reduced PTFE. Barker et al.[7] report that freshly formed films from electrochemical reduction exhibit resistances of 10^{-1}–10^{-2} Ω cm but that this value increases by several orders of magnitude when the film is exposed to air, water, or methanol and slowly increases when exposed to nitrogen or vacuum. We believe that these data are inconsistent because (1) the salts from the reductions were not removed and ionic contributions to conductivity were not addressed and (2) the reactions were not consistently run in inert environments.

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Registry No. PTFE (homopolymer), 9002-84-0; dipotassium benzoin, 16152-63-9.

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(9) Total exclusion of oxygen is necessary. The PTFE film (5 mil, Commercial Plastics/Du Pont Teflon) was extracted with THF for 24 h in a Soxhlet extractor and dried under vacuum at 60 °C to constant weight. Benzoin (Aldrich) was recrystallized twice from ethanol and stored in a vacuum desiccator. Potassium *tert*-butoxide (Aldrich) was sublimed. Doubly distilled water (Gilmont still) was degassed by purging with nitrogen. Tetrahydrofuran was distilled from sodium benzophenone dianion; dimethyl sulfoxide was distilled from calcium hydride at reduced pressure.

(10) Sample resistance was measured with a Fluka multimeter. The samples were mounted on two platinum electrodes with Electrodag under nitrogen. The smallest resistance obtained was 6000 Ω; thus contact resistance could be ignored and four probe measurements were unnecessary. The minimum resistance was used in the formula $\sigma = l/wt\Omega$, where l is the distance between electrodes, w is the width of the sample, and t is the conducting layer thickness.

(11) Iodine doping entailed exposure of the electrode-mounted sample to dry solid iodine at room temperature (initial pressure 0.005 mm). Conductivity normally reached a maximum after 30 min. Quantitative dopant uptake experiments indicated that 0.1–0.19 mol of I_2 per monomer equivalent of reduced PTFE was incorporated.

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Conjugated Polyenes: A Modified Equation To Relate $n_{C=C}$ and $\nu_{C=C}$

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Maddams et al.[1] have recently proposed an exponential equation to establish the accurate relationship between ν_2 (the C=C stretching frequency) and the number of conjugated C=C units, $n_{C=C}$, in polyenes. The aim of this Note is to propose a modification of such an equation that fits experimental data much better than the previously reported equation.

Table I
ν_2 and $n_{C=C}$ Values for Some Conjugated Systems

compd	$n_{C=C}$	ν_2/cm^{-1}	ref
1-hexene	1	1638	7
isoprene	2	1637	
alloocimene	3	1629	
vitamin A acetate	5	1580	
β-carotene	11	1521	
Ph(CH=CH)$_n$Ph	5	1567	4
	6	1552	
EtOOC(CH=CH)$_n$COOEt	1	1664	8
	2	1622	
	3	1621	
	4	1596	
	5	1570	
	6	1562	
	7	1550	
	8	1540	
β-carotene	11	1527	6
lycopene	11	1516	
β-carotene	11	1520	9

The equation of Maddams et al. was of the form $\nu_2 = \nu + ae^{-bn}$, where n stands for $n_{C=C}$, a and b are constants (151.24 cm^{-1} and 0.07808, respectively), and ν corresponds to the limiting value of ν_2 for an infinite length chain of conjugated C=C units; the position of the ν_2 band is very accurately determined in the Raman spectra of polyenes as a consequence of a resonance Raman effect,[2] also observed by us when studying the polymerization of C_2H_2 on TiO_2 (rutile) surface.[3]

The above values for a and b in the exponential equation were derived by Maddams et al. from ν_2 values in the literature[4-6] for low molecular weight polyenes, while the limiting value, ν, was obtained from the Raman spectra of *trans*-polyacetylenes, recorded with the excitation wavelengths at 676.4 and 752.2 nm (when a long-wavelength excitation beam is used, resonance due to long-chain polyenes with low ν_2 values occurs).

The literature data used by Maddams et al. to obtain the above values for a and b have been collected in Table I, together with some other data from the literature.[7-9] However, when the exponential equation, with the constants of Maddams et al.,[1] is applied to these data to obtain the number of conjugated C=C units as a function of the experimental ν_2 values for low molecular weight polyenes (n = 1–11), $n = -\ln((\nu_2 - \nu)/a)/b$, the results shown in Figure 1 (full circles) are obtained. In Figure 1, the number of C=C units, as calculated by applying the equation above to the experimental ν_2 values collected in Table I, n_c, have been plotted vs. the actual $n_{C=C}$ values for these polyenes, n_t. The points fit a straight line defined by the equation $n_c = 1.542n_t - 4.555$, with regression coefficient $r = 0.9839$; i.e., for long chains of polyenes (where the independent term of this equation will be negligible) the $n_{C=C}$ values calculated by using the exponential equation would be ca. 50% larger than the real ones.

The value of $\nu = 1461 \pm 1$ cm^{-1} has been reported by several authors from studies with differently obtained polyenes,[1,10,11] and even lower values have been reported by Kuzmany[12] (1459 cm^{-1}) and Kletter et al.[13] (1457 cm^{-1}). Other authors had previously proposed nonexponential, but reciprocal, equations of the type $\nu_2 = \nu + b/n_{C=C}$ to determine $n_{C=C}$ from ν_2; so, Lichtmann and Fitchen[14] proposed $\nu = 1450$ cm^{-1}, as determined from the wavelength-independent, low-frequency origin of the band, as the limiting value to be used with this reciprocal equation; Kuzmany[12] claims the equation $\nu_2 = 1459 + 720/(n_{C=C} +$

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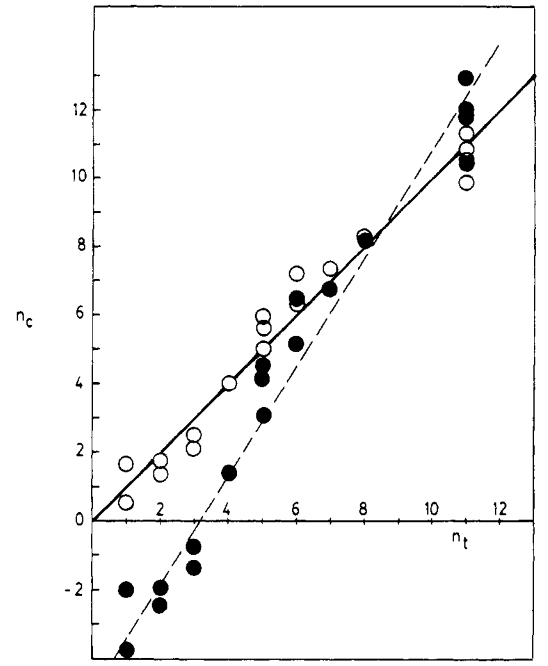

Figure 1. Number of conjugated C═C units in polyenes, n_c, as calculated with experimental ν_2 data and the exponential equation given in ref 1 (full circles) or that proposed here (empty circles), vs. the actual number of C═C units, n_t, in such polyenes. Solid line, equations $n_c = n_t$ and $n_c = 1.000079n_t - 0.001005$; dotted line, equation $n_c = 1.542n_t - 4.555$.

1). However, Maddams et al.[1] have already pointed out that such a reciprocal equation is not satisfactory.

In order to overcome the problems raised when the equation given by Maddams et al. is applied to the experimental data in Table I, an alternative way is proposed here to determine a and b, instead of the asymptotic regression method used by these authors. If the equation is written in logarithmic form as $\ln(\nu_2 - \nu) = \ln a - bn$, by plotting $\ln(\nu_2 - \nu)$ vs. n, a straight line with zero intercept $\ln a$ and slope $-b$ would be obtained; to carry out such a plot, the value of ν should be known beforehand from experimental measurements, and we have used the value of 1461 cm^{-1} given by Maddams et al., more widely experimentally supported than other values given by other authors. When the logarithmic form of the equation is applied with $\nu = 1461$ cm^{-1} to the experimental data in Table I, a straight line with $r = -0.98389$ is obtained, and the values $a = 215.76$ cm^{-1} and $b = 0.12036$ are thus calculated from the zero intercept and the slope, respectively. When these parameters are substituted in the exponential equation and $n_{\mathrm{C{=}C}}$ is calculated for the ν_2 values in Table I, the results in Figure 1 (empty circles) are obtained. These data fit a straight line defined by the equation $n_c = 1.000079n_t - 0.001005$, with $r = 0.9839$; i.e., the calculated (n_c) values will be identical with the actual (n_t) values for $n_{\mathrm{C{=}C}}$.

This same calculation has been performed with the limiting value $\nu = 1450$ cm^{-1} given by Lichtmann and Fitchen,[14] obtaining $a = 223.698$, $b = 0.108$, and $r = -0.98215$. The corresponding n_c vs. n_t plot leads to the equation $n_c = 0.99565\, n_t - 0.0342$, with $r = 0.9821$, slightly worse than that obtained above.

So, the equation $\nu_2 = 1461 + 215.76e^{-0.12036n}$ is proposed to determine the length of conjugated polyenes (as measured by the number of C═C units) from the ν_2 stretching frequency of such a moiety.

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Communications to the Editor

Upper and Lower Critical Solution Temperature Behavior in Polymer Blends

It is well-known that most pairs of high molar mass polymers are immiscible. This is so because the combinatorial entropy of mixing of two polymers is dramatically less than that for two low molar mass compounds.[1] The enthalpy of mixing, on the other hand, is often a positive quantity. Therefore dissimilar polymers are only miscible if there are favorable specific interactions between them leading to a negative contribution to the Gibbs free energy of mixing. Miscible polymers tend to phase separate at elevated temperatures. This lower critical solution temperature (LCST) behavior is typical for miscible polymer blends. The LCST behavior is interpreted in terms of equation of state or free-volume contribution.[2,3] Some miscible polymers also exhibit phase separation at low temperatures. This upper critical solution temperature (UCST) behavior is rather uncommon. It has been observed only when one component has low molar mass, i.e., when one component is an oligomer.[4,5] So far, high molar mass polymers have been found to show only the LCST behavior.

Here we describe results for a mixture of high molar mass polymers which has been found to exhibit both UCST and LCST behavior. To our knowledge, this is the first observation of an UCST in polymer blends of high molar mass polymers.

The polymer specimens used in this study, BR and SBR-45, are commercial polymers supplied by Japan

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