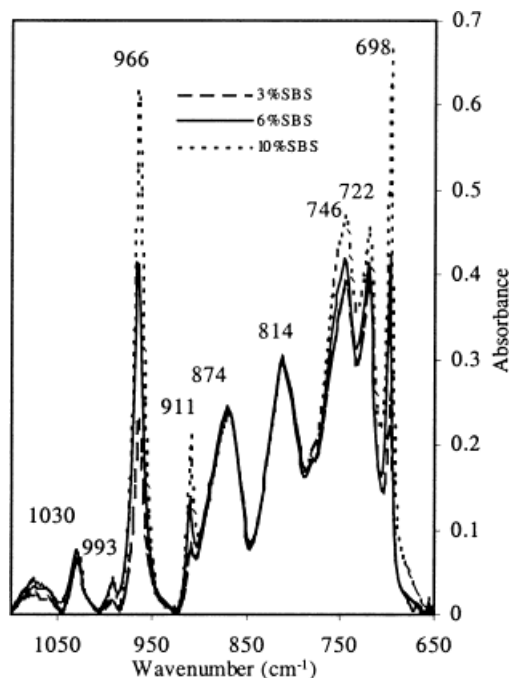
Twenty-four SB-MBs were prepared from the two bitumens and the five copolymers. Copolymer concentrations were 3, 6, and 10% (w/w), except for copolymer L2, which had concentrations of 3

and 5% (w/w). In a typical preparation, 500 g of bitumen was kept under a nitrogen blanket and heated to 170°C in about 30 min. The copolymer was added stepwise in about 5 min with stirring at about 1000 rpm using a Silverson L4RT high-shear mixer. Stirring was continued for an additional 30 min at 185°C and 5000 rpm. To assess blend stability, a 250-g sample of SB-MB was stored without agitation at 165°C.

### FTIR

Typically, 5 g of SB-MB was dissolved in 50 g of carbon disulfide. This solvent was chosen because of its lack of absorbance below 1400 cm<sup>-1</sup> and its ability to dissolve bitumen and copolymer equally well. Carbon disulfide must be handled with care, however, because of its flammability and toxicity. The 10% solution was successively diluted to 5, 2.5, 1.25, and 0.625% (w/w). Homopolymer and copolymer solutions with PS and PB contents close to those in the PMB solutions were obtained by dilution of a polymer stock solution prepared from 1.5 to 3.0 g of polymer dissolved in 38 g of carbon disulfide.

Sealant solutions were prepared from about 350 mg of solid dissolved in about 7 g of carbon disulfide to provide concentrations of 5% (w/w). Each solution was analyzed by transmission and in triplicate by the cell-in cell-out method.<sup>8</sup> The cell path length was 1.25 mm. Fifty scans were coadded on a Bomem MB100 spectrometer operated at a resolution of 4 cm<sup>-1</sup>. The variation of absorbance on the triplicates was less than 1%. The molar absorptivity was obtained for the strongest copolymer absorptions: 966 cm<sup>-1</sup> for PB, and 699 cm<sup>-1</sup> for PS. With solutions of de-



**Figure 1** A portion of the FTIR spectra for bitumen modified with SBS. The peak heights at 966, 911, and 699  $\text{cm}^{-1}$  are proportional to the copolymer content.

creasing polymer concentrations, the absorptivity  $a$  was calculated by application of Beer's law,  $a = A/bc$ , where  $A$  is the absorbance,  $b$  is the cell path length, and  $c$  is the copolymer concentration.

## RESULTS AND DISCUSSION

### Spectral Analysis

FTIR spectra for SB-MB showed absorbances from bitumen and the PS and PB copolymer

units. The region of interest for the quantification of the copolymer was  $650\text{--}1100\text{ cm}^{-1}$  (Fig. 1). The origin of the peaks in this region is shown in Table II. Monitoring the respective PB and PS absorbances at 966 and 699  $\text{cm}^{-1}$  enabled the quantification of the copolymer in SB-MB, and the relative decrease in the PB and PS absorbances, if any, allowed the degradation to be assessed (see Appendix). To quantify the copolymer rapidly with the use of peak absorptivities and circumvent the need for the classical calibration curve,<sup>2</sup> only the respective copolymer units must contribute to the peak height at 966 and 699  $\text{cm}^{-1}$ ; a significant overlap of PS with PB or bitumen, for example, would not allow quantification of the copolymer. Fortunately, there was indeed a negligible overlap between PS, PB, and bitumen (Figs. 2, 3). It was thus possible to proceed with the measurement of the polymer absorptivity in an attempt to develop a rapid quantification method.

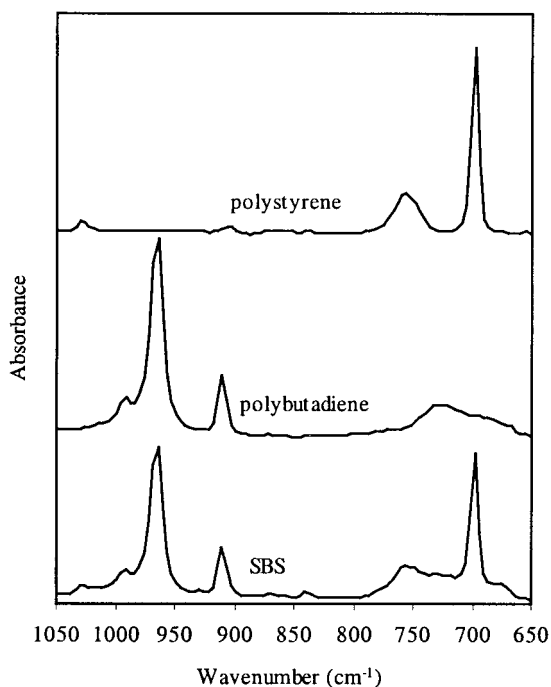
### Polymer Absorptivity

The absorptivities for PB at 966  $\text{cm}^{-1}$  and PS at 699  $\text{cm}^{-1}$  were obtained by measuring the absorbances of successively more dilute solutions and by plotting the absorbance against the concentration (Fig. 4). The slope of the Beer's law curve gives the absorptivity. Values of 266 and 73  $\text{L mol}^{-1}\text{ cm}^{-1}$  were calculated for PS and PB, respectively. These values were then compared to those of the PS and PB units in linear, branched, and star SBS and SB copolymers commonly used to modify bitumen (Table III). The comparison showed that PS and PB absorptivities were affected by the copolymer structure and composition. For example, on the one hand, the PS ab-

**Table II** Absorptions Between  $650$  and  $1100\text{ cm}^{-1}$  in FTIR Spectra of Bitumen, PS, and PB

Compound	Abs. ( $\text{cm}^{-1}$ )	Origin <sup>a</sup>
PS	699 and 750	C—H oop bending in monoalkylated aromatics
PB	993	C—H oop bending of <i>cis</i> -alkene
	966	C—H oop bending of <i>trans</i> -alkene
	911	C—H oop bending of terminal-alkene
	730–650	C—H wagging of <i>cis</i> -alkene
Bitumen	1030	S=O stretching
	874	C—H oop bending in 1,2,4-substituted aromatics
	814	C—H oop bending in 1,2,4- and 1,4-substituted aromatics
	746	C—H oop bending in 1,2-substituted aromatics
	722	Rocking of $(\text{CH}_2)_n$ , $n > 4$

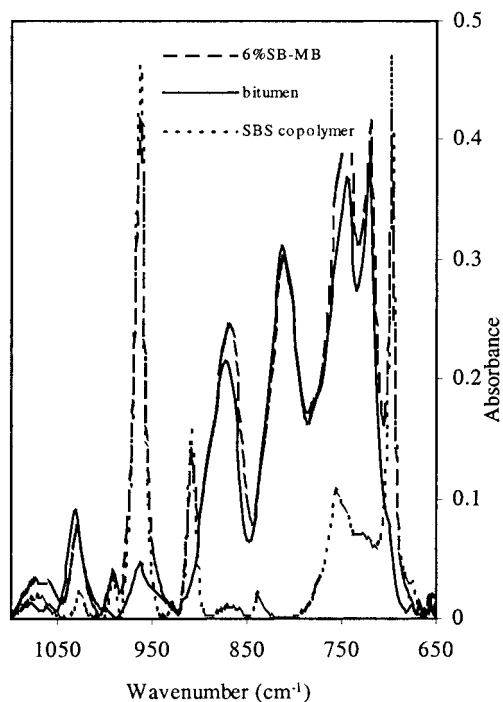
<sup>a</sup>oop, out of plane.



**Figure 2** A portion of the FTIR spectra for PS, PB, and SBS. The  $966\text{ cm}^{-1}$  PB absorbance in SBS is independent of that for PS. That for PS at  $699\text{ cm}^{-1}$  overlaps with a broad PB absorbance, but the baseline is such that the latter can easily be discounted. Hence, the respective PS and PB absorbances can be used for quantification purposes. The origin and band positions are shown in Table II.

sorptivity in linear copolymer L1 was  $30\text{ L mol}^{-1}\text{ cm}^{-1}$  higher (11.5%) than in branched copolymer B1, although both copolymers had an S/B ratio of 30/70. The change stemmed more from the effect of the copolymer structure than from a possible effect from the molecular weight because linear copolymers L1 and L2 with very different molecular weights showed identical PS absorptivities. On the other hand, the PB absorptivity was affected by the block composition (Fig. 5). The absorptivity at  $966\text{ cm}^{-1}$  correlated to the concentration of terminal alkenes that arose from the 1,2-polymerization of butadiene.

Interestingly, branched copolymer B2 did not follow the expected correlation between the PB absorptivity and terminal alkene content (Fig. 5). The reason for the deviation was found in the FTIR and  $^1\text{H-NMR}$  spectra for the copolymer, which revealed the presence of fully saturated units in the copolymer. The PS and PB absorptivities in copolymer B2, which were about 65% of that for the homopolymers (Table II), suggested that the copolymer was 35% hydrogenated, which

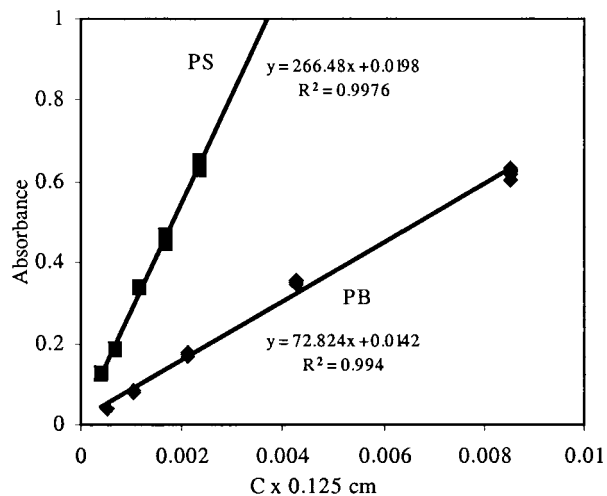


**Figure 3** A portion of the FTIR spectra for SBS, bitumen, and a blend. There is little overlap between the copolymer and bitumen at  $966$  and  $699\text{ cm}^{-1}$ .

meant that its structure contained polyethylene and poly(alkyl)cyclohexane units. Copolymer B2 was not an SB-type copolymer and consequently it was not studied further.

#### Polymer–Bitumen Blends

Bitumen has a complex chemistry (Fig. 6). It contains so-called saturates, aromatics, resins, and



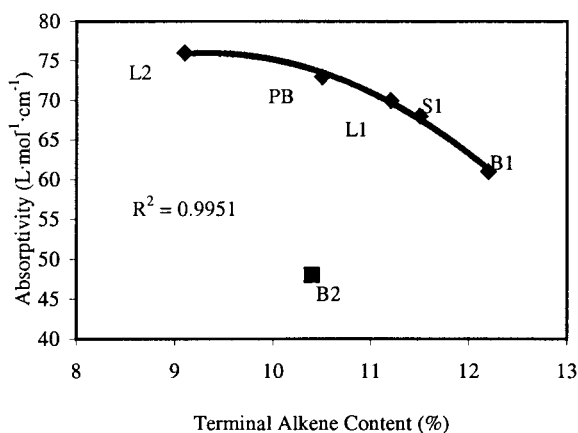
**Figure 4** Beer's law curves for neat PS and PB in carbon disulfide.

**Table III Molar Absorptivity for PB and PS Blocks ( $\text{L mol}^{-1} \text{cm}^{-1}$ )**

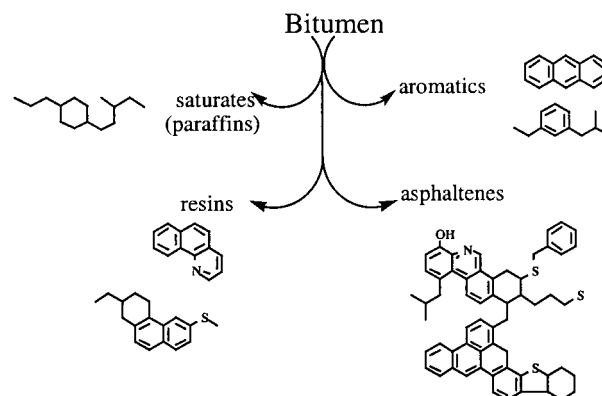
Polymer	S/B Ratio	PB (966 $\text{cm}^{-1}$ )	PS (699 $\text{cm}^{-1}$ )
PS	100/0	—	266
PB	0/100	73	—
L1	30/70	70	290
L2	31/69	76	290
B1	30/70	61	260
B2	44/56	48	169
S1	25/75	68	267

asphaltenes, which may be capable of strongly interacting with a polymer either through dipole-dipole or hydrogen bonds. The interactions may be disruptive and cause deviations from Beer's law. In such a case, the absorption of the polymer in the FTIR spectrum would no longer be linearly correlated to its concentration and it would be impossible to quantify it rapidly and without a calibration curve that accounts for these interactions.

It was thus of interest to investigate the effect of bitumen on PS and PB absorptivities. For that purpose, we measured the absorptivities of the four copolymers used earlier when blended with two bitumens of different compositions (see Experimental section for the composition). The results showed that in the presence of bitumen, the copolymer absorptivity still obeyed Beer's law (Figs. 7, 8). No deviation from linearity was observed, irrespective of the bitumen composition

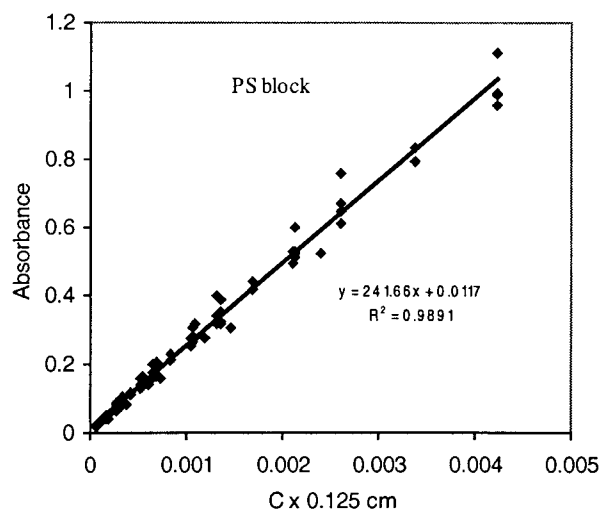


**Figure 5** The relationship between the terminal alkene content and the PB absorptivity at  $966 \text{ cm}^{-1}$ . The curve follows the quadratic equation  $y = -1.8x^2 + 33.3x - 79.5$ . See text for details.

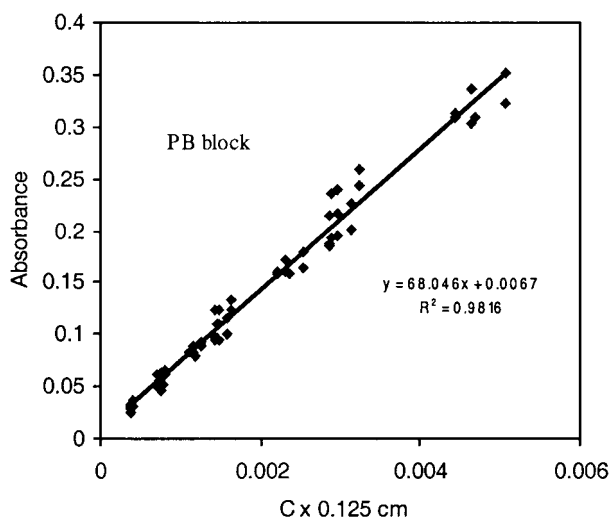


**Figure 6** Representative structures for the four bitumen fractions: the saturates, the aromatics, the resins, and the asphaltenes.

and the copolymer type. There was thus no strong interaction between bitumen and SB-type copolymers in solution. However, a relatively large decrease in the PS absorptivity in blends with bitumen ( $242 \text{ L mol}^{-1} \text{cm}^{-1}$  in blends vs.  $277 \text{ L mol}^{-1} \text{cm}^{-1}$  for the copolymer alone) suggested a weak interaction between PS blocks and bitumen, which is rich in (poly)aromatics. This was in accordance with the good dispersion of SB-type copolymers in bitumen rich in aromatics.<sup>9</sup> The stacking of aromatic rings by  $\pi$ - $\pi$  interactions<sup>10</sup> and induced dipolar interactions<sup>11</sup> could keep PS and bitumen aromatics in close proximity and, as a result, limit the C—H out of plane bending



**Figure 7** A Beer's law plot for blends prepared from two bitumens and five SB-type copolymers. The PS block absorptivity was  $242 \text{ L mol}^{-1} \text{cm}^{-1}$  as obtained from the slope.



**Figure 8** A Beer's law plot for blends prepared from two bitumens and five SB-type copolymers. The PB block absorptivity was  $68 \text{ L mol}^{-1} \text{ cm}^{-1}$  as obtained from the slope.

vibration of PS that would lower the absorptivity at  $699 \text{ cm}^{-1}$ . The effect on the PB block would be similar but much less effective in keeping the more flexible chain in the proximity of bitumen; as a result, the PB remains practically unchanged.

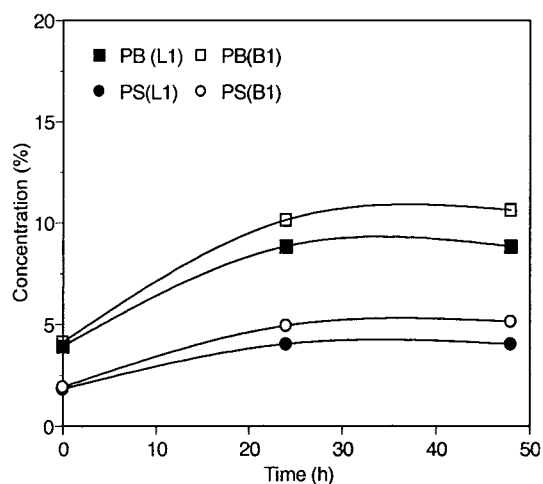
With the average absorptivity for the PS and PB blocks, the copolymer concentrations in all SB-MBs were backcalculated as if each sample had an unknown copolymer concentration (Table IV). This allowed us to assess the accuracy with which we could quantify SBS or SB in SB-MBs prepared from a bitumen and an SB-type copolymer of unknown sources. In all cases, the calculated polymer content was within  $\pm 0.5 \text{ wt } \%$  of

**Table IV** Copolymer Concentrations Calculated with Absorptivity Averages

Copolymer	Bitumen A			Bitumen B		
	3%	6%	10%	3%	6%	10%
L1	2.8	5.7	9.3	3.3	5.7	9.3
L2	2.8	4.7 <sup>a</sup>	ND	ND	ND	ND
B1	3.4	5.7	9.5	3.0	6.4	9.5
S1	3.4	5.5	9.5	3.1	5.7	9.2
Average error	10%	6%	6%	4%	6%	7%

ND, not determined.

<sup>a</sup> This value is for a 5% w/w sample.



**Figure 9** The change in PS and PB concentration at the surface of blends with bitumen A and copolymer L1 or B1 during storage at  $165^\circ\text{C}$ . See text for details.

the expected value. This translated into an average error of 10% or less of the actual polymer contents.

### Practical Applications

With the available average absorptivities for the PS and PB blocks in hand, we applied Beer's law in three practical problems:

1. the stability of a freshly prepared SB-MB during storage at  $165^\circ\text{C}$ , a condition representative of the practice in roadway construction,<sup>12</sup>
2. the quantifying of polymer contents in commercial SB-MBs (crack sealants), and
3. the aging of an SBS copolymer in one of the crack sealants exposed to 5 years of outside weathering.<sup>13</sup>

The SB-MB stability was assessed by measuring the change in polymer concentration at the SB-MB surface during storage at  $165^\circ\text{C}$ . Figure 9 shows the results for blends prepared with bitumen A and copolymers L1 and B1 of identical S/B ratios. Each blend showed segregation over time as seen by a twofold increase in PS and PB concentration at the blend surface. Identical trends for PS and PB indicated that no degradation of the polymer by oxidation or scission occurred (Appendix). In both cases segregation was complete within 24 h, but it was greater with B1 because of its greater molecular weight and the reduced entropy of mixing.<sup>14</sup> The steric effect of the branch

structure may also be partly responsible for the greater segregation. A more detailed study of the effect of copolymer structure on blend stability is underway.

Table V shows the results obtained on commercial SB-MBs (sealants). The polymer concentration varied from about 4 to 18%, the more common concentration of 4–6% being representative of that for SB-MBs used in roadway construction. The method is also useful to assess the resistance of SB-MB to weathering. The results in Table VI show that the initial SBS content of 6.5% in sealant M decreased by about 12% in 5 years of natural weathering. This loss is twice as large as the estimated error of 6% obtained earlier for the SB-MB with 6% copolymer (Table IV). It is likely then that the estimated loss was real. It is also noteworthy that the loss of PS was greater than that for PB. This suggests that the kinetics of PS degradation was greater than that for PB (Appendix) or, alternatively, that the polymer in sealant M was a linear SBS in which PS degradation occurred at both ends of the chains in contrast to PB.

## CONCLUSIONS

The mid-IR absorptivity for PS at  $699\text{ cm}^{-1}$  and PB at  $966\text{ cm}^{-1}$  was obtained on linear, star, and branched SB-type copolymers before and after blending with bitumen. In all cases, Beer's law was obeyed. Before blending, the respective PS and PB absorptivities were  $277$  and  $69\text{ L mol}^{-1}\text{ cm}^{-1}$  and after blending they were  $242$  and  $68\text{ L mol}^{-1}\text{ cm}^{-1}$ . The decrease in copolymer absorptivity in the bitumen blends was attributed to weak interactions between the copolymer and bitumen. Given the applicability of Beer's law, the average absorptivities for PS and PB in blends

**Table V SB-Type Copolymer Concentration in Bituminous Sealants**

Sealant <sup>a</sup>	Concn (%)
A	5.2
D	4.4
E	18.5
F	5.0
J	11.2
K	5.9
M	6.3

<sup>a</sup> From Masson et al.<sup>4</sup>

**Table VI Polymer Contents (w/w %) in Sealant M before and after Weathering**

Block	Weathering		Decrease (%)
	None	5 Years	
PB	4.4	3.9	11.4
PS	2.1	1.8	14.3
Total	6.5	5.7	12.3

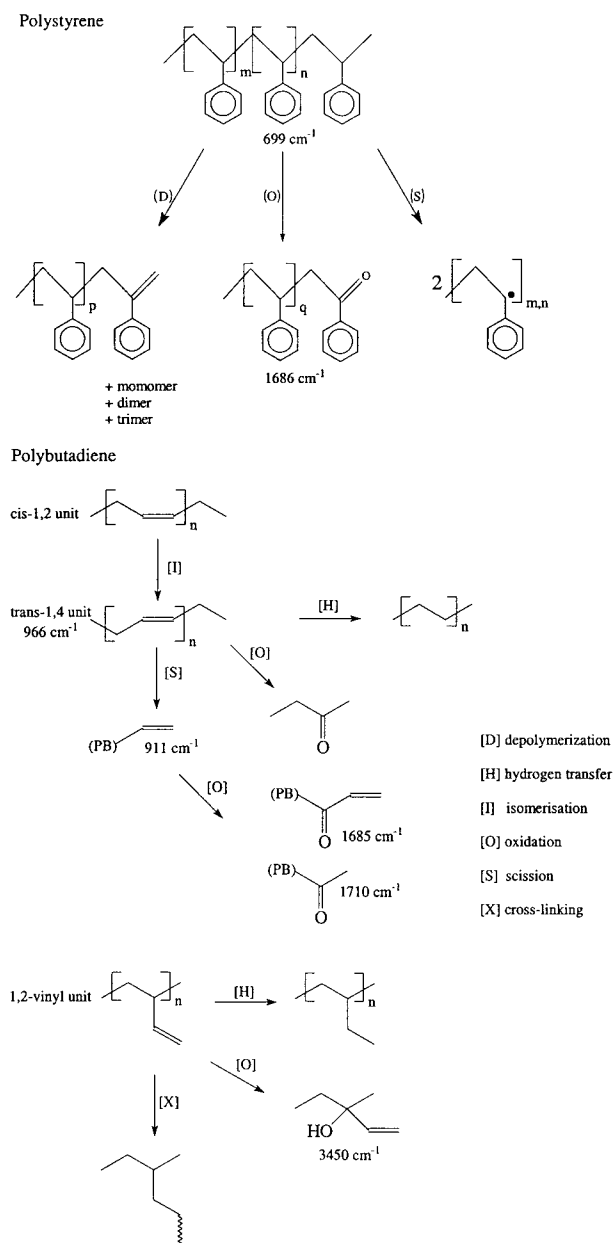
with bitumen were used to measure the concentration of SB-type copolymers in the bitumen with an accuracy of  $\pm 0.4\text{ wt }%$  (or better) of the expected value. The method can be used to

1. quantify SB or SBS contents in bituminous products when calibration standards prepared from the raw materials are unavailable;
2. compare the SB or SBS contents of bituminous products such as crack sealants and polymer modified binders in roadways and roofing applications; and
3. study the effect of weathering, oven aging, or heat storage on polymer concentration in modified bitumen.

The method could be extended to other bitumen-polymer blends that contain a polymer with an IR spectrum distinct from that of bitumen, including styrene-isoprene copolymer, SB rubber, polychloroprene, polyisoprene (natural and synthetic), ethylene-vinyl acetate and S-ethylene-butylene-S polymers. The method cannot be used on bitumen blends with polyolefins, including polyethylene and polypropylene, because they do not have IR absorptions distinct from those of bitumen.

## APPENDIX: DEGRADATION PATHWAYS FOR PS AND PB

Degradation is inseparable from polymer production, transformation, and use. The latter are responsible for the presence of catalytic residues; oxygen into the main chain or a side chain; and weak links, especially at chain ends. Degradation begins at these sites with the rupture of a bond due to a photochemical, mechanical, or thermal action.<sup>15,16</sup> Given the industrial importance of PS and PB, there have been several studies on their degradation pathways.<sup>17–22</sup> The kinetics of degradation is



**Figure A.1** Typical degradation pathways for PS and PB. Adapted from the literature.<sup>13,14,17,19,20</sup>

related to the oxygen concentration within the polymer (i.e., the concentration of oxygen outside the polymer and its rate of diffusion); but if the oxygen concentration is low, the depolymerization of PS and the crosslinking of PB are predominant. Figure A.1 illustrates typical degradation pathways as adapted from the literature.<sup>13,14,17,19,20</sup>

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