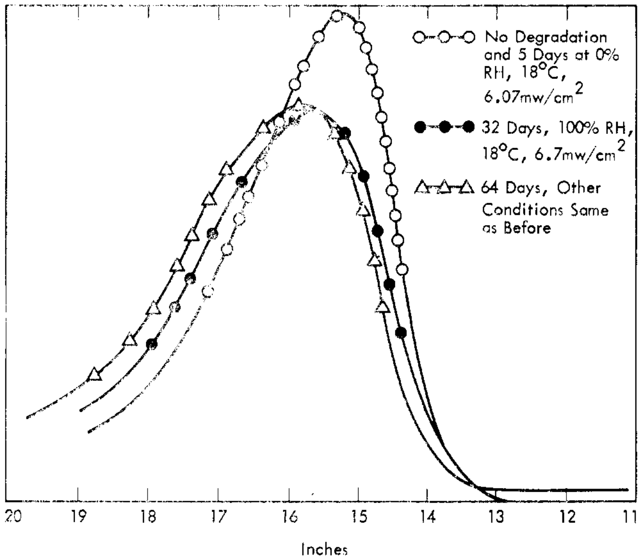

Figure 4. GPC traces of Lexan films after they have undergone photodegradation in the solid state.

benzophenone emits phosphorescence presumably because the intromolecular hydrogen bond is disrupted with resultant increase in the triplet lifetime. Neither the mechanism nor the relative magnitudes of reaction rates change significantly when water is introduced to the system.

It is well known that chain scission is another major mode of photodegradation in this system.[3,10,11] In the radical pair mechanism, these two modes of photodegradation arise from the same primary process, e.g., the C–O bond homolysis. On the other hand, if we propose that the parent excited state of photoFries rearrangement is the first triplet, it is possible that chain scission is an independent process, probably taking place from the $\pi^* \leftarrow n$ singlet. The evidence for chain scission on photodegradation in the solid state is (1) loss of C–O and C–C bond intensities in the FTIR (ATR) spectra, (2) GPC elution profiles of degraded film samples dissolved in $CHCl_3$ (Figure 4), and (3) decrease in T_g and tensile strength as photodegradation proceeds. These plots indicate that chain scission is inhibited as photoFries products build up.

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Why the Phase Boundaries Should be Sharp in Most Phase-Separated Block Copolymers

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Recently, it was found[1] that the glass transition temperatures of the styrene microphases as determined by DSC and DTA measurements in low molecular weight diblock and triblock copolymers of styrene with dimethylsiloxane, butadiene, isoprene, and ethylene oxide depended only on the molecular weight of each styrene block in the block copolymer molecules. The value of this glass transition temperature, T_g, did not depend on the chemical nature of the rubbery blocks, on the position of the styrene block or blocks within the block copolymer molecule, or on the percentage composition of the block copolymer. The chemical nature and/or molecular weight of the rubbery block influenced the T_g of the styrene microphase only when the molecular weight and composition of the block copolymer was near that at which microphase separation no longer takes place.

These data strongly suggest that the nature of the styrene microphase is exactly the same in all the block copolymer samples investigated. If there is any mixing of blocks of different chemical nature in the glassy microphases, it must be exactly the same for all samples. This is highly unlikely for rubbery phases that are as different as butadiene and isoprene are from dimethylsiloxane and ethylene oxide. Among other things, the compatibility of the oligomers of the different rubbers with styrene oligomers is quite different, and this difference should carry over into differences in homopolymer miscibility. For example, it was found that hexamers of styrene and dimethylsiloxane are immiscible at room temperature and have an upper critical solution temperature of 35 °C.[2] A 10-mer of styrene and a 15-mer of isoprene, on the other hand, were miscible at room temperature and had an upper critical solution temperature of −30 °C.[3] In support of the lesser compatibility of poly(dimethylsiloxane) with polystyrene, one may note that the solubility parameter of dimethylsiloxane is much farther from that of polystyrene than are the solubility parameters of polybutadienes or of polyisoprenes,[4] no matter what their microstructure.

It seems to me that the only way to preserve the similar nature of the styrene microphases (made up of styrene blocks with molecular weights 5000 to 20 000) in the different block copolymers in view of the different compatibilities of the respective homopolymers is to assume that there is virtually no mixing between segments of rubbery and glassy blocks in the glassy microphase.

Diameters of these styrene microphases are probably of the order 50–150 Å. It is impossible to avoid mixing completely between the blocks, since there must be some contact between them at the surfaces between microphases, but these surface contacts should be similar in all block copolymers with similar morphology. These inevitable contacts constitute the minimum interface between microphases; the thickness of this minimum interface is hard to assess, but should be of the order of 5 Å.

The preceding considerations lead to the idea that microphase boundaries must be quite sharp in these block copolymers. This appears to be the only way to assure the almost identical nature of the styrene microphases in very different low molecular weight block copolymers, both very different chemically in terms of the chemical nature of the rubbery blocks, and very different physically in terms of the location of the styrene block in the block copolymer molecules, center or end block, and in terms of morphology as indicated by the widely differing percentage compositions of the samples investigated.

There is additional evidence in the literature for the sharpness of microphase boundaries. Skoulios[5] reported some work on X-ray crystallography of a two-block styrene–isoprene copolymer, with $\bar{M}_w = 3 \times 10^5$ and volume fraction per block exactly 0.50. The bulk copolymer had a lamellar morphology in which the thickness of each layer was 450 Å. The X-ray patterns, whose relative intensity was used to calculate a maximum thickness for the diffuse interface between microphases of 12 Å, remained up to the 15th order of diffraction. This value is of the order of the size of a single monomer unit in the block copolymer and therefore denotes a sharp interface. Kim[6] applied a more general two-phase scattering theory to small-angle X-ray scattering from a styrene–butadiene–styrene block copolymer of molecular weight 7.6×10^4 and volume fraction about 13.5:73:13.5 which probably had polystyrene spherical microphases in a polybutadiene matrix. His data also indicated that the interface between microphases was sharp.

More recently, X-ray scattering data on block copolymers have been interpreted somewhat differently to give larger values for the thickness of the interface between microphases. Hashimoto et al.[7] calculated an interface thickness of about 30 Å in two lamellar samples of styrene–isoprene diblock copolymer with (a) 43 wt % styrene and mol wt 5.38×10^5 and (b) 59 wt % styrene and mol wt 1.05×10^5 and with thickness of each lamella about 300 Å. Todo et al.[8] studied styrene–isoprene diblock copolymers with 16–22 wt % isoprene in which spherical microphases of polyisoprene were dispersed in a polystyrene matrix. Copolymer molecular weights ranged from 7.4×10^4 to 6.6×10^5; the radii of the polyisoprene spheres varied concomitantly from 68 to 309 Å. An interfacial thickness of about 20 Å was calculated for each sample from the small-angle X-ray scattering measurements.

In summarizing the small-angle X-ray scattering data on bulk block copolymers, one may state that the interface thickness calculated from the data depends on the investigator and the exact theoretical treatment employed in the calculation much more than it depends on sample morphology, composition, or molecular weight. In the styrene–butadiene and styrene–isoprene block copolymers that have been investigated, a maximum interface thickness of 12 to 30 Å has been calculated by different investigators making the interfaces anywhere from sharp to diffuse. Assuming for the moment that all data and all theoretical analyses of the data were equally excellent, it seems that the analyses that give a sharp interface are more convincing than those that give diffuse interfaces for the following reason. A smooth diffuse interface and a rough but sharp interface should lead to almost the same X-ray scattering data in a large sample. That is, scattering from a group of perfect spherical inclusions with diffuse interfaces should be much the same as scattering from a group of not-quite-spherical inclusions with sharp interfaces, especially if the surfaces of the inclusions have a somewhat wavy shape. Todo et al.[8] found, however, that their calculated interface thickness did not change when the samples were annealed above the polystyrene glass transition temperature even though annealing would be expected to smooth out wavy interfaces.

At any rate, there appear to be sufficient data in the literature that indicate the presence of sharp interfaces in block copolymers to prompt the simple theoretical discussion below. I recognize the existence of various theoretical treatments of microphase separation and of microphase morphology which specifically incorporate a diffuse interface and which even allow calculation of its thickness in some cases.[9-11] Nevertheless, because of the experimental data cited above, I will examine what happens when a diffuse interface is incorporated into a theoretical treatment of microphase separation in which the phase boundaries had been considered sharp.[12] There is another theoretical treatment with sharp interfaces between microphases in the literature,[13] but this will not be considered further here.

Theoretical

In a previous publication,[12] I derived the free-energy change, ΔG, on microphase separation for a system of monodisperse block copolymer molecules with long blocks for which there is no volume change of the mixing. The blocks being considered here are not necessarily very long; they vary down to 50 monomer units, making these considerations only approximate in such cases.

For 1 mol of block copolymer molecules containing repeat groups A and B, each having the same volume as the volume of the lattice site used for calculation of ΔG, and for a lattice coordination number of 8, one obtains[12]

$$\frac{\Delta G}{RT} = -\frac{3n_A{}^c v_B{}^c \chi_{AB}}{4} - \ln\,(v_A{}^c)^{v_A{}^c}(v_B{}^c)^{v_B{}^c} + 2(m-1)(\Delta S\ \mathrm{dis}/R) - \ln\,(m-1) \quad (1)$$

In eq 1, m is the number of blocks in each copolymer molecule, $v_A{}^c$ and $v_B{}^c$ are the volume fractions of A and B in each block copolymer molecule, respectively, $n_A{}^c$ is the number of A repeat units in each block copolymer molecule, $(\Delta S\ \mathrm{dis}/R)$ is essentially equal to the entropy lost when one repeat unit of the block copolymer is immobilized at the sharp interface between microphases (taken equal to 1.0 as discussed earlier[12]), R is the gas constant, T is the absolute temperature, and χ_{AB} is the interaction parameter between A and B units.

The last two terms on the right-hand side (rhs) of eq 1 are concerned with the formation of a sharp interface between microphases and would be expected to decrease as the interface becomes diffuse. The first term on the rhs of eq 1 is the enthalpy of mixing lost during microphase separation assuming a sharp interface. If fraction f_i of the total volume of the sample consists, however, of an interphase in which, on the average, the mixing between A and B units is exactly the same as it would be in the sample in which random mixing of all A and B units occurred, then the enthalpy change on microphase separation of the sample with this kind of diffuse interface would be equal to the first term on the rhs of eq 1 multiplied by $(1 - f_i)$. The second term on the rhs of eq 1 is proportional to the

Table I
Free Energy on Microphase Separation of a Diblock Copolymer with $\upsilon_A{}^c = \upsilon_B{}^c = 0.5$, $n_A{}^c = 1000$

χ_{AB}	f_i	$\Delta G/RT$	χ_{AB}	f_i	$\Delta G/RT$
0.05	0	−16.06	0.007	0.2	+0.011
0.05	0.1	−14.48	0.007	0.3	−0.006
0.05	0.2	−12.89	0.007	0.5	−0.024
0.01	0	−1.06	0.007	0.6	−0.027
0.01	0.1	−0.98	0.007	0.7	−0.024
0.01	0.2	−0.89	0.007	0.9	−0.012
0.008	0	−0.31	0.001	0	+2.32
0.008	0.1	−0.30	0.001	0.1	+2.06
0.008	0.2	−0.29	0.001	0.5	+1.10
0.007	0	+0.068	0.001	0.9	+0.21
0.007	0.1	+0.036			

negative of the entropy lost when one molecule undergoes complete microphase separation. This term was derived with the idea that volume fraction $\upsilon_A{}^c$ of the copolymer suddenly becomes restricted to volume fraction $\upsilon_A{}^c$ of its original volume and volume fraction $\upsilon_B{}^c$ suddenly becomes restricted to $\upsilon_B{}^c$ of its former volume. If volume fraction f_i becomes mixed interphase, then the $\upsilon_A{}^c$ fraction of the block copolymer becomes suddenly restricted to $\upsilon_A{}^c(1 - f_i) + f_i = \upsilon_A{}^c + f_i\upsilon_B{}^c$ of the sample volume while the $\upsilon_B{}^c$ fraction of the block copolymers becomes restricted to $\upsilon_B{}^c + f_i\upsilon_A{}^c$ of the sample volume. The second term on the rhs of eq 1 therefore becomes

$$-\ln \{\upsilon_A{}^c + f_i\upsilon_B{}^c\}^{\upsilon_A{}^c}\{\upsilon_B{}^c + f_i\upsilon_A{}^c\}^{\upsilon_B{}^c}$$

The last two terms on the rhs of eq 1 will not disappear immediately as the interface becomes less sharp, but the exact form of these terms for diffuse interphases becomes difficult to consider. Although it is probably incorrect in detail to multiply these terms by $(1 - f_i)$, this seems like a reasonable way to let them disappear.

In the presence of a diffuse interface of volume fraction f_i, then, eq 1 reads

$$\Delta G/RT \approx \{-{}^3\!/_4 n_A{}^c\upsilon_B{}^c\chi_{AB} + 2(m - 1) - \ln (m - 1)\}\{1 - f_i\} - \ln \{\upsilon_A{}^c + f_i\upsilon_B{}^c\}^{\upsilon_A{}^c}\{\upsilon_B{}^c + f_i\upsilon_A{}^c\}^{\upsilon_B{}^c} \quad (2)$$

Some simple calculations using eq 1 and 2 indicate that free energy considerations of this sort predict sharp boundaries between microphases except when χ_{AB} is close to the value at which complete mixing of the blocks occurs. Calculated values of $\Delta G/RT$ for a diblock copolymer with $\upsilon_A{}^c = \upsilon_B{}^c = 0.5$, $n_A{}^c = 1000$ (a total molecular weight in the vicinity of 200 000), and various values of χ_{AB} and f_i are shown in Table I. For values of χ_{AB} of 0.008 and above, the values of $\Delta G/RT$ are negative for both sharp and diffuse interfaces, but the most negative value is for the sharp interface, thus indicating that free energy considerations favor the sharp interface in these cases. For $\chi_{AB} = 0.007$, $\Delta G/RT$ is positive for the narrow interface, indicating an unfavorable free energy change for microphase separation, and there is a minimum in the negative values of $\Delta G/RT$ at $f_i \approx 0.6$, that is, when 60% by volume of the sample is interphase. That is, the sharp interface hypothesis predicts no microphase separation at all in such a sample, but present considerations indicate a partial phase separation. For $\chi_{AB} = 0.001$, Table I shows positive values of $\Delta G/RT$ for both sharp and diffuse interfaces, so that no phase separation at all is predicted for such a sample.

These calculations may be crude, but they are in accord with experimental observations such as the following. Although T_g's as determined by differential scanning calorimetry (DSC) of microphases generally mimic those of the corresponding homopolymers, the DSC traces of block copolymers that are on the verge of microphase separation show a very broad temperature transition zone which may indicate a diffuse interphase.[14,15]

I have tried to show that both experimental data and theoretical considerations indicate that interfaces between microphases are usually sharp, except when conditions are such that the block copolymer is just on the verge of microphase separation.

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Effect of Stereosequence on Carbon-13 Spin-Lattice Relaxation Times for Poly(vinyl chloride)

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Differences in the spin-lattice relaxation times (T_1) for nuclei in syndiotactic and isotactic configurational sequences have been reported in ^1H and ^{13}C NMR studies on poly(methyl methacrylate)[1-4] and in a ^{13}C NMR study on polypropylene.[5] However, Inoue et al.[6] found no dependence of ^{13}C T_1 values on stereosequence for poly(vinyl chloride) in dimethyl-d_6 sulfoxide at 50 °C. We report in this work the measurement of the ^{13}C spin-lattice relaxation times of poly(vinyl chloride) in 1,2,4-trichlorobenzene/*p*-dioxane-d_8 at 107 °C. The T_1 values of both the methylene and methine carbons are longer for the isotactic sequences than for the syndiotactic sequences.

Experimental Section

The poly(vinyl chloride), Geon 103EP, was obtained from B. F. Goodrich Co. The polymer was observed as a 10% wt/v solution in a 70/20 mixture of 1,2,4-trichlorobenzene and *p*-dioxane-d_8 at 107 °C. An 18-mm capillary cell was used in the