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Pressure-Induced Isomerization of 2-(2′-Hydroxyphenyl)benzoxazole in Solid Media

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2-(2′-Hydroxyphenyl)benzoxazole (HBO) has three isomers: a ketone (Kt), an enol (1) which is intramolecularly hydrogen bonded, and a second enol (2) which is not. Enol 1 does not emit but transforms in the excited state to the ketone Kt which can emit fluorescence or return by various paths to the ground state of enol 1. Enol 2 fluoresces but at atmospheric pressure is present, in general, in very low concentration except in hydrogen-bonding media. The fluorescence of HBO was measured as a function of pressure to 60 kbar in five media: poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(butyl methacrylate) (PBMA), poly(2-hydroxyethyl methacrylate), (PHEMA), and poly(vinyl chloride) (PVCl). In all cases enol 2 is stabilized relative to enol 1 by pressure. With reasonable assumptions it was possible to extract $\Delta\bar{V}$, the difference in partial molar volume of enol 1 − enol 2, as a function of pressure. For the methacrylates $\Delta\bar{V}$ decreases strongly with increasing pressure. The indications are that enol 2, which hydrogen bonds to the methacrylate, has initially a smaller $\Delta\bar{V}$ but also the configuration has a smaller compressibility. In PVCl $\Delta\bar{V}$ is relatively small but independent of pressure.

Introduction

The isomerization of 2-(2′-hydroxyphenyl)benzoxazole (HBO) has been widely studied as a function of solvent and temperature at atmospheric pressure (refs 1−6 and references therein). The basic processes are shown in Figure 1. The excitation is via the intramolecularly hydrogen bonded enol (E_1). The excited state $^1E_1$ rapidly converts to the excited state of the keto form ^{1}Kt, although it may decay thermally to the ground state—$^1E_1$ does not emit radiation. ^{1}Kt emits radiation, generally around 16 000−17 000 cm^{-1}, but it may also decay thermally, ultimately back to $^0E_1$. Since, at low temperature, two phosphorescent decays have been observed,[4] at least part of the thermal decay at room temperature is via the triplets along the $^3\mathrm{Kt} \rightarrow {}^3E_1$ pathway.

There is a second fluorescence of the enol E_2 which does not exhibit intramolecular hydrogen bonding and thus is free to hydrogen bond to the medium. In most media that exhibit little or no hydrogen-bonding potential the amount of E_2 observed is very small. The assignments of E_1 and E_2 are from ref 1. The amount of this isomer increases with pressure in all media as determined by the increase in emission at ∼26 000 cm^{-1}, which indicates that the partial molar volume of E_2 is smaller than that of E_1 in these media.

Our studies of the emission characteristics of this molecule involved five solid polymeric media: poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(butyl methacrylate) (PBMA), poly(2-hydroxyethyl methacrylate) (PHEMA), and poly(vinyl chloride) (PVCl).

Experiment

2-(2′-Hydroxyphenyl)benzoxazole (HBO) was purchased from Aldrich and was purified by multiple recrystallizations from methanol. PMMA (medium molecular weight) and PVCl (high molecular weight) were purchased from Aldrich. PEMA (MW = 250 000), PBMA, and PHEMA were purchased from Polysciences, Inc. None of the polymers gave any emission when irradiated at the excitation energy employed (325 nm) so they were used without further purification.

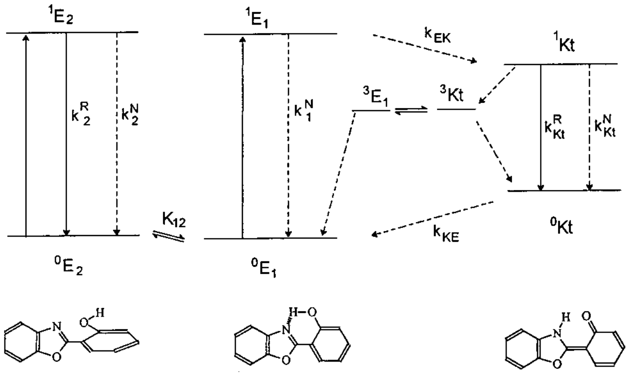

Figure 1. Diagram of the structures and processes involved in HBO isomerization.

HBO and the polymer were dissolved in a spectral grade solvent (1,2-dichloroethane or dichloromethane for PMMA, PEMA, and PBMA, THF for PVCl, and ethanol for PHEMA), and the solution was then poured in a glass dish to form a transparent film after the solvent evaporation at room temperature. The optically clear film obtained then was placed in a vacuum oven for a few days at 45 °C. The concentration of HBO in the polymers was (2−3) × 10^{-3} mol/dm^3, and the thickness of the samples was 50−80 μm.

All of the experiments (including those at 1 atm) were performed in a Merrill-Bassett diamond anvil cell (DAC), utilizing low fluorescent and UV transmitting diamonds. The hole diameter of the gasket was approximately 0.3 mm. The sample and a tiny ruby chip were placed in the hole, and light mineral oil (Aldrich 33077-9) was used as quasi-hydrostatic medium. The pressure was determined by the ruby fluorescence shift.[7] The application of the DAC to high-pressure luminescence and absorption experiments as well as the experimental setup for these measurements has been described before.[8,9] The excitation for emission was by means of the 325 nm line of a Model 3056 Omnichrome Inc. He−Cd laser in conjunction with various filters to cut extraneous radiation from the emission path

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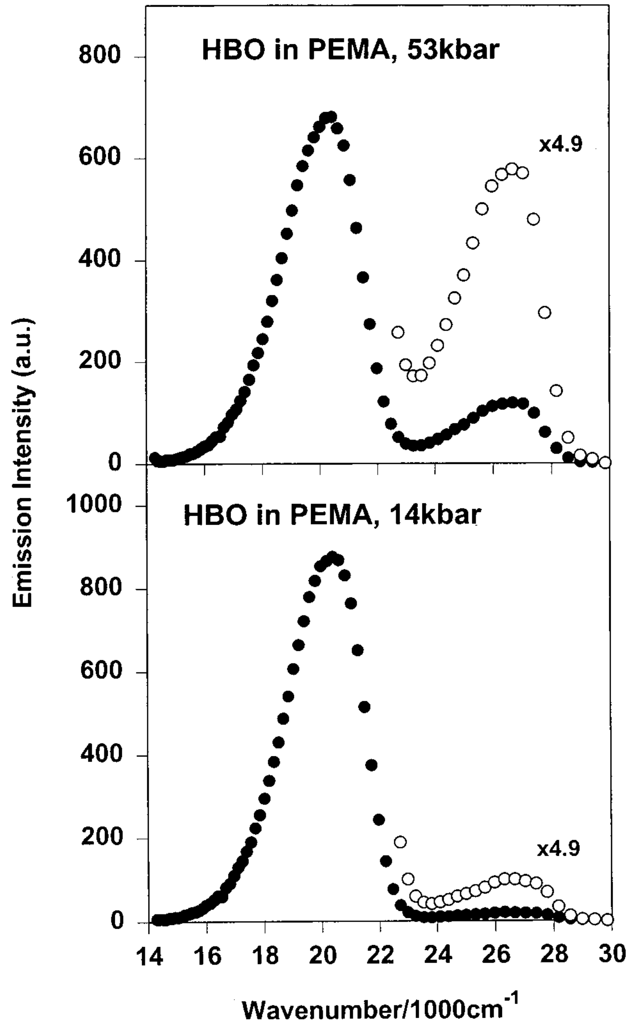

Figure 2. Spectra of HBO in PEMA at 14 and 53 kbar.

TABLE 1: Ratio of Emission Intensities—Low Energy (Kt Emission) to High Energy (E_2 Emission) in Various Media at 1 atm Pressure

medium	ratio	medium	ratio
PMMA	159	PHEMA	15.9
PEMA	167	PVCl	113
PBMA	4.9		

and to control the intensity of the excitation light. The emission at the chosen energy was measured by a single photon counter and computer on line with a reading interval of 2 s. A GG19 Schott filter was taken out from the excitation beam path to measure the weaker intensity of the higher energy emission. The intensities of the higher energy peak emission were obtained from the results divided by a factor of 4.9 to correct for the absorption of the filter at 325 nm. All results were corrected in the program for recording the data for the wavelength-dependent response of the monochromator grating, the photomultiplier and detection system, the filters, and the absorption and emission effects of each diamond cell used.

Results

The ratio of intensities of the LE(Kt) emission to the HE(E_2) emission at 1 atm appear in Table 1. For PMMA, PEMA, and PVCl the emission from E_2 is very small, while there is significantly more for PHEMA and PBMA. PHEMA tends to hydrogen bond to E_2 which stabilizes this isomer. The reasons for the relatively high initial yield for PBMA are not obvious.

Typical spectra (uncorrected for absorption) are shown in Figures 2 and 3 at two pressures for PEMA and PHEMA. In

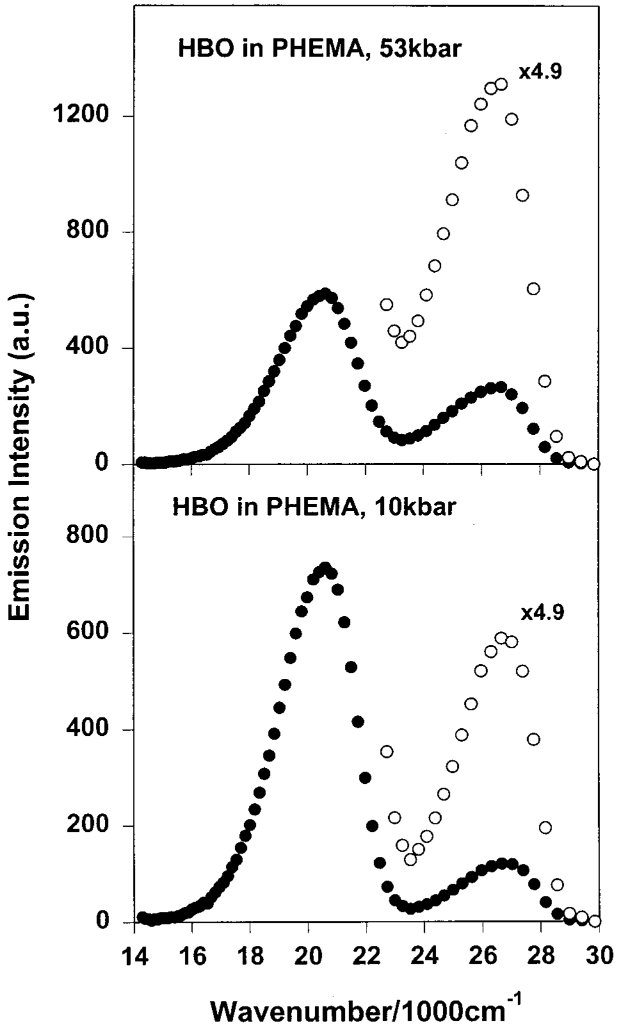

Figure 3. Spectra of HBO in PHEMA at 10 and 53 kbar.

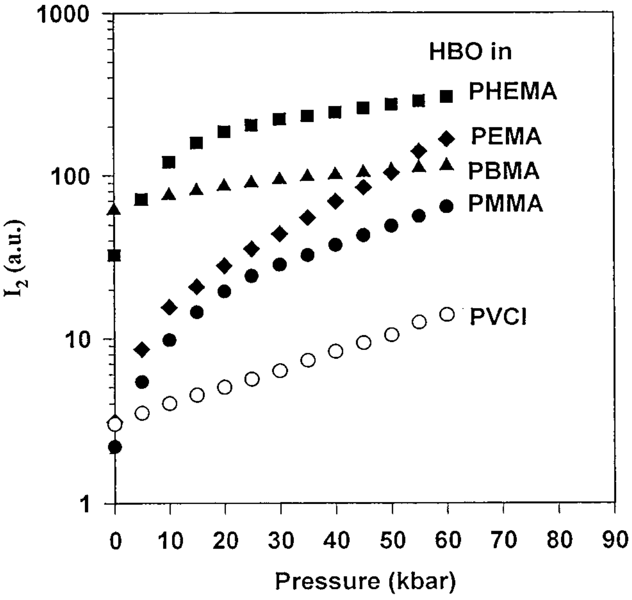

Figure 4. Change of intensity with pressure for the high-energy band (emission from enol 2) of HBO: ■, PHEMA; ◆, PEMA; ▲, PBMA; ●, PMMA; ○, PVCl.

all cases the effect of pressure is to increase significantly the relative intensity of the E_2 emission. Figures 4 and 5 exhibit the change of intensity with pressure for the ketone (Kt) and the non-hydrogen-bonded enol (E_2). While the intensities are given in arbitrary units, the relative values for I_{Kt} and I_2 are meaningful. In particular, the E_2 emission and the Kt emission

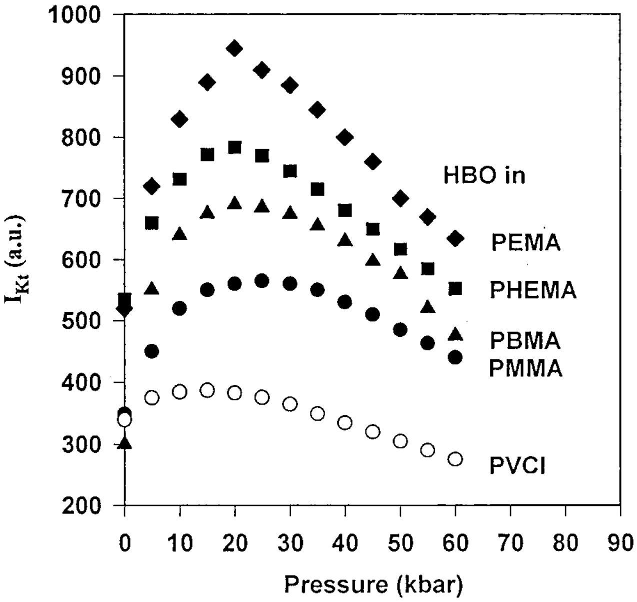

Figure 5. Change of emission intensity with pressure for the low-energy band (emission from the ketone Kt) of HBO: ■, PHEMA; ♦, PEMA; ▲, PBMA; ●, PMMA; ○, PVCl.

TABLE 2: Absorption Coefficients at 325 nm vs Pressure (Normalized to 1 atm)

p	PMMA	PEMA	PBMA	PHEMA	PVCl
0	1.00	1.00	1.00	1.00	1.00
10	1.07	1.07	1.10	1.02	1.14
20	1.13	1.12	1.16	1.06	1.27
30	1.18	1.13	1.19	1.11	1.28
40	1.21	1.12	1.16	1.10	1.26
50	1.19	1.08	1.10	1.10	1.19
60	1.14	1.04	1.03	1.09	1.12

in each polymer were taken on the same load at each pressure. The values shown in Figures 4 and 5 are averaged from at least three loads for each polymer. The scatter at any pressure was never over ±4% and was mostly considerably less.

The E_2 emission increases monotonically for all polymers by a factor of from 2 (PBMA) to 60 (PEMA) in 60 kbar. The behavior of the Kt emission (Figure 5) is more complex with a significant increase, a maximum near 20 kbar, and then a decrease.

Our goal is to establish the equilibrium constant K_{12} between the two enol forms as a function of pressure. In addition to the emission data of Figures 4 and 5, we measured the absorption spectra as a function of pressure. The absorption spectra have several peaks. The shape of the spectra did not vary significantly with pressure or medium. The main maximum was a little higher in energy than the exciting light (325 nm = 30.770 cm $^{-1}$) and shifted to lower energy in 60 kbar by 600−1000 cm^{-1} depending on the medium. Relative to the 1 atm value the absorption intensity at 325 nm is shown in Table 2.

A significant part of the decrease in Kt emission above 20 kbar is due to increasing conversion of the E_1 enol to E_2. To test the degree that this conversion accounts for the drop in Kt emission intensity, in Figure 6 we plot $I_T = I_2 + I_{Kt}$, corrected for the absorption at 325 nm vs pressure. For the methacrylates the increase at low pressure is present as in Figure 5. From the maximum near 30−60 kbar there is a drop of 5−10% depending on the polymer. In PVCl there is a small maximum at 5−10 kbar and then a somewhat larger decrease.

The most likely cause of the increase in intensity at lower pressure is an increase in the efficiency of the crossing from $^1E_1$ to ^{1}Kt (Φ_{EK}). The emission peaks from E_2 and Kt shift to lower energy less than 300 cm^{-1} in 60 kbar, so any decrease in efficiency due to the energy gap law[10] is trivial. However, nothing is known about the nonradiative rate from E_1, and the literature[4] indicates that the nonradiative rate from the excited state ^{1}Kt to $^0E_1$ may be via ^{3}Kt and $^3E_1$. It has been shown that, given the lifetime of triplet states, much of the quenching is via vibrational coupling to the matrix which coupling increases with compression.[11] If the emission efficiency from E_2 is less than that for Kt, the increasing fraction of E_2 at higher pressures could contribute to the modest decrease in I_T observed from 30 to 60 kbar.

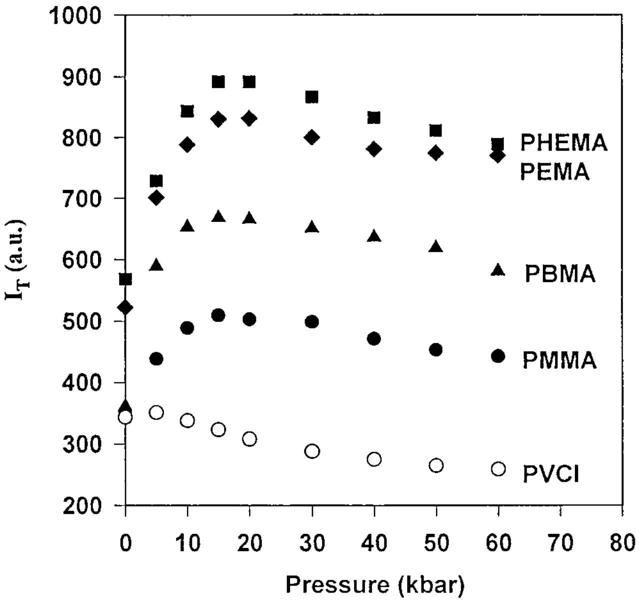

Figure 6. Change in total emission ($I_T = I_2 + I_{Kt}$) corrected for the change of absorption at 325 nm vs pressure: ■, PHEMA; ♦, PEMA; ▲, PBMA; ●, PMMA; ○, PVCl.

Discussion

As indicated above, the basic problem is to describe the change in K_{12} with pressure where K_{12} is the equilibrium constant between E_1 and E_2. Our nomenclature, following Figure 1, is as follows: k_2^R and k_2^N are the radiative and nonradiative rates for E_2; k_{Kt}^R and k_{Kt}^N are the analogous rates for the ketone Kt. k_{Kt}^N includes both paths shown in Figure 1 for return to $^0E_1$. k_{EK} is the rate of transfer of excitation from $^1E_1$ to ^{1}Kt, while k_1^N is the nonradiative rate from $^1E_1$ to $^0E_1$.

Then

$$\Phi_2 = \frac{k_2^R}{k_2^R + k_2^N} \qquad (1)$$

$$\Phi_{Kt} = \frac{k_{Kt}^R}{k_{Kt}^R + k_{Kt}^N} \qquad (2)$$

$$\Phi_{EK} = \frac{k_{EK}}{k_{EK} + k_1^N} \qquad (3)$$

The emission from E_2 (the high-energy peak) is given by

$$I_2 = \alpha_2 I_{ex} \Phi_2 [E_2] \qquad (4)$$

where I_{ex} is the intensity of the exciting light and α_2 is the absorption cross section for E_2. The bracketed expressions are concentrations. For the ketone emission (low-energy peak), by straightforward rearrangement

$$I_{Kt} = \alpha_1 I_{ex} \Phi_{Kt} \Phi_{EK} [E_1] \qquad (5)$$

One can write the equilibrium constant $K_{12} = [^0E_1]/[^0E_2]$ in terms of eqs 4 and 5, but the coefficient in front has a complex and undetermined pressure dependence.

The absorption cross section at 325 nm has only a modest pressure dependence, but we cannot separate α_1 and α_2 because of the overlap in absorption bands. We assume that α_1/α_2 is not pressure dependent, and since we will be interested only in the change of K_{12} with pressure, not its absolute value, we set this ratio equal to one. As we indicated in the previous section the emission peaks shift less than 300 cm^{-1}; therefore, k_2^N is independent of pressure. All radiative rates can be assumed pressure independent in this modest pressure range; therefore, Φ_2 is constant.

We consider for each medium the concentrations at the pressure where I_{Kt} is a maximum using the subscript M for this pressure.

$$[E_1]_M = \frac{(I_{Kt})_M}{(\Phi_{Kt}\Phi_{EK})_M\alpha_1 I_{EX}} \qquad (6)$$

$$[E_2]_M = \frac{(I_2)_M}{\Phi_2\alpha_2 I_{EX}} \qquad (7)$$

Similar equations can be written for $[E_2]_0$ and $[E_2]_p$, the concentration of E_2 at 1 atm and any pressure p, using $(I_2)_0$ and $(I_2)_p$.

By straightforward reorganization we obtain for K_{12}

$$K_{12} = \frac{(I_2)_M + \beta(I_{Kt})_M}{(I_2)_p} - 1 \qquad (8)$$

where

$$\beta = \frac{\Phi_2}{(\Phi_{Kt}\Phi_{EK})_M} \qquad (9)$$

β is not dependent on pressure, but its value is not known. The assumption $\beta = 1$ is one solution. If $\beta \gg 1$

$$K_{12} = \frac{(I_{Kt})_M}{(I_2)_p}\beta \qquad (10)$$

It is possible to set a reasonable minimum value for β as follows. K_{12} must be greater than zero at any pressure. For $K = 0$

$$\beta = \frac{(I_2)_p - (I_2)_M}{(I_{Kt})_M} \qquad (11)$$

It is difficult to set an exact maximum for $(I_2)_p$ as it is increasing monotonically, but reasonable lower limits for β can be approximated. Calculations of $K_{12}(p)/K_{12}(0)$ were made for the following cases:

PMMA: $\beta \gg 1, \beta = 1, \beta = 0.6, \beta = 0.5$

PEMA: $\beta \gg 1, \beta = 1, \beta = 0.5$

PBMA: $\beta \gg 1, \beta = 1, \beta = 0.5, \beta = 0.3$

PHEMA: $\beta \gg 1, \beta = 1, \beta = 0.75, \beta = 0.5$

PVCl: $\beta \gg 1, \beta = 1, \beta = 0.5$

From Figures 7−9 it can be seen that the value of β has little effect on $K_{12}(p)/K_{12}(0)$ for PMMA, PEMA, and PVCl. There is a measurable effect for PBMA and PHEMA although the trends are similar for all values of β.

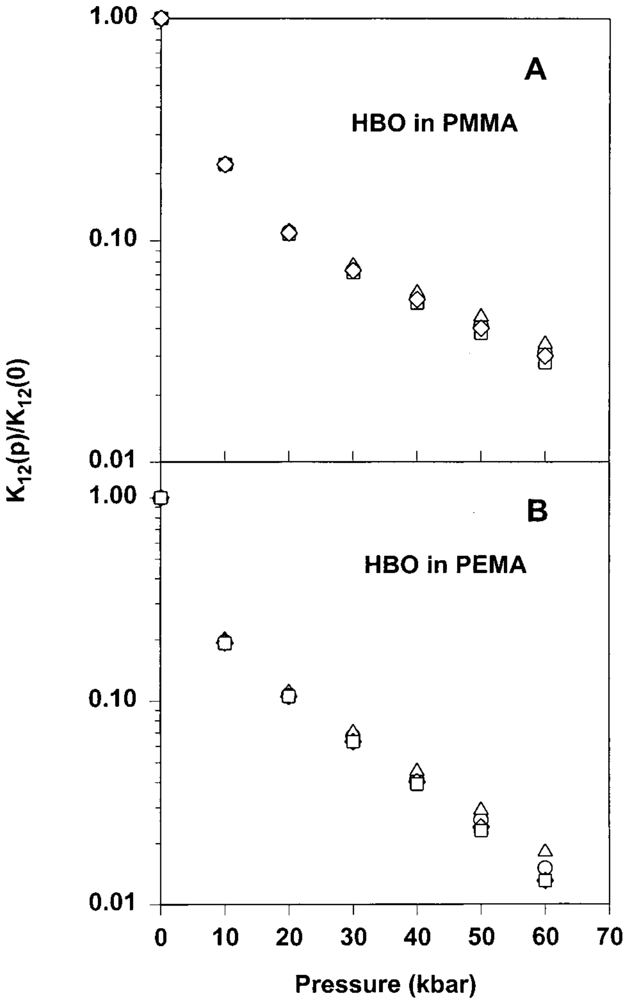

Figure 7. (A) $K_{12}(p)/K_{12}(0)$ vs pressure for HBO in PMMA: △, $\beta \gg 1$; ○, $\beta = 1$; ◇, $\beta = 0.6$; □, $\beta = 0.5$. (B) $K_{12}(p)/K_{12}(0)$ vs pressure for HBO in PEMA: △, $\beta \gg 1$; ○, $\beta = 1$; ◇, $\beta = 0.75$; □, $\beta = 0.5$.

From elementary thermodynamics

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = \frac{-\Delta\bar{V}}{RT}$$

where $\Delta\bar{V}$ is the difference in partial molar volumes associated with products and reactants. $\Delta\bar{V}$ was calculated for each polymer using $K(p)/K(0)$ averaged for all values of β. The results are shown in Figure 10. The values represent the difference in partial molar volume $\Delta\bar{V}$(enol 1) − $\Delta\bar{V}$(enol 2). It is clear that the ability of the non-intramolecularly-bonded isomer (enol 2) to hydrogen bond to the methacrylate reduces the volume of the system in the neighborhood of this isomer. However, this bonding to the medium also reduces the local compressibility so that $\Delta\bar{V}$ decreases rapidly with increasing pressure. Although PBMA exhibits the same trend with pressure as the other methacrylates ($\Delta\bar{V}(55)/\Delta\bar{V}(5)$ equals 0.18 for PMMA, 0.29 for PEMA, 0.11 for PHEMA, 0.28 for PBMA, and 1.0 for PVCl), it has a much smaller initial $\Delta\bar{V}$. T_g for PBMA is ~20 °C while for the other polymers it is in the range 80−120 °C. This may be a factor, although T_g increases rapidly with pressure for most polymers. It is also possible that the large butyl groups inhibit the hydrogen bonding of enol 2 to the methacrylate.

The behavior in PVCl is markedly different. The initial value (0.62 cm^3) is quite small, and there is virtually no pressure effect on it. No hydrogen bonding to the medium is possible so ΔV represents the difference in polarizability interactions of the two enol isomers with the medium. Since 0.62 cm^3 must be

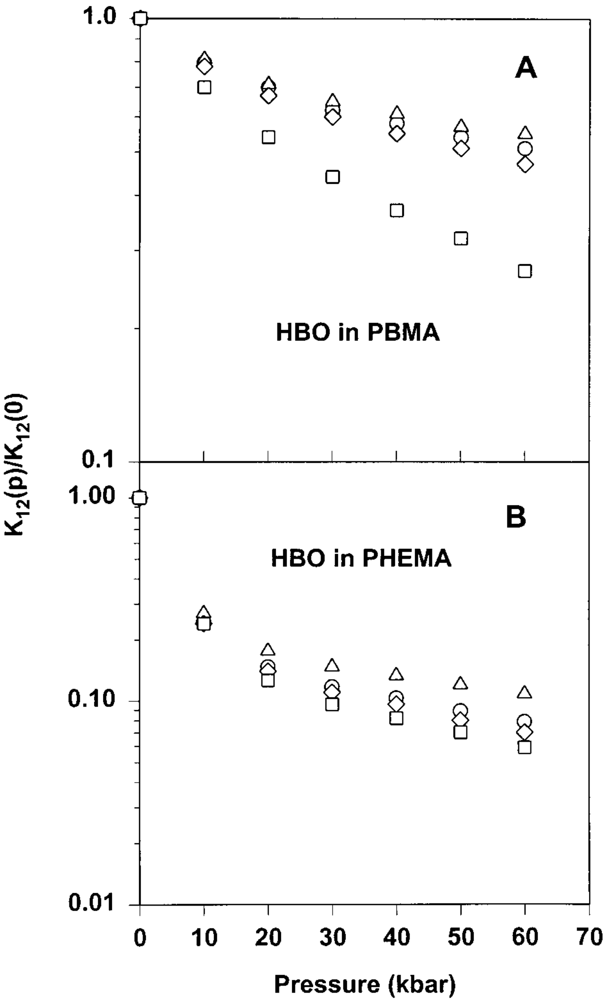

Figure 8. (A) $K_{12}(p)/K_{12}(0)$ vs pressure for HBO in PBMA: △, $\beta \gg 1$; ○, $\beta = 1$; ◇, $\beta = 0.5$; □, $\beta = 0.3$. (B) $K_{12}(p)/K_{12}(0)$ vs pressure for HBO in PHEMA: △, $\beta \gg 1$; ○, $\beta = 1$; ◇, $\beta = 0.75$; □, $\beta = 0.5$.

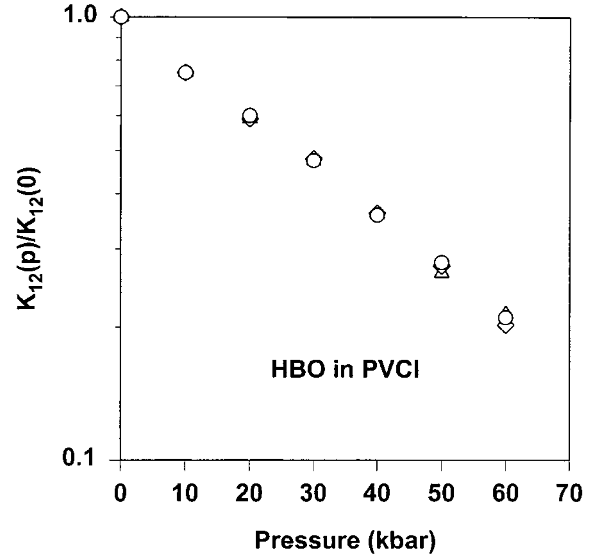

Figure 9. $K_{12}(p)/K_{12}(0)$ vs pressure for HBO in PVCl: △, $\beta \gg 1$; ○, $\beta = 1$; ◇, $\beta = 0.5$.

considerably less than 0.5% of the molar volume of either isomer, this difference must be small.

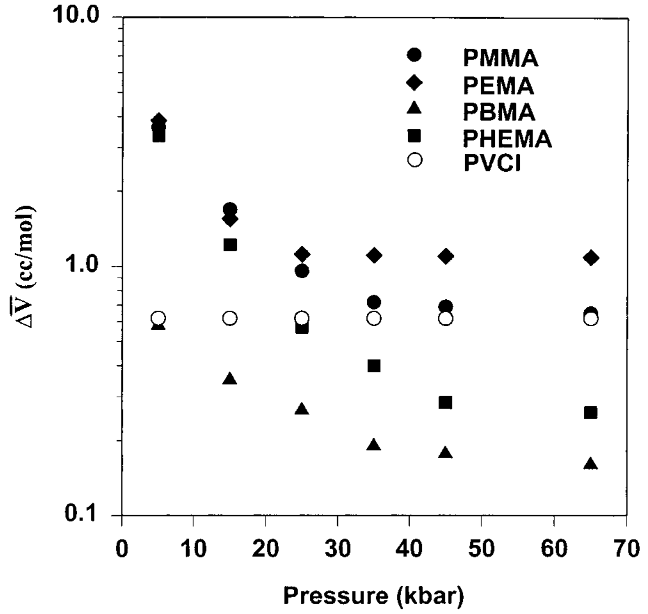

Figure 10. $\Delta\bar{V}$ (cm^3/mol) vs pressure: ●, PMMA; ♦, PEMA; ▲, PBMA; ■, PHEMA; ○, PVCl.

Summary

The emission spectra of HBO permit us to extract the changes of equilibrium constant K_{12} between the intramolecularly-hydrogen-bonded enol (1) and the non-internally-bonded isomer enol (2). The equilibrium constants were obtained in four solid methacrylate polymers and in PVCl. From the pressure dependence of K_{12} we extracted the difference in partial molar volume between enol 1 and enol 2. In PMMA, PEMA, and PHEMA $\Delta\bar{V}$ was on the order 3.5 cm^3/mol at 5 kbar and decreased by a factor of 4−8 over the range from 5 to 55 kbar. In PBMA the initial value was significantly smaller, but the fractional decrease was comparable. In PVCl $\Delta\bar{V} \simeq 0.6$ cm^3/mol independent of pressure. For the methacrylates the initial smaller volume for enol 2 results from hydrogen bonding of the isomer to the methacrylate. The decrease in $\Delta\bar{V}$ with pressure indicates a lower compressibility for the externally-hydrogen-bonded configuration. Since no hydrogen bonding to PVCl is possible, the $\Delta\bar{V}$ represents the difference in interaction with the medium due to different polarizabilities and polarities of the two isomers.

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