Table I
Glass Transition Temperature of Polyisoprene and Its Photochemical Adduct with Benzophenone Determined by DSC

Irradiation time, min	Residual double bonds, mol %	T_g, °C
0	100	−64.9
15	70.4	31
30	61.8	37.8
45	58.0	37.6
60	51.5	41.2
120	42.6	45.8

is quite rapid, as shown in Figure 1. Most of the reaction takes place within 1 h after which no further radiation seems to occur. The extent of reaction increases with the initial concentration of benzophenone. Figure 2 shows the infrared spectra of the extracted films taken after various times of irradiation. They are qualitatively similar to those of the polymers made in solution and should therefore have similar structures, although it is not possible to check this by NMR because of the insolubility of the films. The maximum conversion to cyclic products, as estimated from the removal of internal double bonds in the polyisoprene, seems to level out at about 70%, as shown in Figure 1. It is not known whether this is a limit imposed by steric requirements in the chain or by the fact that the benzophenone is no longer soluble in the polymer at high degrees of conversion. Furthermore, an equimolar mixture of polyisoprene and benzophenone contains 73 wt % benzophenone, and the benzophenone tends to crystallize out at these high concentrations.

The inclusion of bulky phenyl groups into the polyisoprene chain, in addition to the "stiffening" effect of the oxetane ring, would be expected to raise the glass transition of the polymer. Measurements of T_g on a series of films made by irradiation of equimolar mixtures of benzophenone and polyisoprene for various times at 110 °C are given in Table I. The measurements were made using a Perkin-Elmer DSC IB differential scanning calorimeter. Addition of only 30 mol % benzophenone gives an increase of more than 100 °C in the glass transition, confirming the expected effect of inclusion of ring structures in the polymer chain. Increases in benzophenone units above this amount apparently do not increase T_g further, for reasons which are not obvious. It is possible that the double bond analysis overestimates the yield of cyclic products, and that toward the end of the reaction double bonds are removed by mechanisms other than cyclization, such as cross-linking.

In conclusion, these studies have shown that it is possible to add appreciable quantities of benzophenone to *cis*-polyisoprene to form novel polymer structures in which an oxetane ring replaces a double bond in the backbone of the polyisoprene chain. Presumably this reaction could be used with other polydienes and carbonyl compounds to make polymeric structures unattainable by conventional polymerization reactions. This reaction might be considered as a new type of photopolymerization in which the polydiene acts as a "template" and the rings are formed by successive addition of a photoexcited intermediate.

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Trace Element Characterization of Thin Polymer Films by Proton-Induced X-Ray Emission Spectrometry

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Trace element levels in polymers reflect the concentrations of certain polymer constituents including catalysts, stabilizers, and fire retardants. Their characterization is of interest because these constituents affect the physical, chemical, and electrical properties of polymers. Another interest in monitoring trace constituents of polymers arises out of the medical concern that certain toxic constituents of plastics can leach out when the plastics come into contact with food or body fluids. There is also a need to know the trace element levels in selected thin plastic films which can serve as clean backing materials on which samples can be deposited for trace element analysis by x-ray and proton-induced x-ray fluorescence.

Proton-induced x-ray emission spectrometry (PIXE) is a technique which has been developed and applied to the trace element analysis of environmental samples (e.g., air particulates and trace elements in water) and biomedical samples.[2–8] The references cited in these articles provide a good guide to the literature describing PIXE and its applications. We wish to point out that this technique is particularly well-suited for the simultaneous quantitative analysis of trace elements in thin plastic films.

In PIXE, the characteristic x-ray emissions of interest accompany transitions of electrons into inner atomic shell vacancies created by bombardment by protons with energies of several MeV. These high-energy protons can be produced by Van de Graaff accelerators which exist at a number of laboratories. The energy of a characteristic x ray is determined uniquely by the atomic number of the element from which it emerges. These x rays are individually detected by a lithium-drifted silicon (Si(Li)) semiconductor detector and generate signal pulses which are linearly proportional to their energy. By counting and measuring the number and amplitude of these signal pulses with a multichannel analyzer, one obtains multielement spectra. In Figure 1 we see a typical pulse-height spectrum obtained from a Nuclepore[10] film.

The analysis procedure is calibrated by making measurements on known quantities of selected elements deposited on thin plastic films. These deposits result from solutions which contain the elements of interest at known concentrations. The uniform proton beam includes the area of the dried solution deposit so that for fixed integrated charge (known number of protons) and fixed geometrical configuration, one obtains a calibration in terms of counts per nanogram for each element of interest. Analyses of thin plastic materials are then made

Table I
Fe, Cu, and Zn Impurities in Several Thin Backing Materials (Mean Value and Range in Parentheses)[a]

Type of backings (No. of backings analyzed)	[Fe], ng/cm^2	[Cu], ng/cm^2	[Zn], ng/cm^2	Areal mass, mg/cm^2
Polycarbonate, Nuclepore (6) (blue separators)	9 (8–10)	5 (4–6)	1.5 (1–3)	1.0
Polycarbonate, Nuclepore (6) (green separators)	31 (16–50)	12 (8–18)	14 (6–24)	1.0
Cellulose acetate, Millipore (4)	21 (14–25)	35 (19–48)	24 (17–32)	1.0
Polypropylene (6)	5 (4–7.5)	4 (2–9)	6 (1.5–11)	1.2
Polyester, Mylar (3) 0.000 15 in.	6.5 (4.5–12.5)	6 (2–13)	44 (35–69)	0.5
Kodak paper (2)	56 (54–58)	88 (86–90)	129 (95–163)	1.0
Filtrator coffee paper (2)	98 (96–100)	73 (72–74)	17 (14–20)	1.6

[a] Uncertainties in the above numbers are on the order of 20%. Measurements were by proton-induced x-ray fluorescence using 2.5 MeV protons at beam currents of 50–100 nA. Sample analysis times were on the order of 5–10 min.

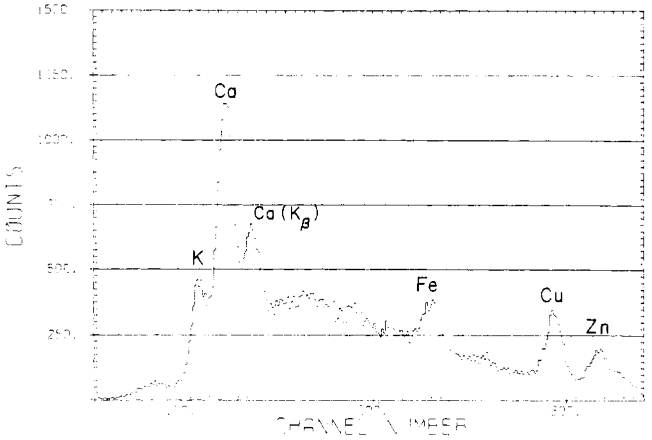

Figure 1. Pulse height spectrum obtained during the analysis of a blank Nuclepore polycarbonate film by 2.5 meV protons for a total integrated charge of 90 μC.

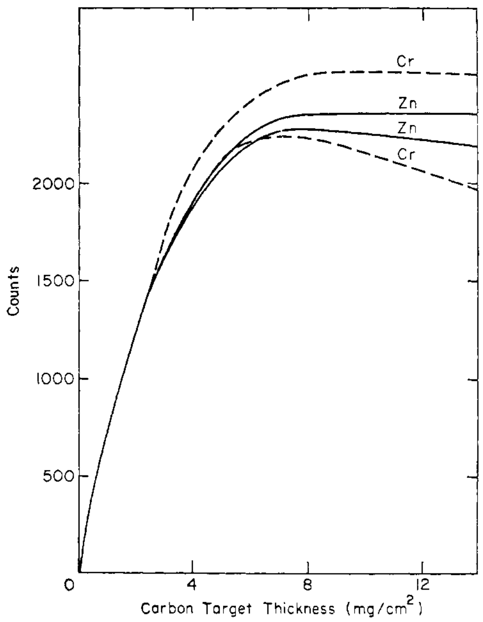

Figure 2. Relative numbers of chromium and zinc x rays emerging from carbon films of varying thickness with fixed concentrations of Cr and Zn. Decreasing x-ray production cross sections due to proton deceleration of incident 2.5 MeV protons are taken into account in the upper two curves. The lower Zn and Cr curves show the additional effect of x-ray absorption by the sample.

by bombarding a defined area of the material for a fixed integrated charge. In all cases, the continuous x-ray background was subtracted. By combining the resulting information on counts per square centimeter with the calibration results in counts per nanogram, the trace element composition of the films in units of nanograms per square centimeter can be determined.

Use of the technique of PIXE for trace element analysis of thin polymer films is not complicated by severe matrix effects. We have studied the effect of x-ray absorption within samples and of proton energy loss along the path of the protons in order to make corrections where required. Our study of these effects is based upon consideration of a model for varying thickness carbon films which are doped with traces of chromium and zinc. The matrix of carbon provides a good representation of polymers of various composition if thicknesses are compared in units of mg/cm^2. The chromium and zinc concentrations are chosen so that for thin targets the intensities in counts are the same for chromium and zinc and comparisons are thereby simplified. As protons lose energy in penetrating a sample, the cross section for characteristic x-ray production decreases and the yield of x rays does not continue to increase linearly for increasing thickness. This effect is demonstrated by the top two lines for chromium and zinc in Figure 2 for protons with an incident energy of 2.5 MeV. The curves result from calculations[9] based upon a proton beam entering the film at an angle of 45° with respect to the normal and an x-ray detector located behind the film at right angles to the proton beam so that the x rays detected also emerge at an angle of 45° with respect to the normal. The lower two curves for chromium and zinc also include the additional effect of x-ray absorption within the films. Calculations of this type allow corrections to be made for films of thicknesses of a few mg/cm^2. We note that, for elements falling between chromium and zinc in atomic number, linearity of intensity with thickness is good to within 5% for films of 0.5 mg/cm^2 thickness. As can be seen from the graph, linearity of intensity ratios (e.g., Cr/Zn) with thickness is good over a considerably greater thickness range.

Results

The results obtained for the levels of iron, copper, and zinc in batches of several different polymer films and thin papers are presented in Table I. These results are presented only to give an idea of the ranges of iron, copper, and zinc present and the capabilities of this technique for this type of measurement. We have often found considerable variations from batch to batch so that these values should not be assumed to be generally valid for the materials mentioned in the table. At these levels, contamination can be a serious problem and care must be exercised in the handling of materials.

Proton-induced x-ray emission spectrometry is well-suited to the quantitative analysis of trace elements in thin polymer films. This is because of the technique's high sensitivity and because trace element analyses of thin films of low atomic number material are not significantly affected by errors associated with x-ray absorption and proton energy loss.

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Interpretation of the Gibbs Phase Rule in the Presence of a Block Copolymer

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It is known that most block copolymers, even if quite monodisperse, form domains or microphases in bulk samples or films. In an A–B block copolymer, these domains or microphases exhibit many of the properties of bulk phases of homopolymers A and B, for example, glass transition temperatures or crystalline melting points. One is therefore inclined to attribute *all* properties of macroscopic bulk phases to these domains. This, however, is not always possible, and is particularly inappropriate in considerations involving the Gibbs Phase rule.

When using the Gibbs Phase rule, one considers phases that are in equilibrium with each other, whether these be bulk phases or surface phases. In the absence of chemical reactions or of surface phases, one uses[1]

$$f = c - p + 2$$

where f is the number of degrees of freedom or independent variables which may describe the system, c is the number of independent components in the system, and p is the number of phases in equilibrium. If the system consists solely of a monodisperse A–B block copolymer which exhibits microphase separation, the number of phases, p, in equilibrium with each other must be considered to be *one*, not two. This is because the presence of microphases of type A and of type B represents a minimum in the possible free energy of the system; it does *not* represent two phases in equilibrium.[2] In such a system, $c = p = 1$, and $f = 2$. In other words, microphase separation may be observed at a variety of temperatures and pressures. If an equilibrium should be possible between a condition in which the A and B blocks of the block copolymer are uniformly mixed and a condition in which both A and B domains exist, then $c = 1$, $p = 2$, and $f = 1$. At a fixed pressure, therefore, such an equilibrium can only exist at a single temperature.

When a second component, polymer or solvent, is added to an A–B block copolymer, the same considerations apply. For example, if the second component is homopolymer A, it may mix completely with the block copolymer domains of type A. Then again only a single "phase" is present as far as the phase rule is concerned and $c = 2$, $p = 1$, and $f = 3$. This means that such complete mixing of homopolymer A with the A domains of the block copolymer may be observed over a range of temperature, pressure, and weight fraction of homopolymer A in the block copolymer. When macroscopic phases of homopolymer A are present in equilibrium with block copolymer which may or may not contain homopolymer A mixed with its A domains, then $p = 2$, $c = 2$, and $f = 2$, that is, this condition may be observed over a range of temperatures and pressures, but the weight fraction of homopolymer A in the A domains will be fixed at any particular T and P.

If the second component in the system is a solvent that may partition between the A and B domains of the block copolymer, $c = 2$, $p = 1$, and $f = 3$. This condition is similar to that in which homopolymer A enters only the A domains. If, however, sufficient solvent is present that it cannot all enter the microphases, then there will probably be an equilibrium between block copolymer solution and micelles. Now $p = 2$ and $c = 2$, and $f = 2$, that is, at any fixed temperature and pressure the concentration of solvent in both solution and micelles is fixed when these phases are in equilibrium. Presumably, the concentration of block copolymer in the solution phase would be equal to the critical micelle concentration at that T and P.

One might continue these arguments with more and more components in the system, but it is of greater interest to consider the phase rule in a case in which the block copolymer acts as a surface active agent between two macroscopic phases made up of two other components. We now have $c = 3$ and $p = 2$ but must use the phase rule as modified for considerations of surface phases. If the interface between macroscopic phases is curved and if there are no chemical reactions between components, then the phase rule may be written[3]

$$f = c - \psi + s + 1$$

where ψ is the number of surface phases present and s is the number of types of surface present. Between two macroscopic phases, there is only one type of surface, so that $s = 1$. The surface phase may have a gas-like, a liquid-like, or a solid-like character, and several of these may be present on any type of surface. Assuming that only a single such surface phase is present, $\psi = 1$, and then $f = 4$. Presumably, the block copolymer could act as a surface active agent at a range of temperature, pressure, radius of curvature of the interface, and concentration of block copolymer at the interface. Again, in this last consideration, the block copolymer is treated as a single entity, and the different domains inhabited by the A and B blocks are not treated as if they were different phases.

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(1) J. W. Gibbs, "The Scientific Papers of J. Willard Gibbs", Vol. I, Dover Publications, New York, N.Y., 1961, Chapter III.

(2) The use of the word "phase" for this condition of minimum free energy of the block copolymer may be somewhat confusing since this condition in-