structure for both the blends and the block copolymers of BPAC/DMS. By combining the data from several techniques (ESCA, ISS, and SEM), we see that while the surface concentration of the blends and block copolymers differs greatly from that of the bulk, the morphology of this region is consistent with those found in bulk samples with a concentration equivalent to the surface concentration.[14]

It is interesting to compare the findings of this work on the BPAC/DMS system with the work published by Thomas and O'Malley[4,5] on blends and block copolymers consisting of poly(ethylene oxide) (PEO) and polystyrene (PS). By the use of angle-resolved ESCA they showed the surface region of the block copolymers to contain an excess of the lower surface energy PS component, which is consistent with the results obtained for BPAC/DMS block copolymers.[1] However, for blends of PEO/PS the amount of surface segregation present was less than that found in the block copolymers. This is the opposite of that found for the BPAC/DMS system, even though the differences in the surface energy for each system were approximately the same (PEO/PS = 44/36 dyn/cm, BPAC/DMS = 34/24 dyn/cm).[6]

This analysis demonstrates that while surface energy values are useful for predicting which species should show a surface preference, they alone are not useful for predicting the degree of surface enrichment expected. The amount of surface segregation appears to be dependent on the degree of "compatability" (by any definition) present in the system and the final morphology of the sample.

Conclusions

In this work we employed a multitechnique approach to gain a detailed understanding of the surface region for blends of BPAC/DMS. This approach leads to a quantitative understanding of the degree of surface enrichment present for the lower surface energy DMS component. The ESCA quantification was accomplished without the need to use sensitivity factors or electron mean free paths, which can complicate the accuracy of results. In addition to quantitative descriptions of the surface concentration of each component, the multitechnique approach allowed for the elucidation of the surface morphology of these samples. All samples containing 1.4–10.8% bulk DMS showed equivalent surface composition and morphology.

When the results obtained for blends of BPAC/DMS are combined with previous work on block copolymers of BPAC/DMS, a detailed understanding of the surface region is obtained for these materials. In the block copolymers the surface region shows a increased concentration of the DMS component and has a morphology similar to that of the bulk. However, for the blends of BPAC/DMS the surface segregation of the DMS component is much greater than that seen for the block copolymers. Also, the morphology of this surface region is different than that of the bulk.

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Registry No. Bisphenol A polycarbonate (SRU), 24936-68-3; (bisphenol A)·(carbonic acid) (copolymer), 25037-45-0.

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Polymer Swelling. 3. Correlation of Aromatic Carbon-13 NMR Line Width with Cross-Link Density in Poly(styrene-*co*-divinylbenzene)

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ABSTRACT: The aromatic carbon-13 NMR line widths ($\nu_{1/2}$) of ten styrene–divinylbenzene copolymers, swelled to equilibrium in $CDCl_3$, were measured at +21 °C. The line width (in Hz) increases exponentially with cross-link density $\tilde{\chi}$ and is given by $\nu_{1/2} = 6 \times 10^4 \tilde{\chi}^{1.6}$.

Introduction

We have reported[1-3] that the volume of liquid, S, absorbed per gram of cross-linked polymer at equilibrium swelling increases with the average number of atoms λ in the backbone of the polystyrene segments between cross-link junctions in accordance with the equation

$$S = C(\lambda^{1/3} - \lambda_0^{1/3}) = C(\tilde{\chi}^{-1/3} - \tilde{\chi}_0^{-1/3}) \qquad (1)$$

where C is a constant characteristic of the swelling liquid, λ is the average number of carbon atoms in the polymer

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Table I
Swellability and Carbon-13 Line Width (Hz) of Styrene–Divinylbenzene Copolymers

source	cross-link density	S^a	^{13}C line width
Rohm and Haas Co.[b]	0.007[c]	8.14	15
Dow Chemical Co.[b]	0.009[c]	7.19	33
Bio-Rad Laboratories (SX-1)	0.010	6.95	32
Rhom and Haas Co.[d]	0.014[c]	5.82	49
Bio-Rad Laboratories (SX-2)	0.023	4.13	250
Bio-Rad Laboratories (SX-3)	0.034	3.02	320
Bio-Rad Laboratories (SX-4)	0.042	2.44	360
PolyScience Corp.[d]	0.07[c]	1.65	620
Bio-Rad Laboratories (SX-8)	0.08	1.48	900
Bio-Rad Laboratories (SX-12)	0.112	0.94	2400

[a] In milliliters of CHCl$_3$ per gram of polymer. [b] 0.001 cross-link density claimed by manufacturer. [c] Determined on the basis of observed S using eq 2. [d] 0.005 cross-link density claimed by manufacturer.

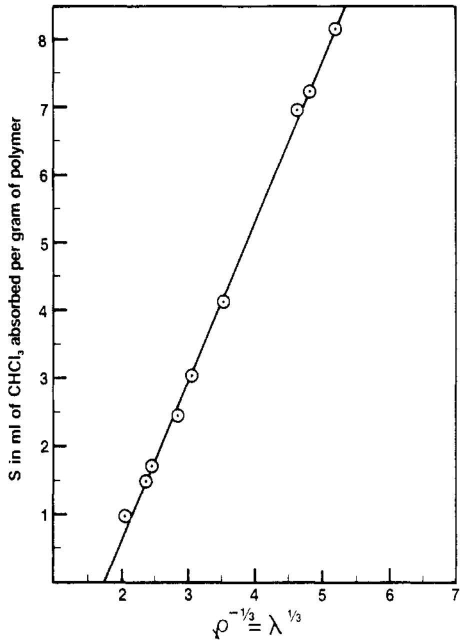

Figure 1. Volume of CHCl$_3$ absorbed at equilibrium swelling per gram of polymer for styrene–divinylbenzene copolymers as a function of $\tilde{\chi}^{-1/3} = \lambda^{1/3}$.

backbone between cross-link junctions and $\tilde{\chi}_0 = 1/\lambda_0$ is the critical cross-link density at or above which $S = 0$.

Several papers have been published reporting that high-resolution carbon and proton NMR spectra could be obtained on cross-linked polystyrenes or styrene copolymers.[4-9] Manatt et al.[6] proved that the chloromethyl level in chloromethylated, divinylbenzene-cross-linked polystyrene could be quantitatively determined in 1 or 2% cross-linked polystyrene gel systems. The spectra also proved that chloromethylation gave exclusively the para isomer. Ford and Balakrishnan[7,8] added an internal reference to a series of divinylbenzene-cross-linked 75:25 poly(styrene-*co*-(chloromethyl)styrene) samples and showed that the aromatic carbons were quantitatively observed on gel polymers that were up to 6% cross-linked but claimed that only 50% of the aromatic carbons contribute to the high resolution spectrum at 10% cross-linking. They also measured the carbon-13 NMR spin–lattice relaxation time (T_1), nuclear Overhauser enhancement (NOE), and line widths. They found T_1 to be independent of cross-link level but observed a good correlation of line width and poor correlation of NOE with cross-link density. These works indicated that good quantitative ^{13}C spectra could be obtained on cross-linked polystyrenes. It was of interest to us to see if the ^{13}C line width could be correlated quantitatively with the cross-link density determined on the basis of swelling measurements in chloroform.

Experimental Section

Experimental Determination of Cross-Link Density. Ten samples of styrene–divinylbenzene copolymer were obtained in the form of microbeads from various commercial sources as noted in Table I. The samples with average diameter greater than 50 μm were pulverized further before mixing with Teflon 30B aqueous emulsion and subsequent conversion to the corresponding thin (<0.3 mm) microporous film as described in detail elsewhere.[1,2] These microporous composite films have a >50% void volume and consist of >80 wt % polymer particles enmeshed in <20 wt % PTFE microfibers. Aliquot samples cut from each of these 10 microporous films were allowed to swell overnight in chloroform at 21 °C. The corresponding volume of absorbed liquid, S, in milliliters per gram of each copolymer, was determined gravimetrically in the usual way.[1-3] The composition of the six Bio-Rad samples was determined by the manufacturer from the ratio of *p*-diethylbenzene to ethylbenzene obtained via thermal degradation of the copolymer. The S data obtained on these six samples were used to establish the characteristic linear relationship of swelling in chloroform as a function of $\tilde{\chi}^{-1/3} = \{1/(1+x)\}^{-1/3}$ (Figure 1), where x is the mole fraction of divinylbenzene in the copolymer. The cross-link density, $\tilde{\chi}$, of the other copolymers, obtained from different commercial sources (Table I), was calculated on the basis of the rearranged form of eq 1

$$\tilde{\chi} = \left\{\frac{C}{S + C\tilde{\chi}_0^{-1/3}}\right\}^3 \tag{2}$$

where C and $\tilde{\chi}_0^{-1/3}$ for swelling in chloroform was observed to be 2.32 and 1.72, respectively. The $\tilde{\chi}$ for these copolymer samples determined in a like manner with 14 other solvents were in good agreement with the corresponding data determined with chloroform. The cross-link density determined in these other four samples differed up to a factor of 14 from the manufacturer's stated composition, presumably made on the basis of monomer charge ratio. However, the linear relationship of S observed in eq 2 for 14 different solvents confirms the analysis of these six copolymers reported by Bio-Rad.

NMR Analysis. NMR samples were prepared by weighing into a 10-mm-o.d. NMR tube a 400-mg aliquot of the same polymer microbeads used to fabricate the above composite film. Approximately 4 mL of CDCl$_3$ was added and the sample allowed to swell to a homogenous gel. Excess CDCl$_3$ was removed with a long pipet to center the gel in the receiver coil. ^{13}C NMR spectra were obtained at 50.3 MHz at room temperature (22 °C) on a Varian XL-200 spectrometer, using the solvent for a ^{2}H lock. Between 1000 and 6000 transients were collected with a 10000-Hz sweep width and 8192 data points with 8-μs (40°) pulses and a 0.4-s recycle time. The line broadening used was 10 Hz for all samples except those with greater than 6% cross-linking, in which case 100-Hz line broadening was necessary for a reasonable signal/noise ratio. Line widths at half-height were measured on spectra expanded to 4 Hz/mm for widths under 400 Hz. The observed line widths in Table I have been corrected for the 15-Hz chemical shift difference between the ortho and meta carbons by subtracting 15 Hz from the measured line width of the combined pair of peaks.

Results and Discussion

The observed linear relationship of S as a function of $\lambda^{1/3} = \tilde{\chi}^{-1/3}$, i.e.

$$S = 2.32(\lambda^{1/3} - 1.72) = 2.32(\tilde{\chi}^{-1/3} - 1.72) \tag{3}$$

showed that even in this excellent solvent for polystyrene less than 0.5 mL of chloroform is absorbed per gram of polymer when the divinylbenzene mole fraction of that

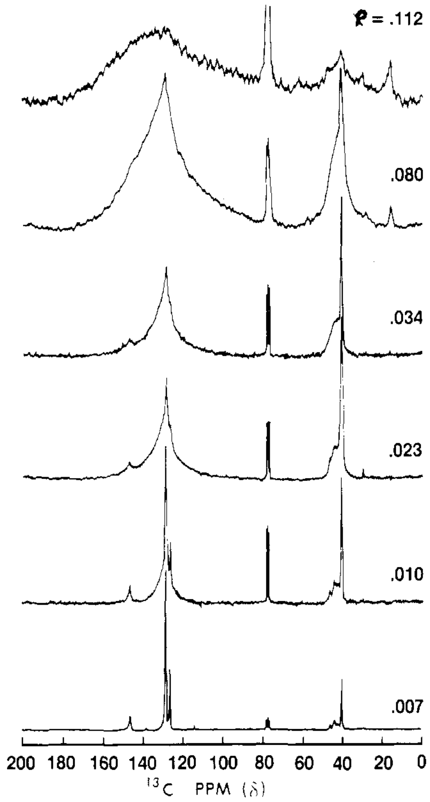

Figure 2. 50-MHz ^{13}C NMR spectra of styrene–divinylbenzene copolymers gelled in $CDCl_3$ as a function of cross-link density $\tilde{\chi}$.

polymer is greater than 0.12. This was taken to be the upper limit for the extent of cross-linked polymer that might lead to meaningful ^{13}C NMR measurements. Also, copolymer samples with $\tilde{\chi} > 12\%$ or $\tilde{\chi} < 0.7\%$ were not commercially available.

The high-resolution ^{13}C NMR spectrum of polystyrene shows a pair of absorptions for the ortho and meta carbons at 127.8 and 128.1 ppm, separated by 15 Hz at 50 MHz (see lower spectrum, Figure 2). The para carbon, at 125.8 ppm, is 105 Hz upfield, and the ipso carbon, at 145.3 ppm, is 800 Hz downfield. All the peaks broaden in cross-linked polystyrene. The pair of ortho and meta carbons overlap and are not distinguishable at cross-link densities greater than 0.5%. The para absorption is distinguishable but is 2-fold lower in intensity than the absorption due to the nearly degenerate ortho and meta carbons. To a first approximation, the line width of the aromatic carbon absorption is determined solely by the ortho and meta carbons. At line widths greater than 100 Hz it is not possible to observe the para carbon as a separate peak. However, since its intensity is only 25% of the combined intensity of the major aromatic absorption, it does not contribute significantly to the line width, measured at half-height, of the major aromatic absorption, even for line widths that exceed the ortho–para chemical shift difference. Typical spectra as a function of cross-link density are shown in Figure 2.

Line widths in Hz ($\nu_{1/2}$) for the aromatic carbons in the poly(styrene-*co*-divinylbenzene) samples, measured in $CDCl_3$ (Table I), increase monotonically with cross-link density $\tilde{\chi}$. The log–log plot of these data (Figure 3) shows an empirical exponential relationship of $\nu_{1/2}$ to $\tilde{\chi}$. The least-squares fit to the observed log–log plot, given in eq 4, has a correlation coefficient of 0.97. Equation 5 is the

$$\log(\nu_{1/2}) = 1.6 \log \tilde{\chi} + 4.8 \qquad (4)$$

$$\nu_{1/2} = 6 \times 10^4 \tilde{\chi}^{1.6} \qquad (5)$$

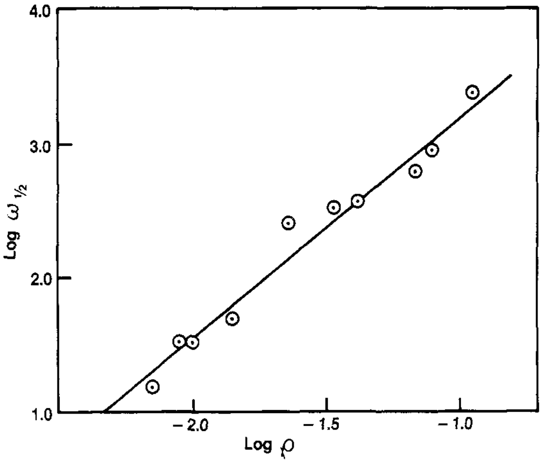

Figure 3. log–log plot of aromatic carbon line width as a function of cross-link density, $\tilde{\chi}$.

exponential equivalent of eq 4, giving explicitly the power dependence of ν. The spectrum of the $\tilde{\chi} = 0.12$ sample (top spectrum, Figure 2) shows a very poor signal/noise ratio compared to the other spectra but still fits within experimental error the line which would be determined if this point were excluded from the correlation.

These results confirm those of Ford and Balakrishnan that the changes in line width are due to cross-linking and not just to increased concentration of polymer in the gel. Although Live and Kent[9] report that the line width for a 1% cross-linked polystyrene varies proportionally with magnetic field, the increase in line width with cross-link density up to line widths in excess of 25 ppm indicates the increase must be attributed to a relaxation phenomenon (probably chemical shift anisotropy) rather than a distribution of chemical shifts in the cross-linked gel. The variation in line width is inversely proportional to the spin–spin relaxation time, T_2. The decrease in T_2 with cross-linking has been attributed to incomplete motional averaging of low-frequency motions, leading to near-static dipolar interactions, but the invariance of T_1 with cross-link density requires that rapid segmental motion be maintained in the gels.[7]

Marchenkov and Khitrin[10] have performed a theoretical analysis relating the line width to intramolecular dipole–dipole interactions. They claim $\nu_{1/2}$ should be proportional to the fourth root of $\tilde{\chi}$ when, as is the case for divinylbenzene-cross-linked polymers, the length of the cross-linkage is less than the average chain length between cross-links. Cohen-Addad, Domard, and Herz[11] have discussed the theoretical dependence of T_2 on gel samples and considered the effect of entangled chains as well as cross-links. They find that T_2 should vary as $\tilde{\chi}^{4/3}$ but observe that the dependence on $\tilde{\chi}$ is somewhat less for poly(dimethylsiloxane) gels and attribute the difference to chain entanglements. The experimental observations reported here confirm the proportionality of $\nu_{1/2}$ and $\tilde{\chi}$ but indicate the dependence on $\tilde{\chi}$ is approximately the $^3/_2$ power in divinylbenzene-cross-linked polystyrenes.

It should be noted that measurement of line widths in cross-linked systems is valid only if the gel is homogenous. In nonhomogenous gels a sharp absorption is observed for the less cross-linked portion superimposed on a very broad absorption from the portion with greater cross-links.[7]

In summary, we have observed an excellent correlation of NMR line width, cross-link density determined experimentally by swelling measurements, and cross-link density determined by pyrolytic degradation (as carried out by Bio-Rad Laboratories). However, there is no correlation between NMR line width and monomer charge ratio reported by the other manufacturers (Table I), emphasizing that the charge ratio of the comonomers made to undergo polymerization cannot be used as a reliable measure of the composition of the polymeric product.

Registry No. (Styrene)·(divinylbenzene) (copolymer), 9003-70-7.

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Polymer Swelling. 4. A Reexamination of Reported Polymer Swelling Studies for Conformance to Equations That Relate Swellability to Cross-Link Density

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ABSTRACT: The styrene–divinylbenzene copolymer swelling studies reported years ago by Staudinger, Boyer, and Rempp have been reexamined to test the validity of the observation made recently that swelling, S, of such polymers is given in terms of cross-link density, $\tilde{\chi}$, by the general equation $S = C(\tilde{\chi}^{-1/3} - \tilde{\chi}_0^{-1/3}) = C(\lambda^{1/3} - \lambda_0^{1/3})$, where $\lambda = 1/\tilde{\chi}$ is the average number of carbon atoms in the "backbone" of the polystyrene segments between cross-link junctions, C is a constant characteristic of the swelling power of the liquid for the kind of polymer being investigated at temperature T, and $\tilde{\chi}_0$ is the critical cross-link density of the polymer at or above which $S = 0$. In every reexamination, S, calculated from the reported swelling data, was a linear function of $\lambda^{1/3}$, calculated from the corresponding reported polymer molecular weight data, but the constants C and $\lambda_0^{1/3}$ depended upon the conditions of copolymerization that affect the λ-distribution. Similar linear relationships appear to obtain for swelling studies of "macronet" cross-linked polyesters reported by Takahashi and perhaps for water-swellable "macronet" cross-linked polyacrylates reported by Refojo. It is concluded that the above linear relationship may be general for cross-linked polymer networks and therefore useful in the planning of future studies aimed at a better understanding of polymer swelling in terms of the molecular structures of the polymer and the swelling liquid.

Introduction

We have reported[1] that thin but tough microporous composite films can be made from particulate cross-linked polymer and poly(tetrafluoroethylene) [PTFE] by a work-intensive procedure using an ordinary rubber mill. Because the particles (>80% by weight) are isolated, evenly distributed in three dimensions, and irreversibly enmeshed in an "open-celled" network of PTFE microfibers (<20%) as shown in Figure 1 of ref 1, these composite films are ideal for studying the absorption of liquids and/or vapors by the major component. Such microporous films made from *non-cross-linked* polymer particulates were used by Fowkes[2] to monitor absorption of organic vapors in his study of acid–base complexes of polymers, and we have used such microporous films made from *cross-linked* polystyrene particles[3] to study polymer swelling in excess liquid as a function of cross-link density $\tilde{\chi} = 1/\lambda$, where λ is the average number of carbon atoms in the "backbone" of the polystyrene segments between cross-link junctions.

It was shown[3] in the latter study that the volume, S, of liquid absorbed by a unit weight of poly(styrene-*co*-divinylbenzene) [poly(Sty-*co*-DVB)] at swelling equilibrium in excess liquid is given by the general equation

$$S = C(\lambda^{1/3} - \lambda_0^{1/3}) = C(\tilde{\chi}^{-1/3} - \tilde{\chi}_0^{-1/3})$$

where C is the swelling power of the liquid at temperature T for the copolymer, and $\tilde{\chi}_0$ is the critical cross-link density of the copolymer, above which $S = 0$ (i.e., not measurable with the experimental procedure of this investigation). It was also shown[4] that the aromatic ^{13}C NMR line width, $\nu_{1/2}$, is related to the cross-link density, determined by means of the above swellability–cross-link density relationship, by the equation

$$\nu_{1/2} = 4.8 \times 10^4 \tilde{\chi}^{-1.62}$$

The purpose of this publication is to report tests of the validity of these equations using swelling data already reported for poly(Sty-*co*-DVB) and "macronet" cross-linked polymers prepared by earlier investigators.

Results and Discussion

(A) Sty-DVB Copolymers Made via Anion Polymerization. Swelling data for Sty–DVB copolymers that have very narrow range molecular weight distributions of the polystyrene segment between "nodules" of divinylbenzene have been reported by Rempp[5-7] and his coworkers. These copolymers were made via anionic polymerization[8] with an efficient bifunctional initiator to produce a very narrow range molecular weight distribution (determined by the monomer-to-initiator ratio) of polymer with "living" carbanions at both ends of its linear chain. Divinylbenzene was then added to produce the corre-

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