Molecular and Spectroscopic Properties of a Polarizer Based on a Block Copolymer of Vinylalcohol and Acetylene

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Summary: The preparation of a high efficiency polarizer derived from the block copolymer, poly(vinylalcohol-b-acetylene) will be described. The orientations of the polyacetylene chromophore and the polyvinylalcohol matrix have been analyzed by polarized UV/Vis and FTIR spectroscopy, respectively. For moderately stretched films (L/Lo = 3.0-7.0), the degree of orientation for the polyacetylene segments greatly exceeds that predicted from a simple, pseudoaffine deformation model. For the visible spectral region, dichroic ratios in the range of 60 to 100 are easily achieved, thus permitting films of this polymer to function as a high efficiency, polarizing optical element. Data from a series of sample tilting experiments utilizing polarized UV/Vis radiation are consistent with the polyacetylene segments being distributed uniaxially about the stretching direction. However, analogous experiments in the infrared indicate that the PVA matrix has significant biaxial character. Other novel characteristics of this polarizer will be discussed, such as its thermal and chemical stability.

Introduction

Synthetic sheet polarizers have been important components in a variety of optical display applications for over 25 years. In addition to their notable use in liquid crystal displays, they have also gained widespread acceptance in anti-glare, contrast enhancing and 3D applications. The polarizer most commonly employed in these applications is the H-type polarizer, invented and commercialized by Land and Rogers[1-3)] over 50 years ago. The light absorbing properties of the H-type polarizer are derived from a complex that forms when a solution of I_2/KI is absorbed into an oriented film of polyvinylalcohol (PVA). The complex is believed to involve tri-iodide ion (I_3^-) as well as higher oligomers[4,5)]. The H-polarizers are renowned for achieving polarization efficiencies in excess of 99.9% with high light transmission (42-43%). However, the thermodynamics of PVA-I_3 complexes are such that these complexes are quasi-stable at best, particularly at high temperatures and humidity. This has limited their application in such areas as automotive, avionics and LCD projection systems where the display must function over broad environmental extremes.

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One approach chosen to mitigate this shortcoming has been to replace I_2/KI with certain organic dyes6) which, when absorbed or dispersed within the oriented PVA matrix, exhibit dichroism throughout the visible spectrum. While this does significantly improve the thermal stability of the resulting polarizer, such systems remain inferior to the H-type with respect to the polarization efficiency. An alternative approach1-3) is the incorporation of a light absorbing chromophore directly into the PVA backbone, and this can be readily achieved by thermal dehydration of oriented PVA films with a strong acid catalyst (Fig. 1). This reaction efficiently generates $-(-C{=}C-)_x-$ conjugation along the polymer backbone7,8), and the polarizer made in this fashion is referred to as K-type. The resulting polymer is in fact a block copolymer of vinylalcohol and acetylene (PVA/PAC).

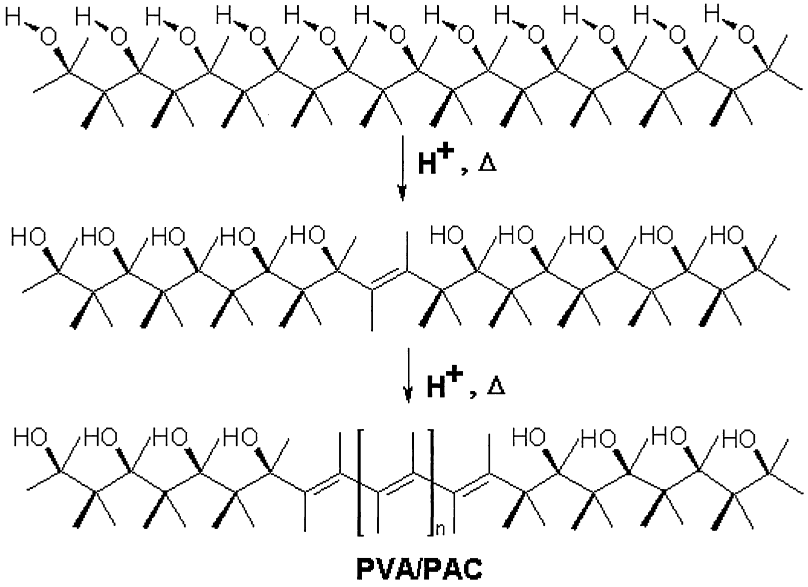

Fig. 1: Reaction scheme for the preparation of poly(vinylalcohol-b-acetylene).

While K-type polarizers are stable to high temperatures and humidity, they are typically also inferior in polarization efficiency relative to the H-type, and this limits their acceptance into market applications where high polarization efficiency is required. Recently, we demonstrated significant improvements in polarization efficiency for K-type polarizers9-11) which result from a number of proprietary advances. One is a newly developed stretching scheme for PVA films or sheets, which achieves the necessary, high degree of molecular orientation for the polymer chains. Another is the ability to control the dehydration kinetics, and which allows control of the distribution of conjugation lengths of the polyacetylene segments formed within the PVA molecule. The latter is particularly important for the optical performance of the polarizer since conjugation length ultimately determines the spectral region in which the chromophore absorbs light. This new, high efficiency K-polarizer is referred to as KE.

Materials and Methods

The preparation of a polarizer containing the PVA/PAC block copolymer requires initially stretching a film of PVA (38-75 μm thickness) at elevated temperatures such that the extension ratio, L/Lo = 3.6 or higher. Lo and L are the initial and final film lengths, respectively, and we denote this step in the process as pre-stretch. The PVA should have a degree of polymerization of 1400 or higher with a degree of hydrolysis of at least 98%. While not essential, we have found it helpful to fix or laminate the stretched PVA to a more rigid plastic support after this pre-stretch step, which facilitates subsequent sample handling. In the next step the acid catalyst in the vapor phase is absorbed into the PVA. This is accomplished by suspending the PVA film in the headspace above a solution of HCl (25% wt/vol.) for a period of 1.0-1.5 minutes. The temperature of the HCl can range from 35°C to 60°C but should be kept constant. After absorbing the HCl, the PVA is then immediately placed in an oven for 2-3 minutes at 150°-175°C to affect the dehydration reaction. While it is difficult to assess the exact degree of conversion resulting from dehydration, our best estimates are that only ~1% conversion has resulted. The oriented PVA at this stage has been transformed from colorless to a distinctive, reddish brown. We refer to the polarizer at this point in the process as Raw-K. The specific conditions of heating time, temperature and acid concentration are not particularly critical. Considerable latitude in these process parameters exists without detriment to the formation of the copolymer and its resulting polarization properties.

The final stage in the preparation of a high efficiency KE polarizer requires a second stretching step. Raw-K is removed from its plastic support and unidirectionally restretched an additional 10% to 60% such that the final extension ratio is at least 4.8 times (and preferably much higher) the sheet's original, unstretched length. This restretch step is performed in an aqueous solution of boric acid and borax (9% and 3% wt/vol), maintained at 70-80°C. The Raw-K film or sheet is resident in this solution for 5 to 10 minutes, and a significant fraction of this time is required to allow the film to swell and soften prior to restretching. After removal from the solution, the resulting KE polarizer is washed with distilled water and allowed to dry. A consequence of the additional molecular orientation imparted by the restretch step is the improvement in polarization efficiency that was lacking in the original K-type polarizers. Also, the color has changed from a reddish brown to a preferred neutral gray, and this is acceptable for display applications.

Spectroscopy

Polarized UV/Vis spectra were recorded on a Cary 5E spectrophotometer using a Glan-Thompson analyzer. Similarly, polarized IR spectra were recorded on a Nicolet FTIR spectrophotometer with a wire grid polarizer. Absorbance spectra obtained with the incident plane of polarization parallel to the stretching axis of the sample are denoted as A_z, while those obtained with the plane of polarization parallel to the transverse direction are denoted as A_y. In order to gain information on the absorption component in the thickness direction, A_x, a special sample holder was constructed which allowed spectra to be recorded from tilted samples. All spectra were corrected for surface reflections (σ and π), and in the case of spectra obtained from tilted samples, corrections for refraction were also applied12).

Results and Discussion

In Fig. 2 are shown representative polarized UV/Vis spectra for a KE polarizer prepared from an initial pre-stretch of 4.8X and a subsequent restretch of 15% (i.e., total stretch ratio = 5.5X). Since PVA is essentially transparent throughout this spectral region, the respective spectra are attributable to the polyacetylene segments in the copolymer. As can be seen the dichroism is high, indicating a high degree of PAC segment orientation, with maximum absorption occurring when the plane of polarization is parallel to the stretch direction. In the case of the A_z spectrum, optical densities in excess of 2.0 are attained throughout most of the visible region of the spectrum. By taking the ratio of the two spectra the dichroic ratio, A_z/A_y, may be obtained as a function of wavelength; this is depicted in Fig. 3. In the UV region the dichroic ratios are initially low and increase slowly to ~400 nm, whereupon they increase more rapidly throughout the visible region. A_z/A_y ranges from 17 at 400 nm to 145 at 700 nm. The apparent noise in the 600-700 nm region is the result of a low level of interference fringes present in the original A_y spectrum. Since it has been well established that λ_{max} increases with the PAC conjugation length, then the increase in dichroic ratio with increasing wavelength

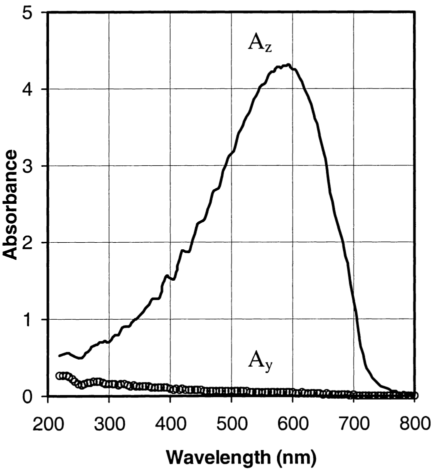

Fig. 2: A_z and A_y spectra for KE.

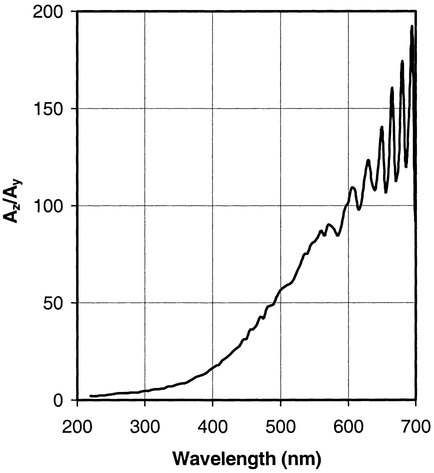

Fig. 3: A_z/A_y vs. wavelength for KE.

certainly suggests that longer PAC segments are more highly oriented than shorter PAC segments. However, another factor contributing to this behavior is the angle between the transition moment vector and the PAC molecular axis. This angle decreases as the conjugation length increases, and as a result, the dichroic ratio should increase with wavelength.

The effect of varying PVA pre-stretch on the resulting A_z spectra for KE is shown in Fig. 4. The results are dramatic with both absorbance and λ_{max} increasing significantly. An increase in absorbance with pre-stretch is what one should expect as the overall degree of molecular orientation is increased. However, there was no *a priori* reason to suspect that an analogous increase in λ_{max} should or would occur. Given the reaction scheme of Fig. 1, the result can be rationalized, and one possibility is that longer PVA chain segments simply facilitate the overall amount and extent of dehydration proceeding along the PVA backbone. Alternatively, the phenomenon may be related to the degree of crystallinity of the PVA. Unpublished results from our laboratory indicate that as L/Lo increases in the pre-stretch step, the PVA degree of crystallinity also increases, as measured by calorimetry and X-ray diffraction. Whether the PAC chromophore resides in the crystalline, amorphous or both phases is still a matter for conjecture.

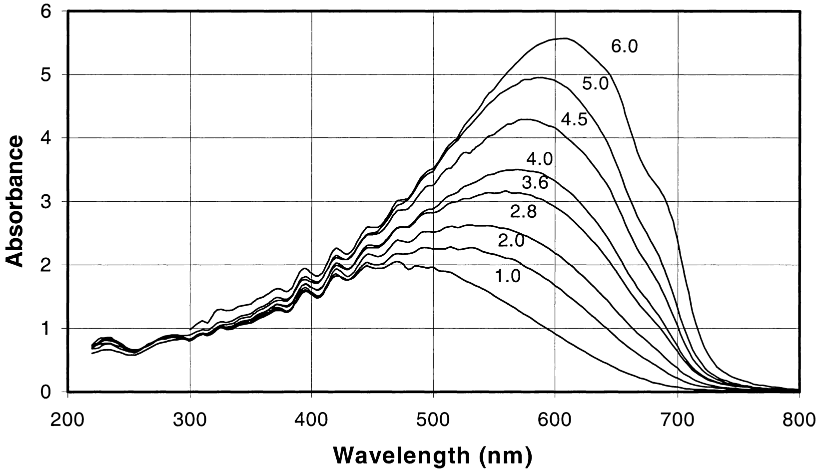

Fig. 4: A_z spectra as a function of pre-stretch for KE.

While our focus up to the present time has been on KE spectra, it is important to note that spectra and trends similar to those in Fig. 4 are also obtained for Raw-K. The main difference in spectral features between the two polarizers is that A_z is reduced (with a concomitant increase in A_y) for the Raw-K samples, and this is expected given their lower degree of orientation. While the distribution of PAC chain lengths is totally determined at the Raw-K stage of the process, the distribution of chain orientations is determined by the combined steps of pre-stretch and restretch.

In order to understand the dichroic properties of the KE polarizer, we now compare our results with model calculations of the orientation process. The model we have chosen is the Kratky pseudoaffine deformation model13) for a system conforming to partial axial orientation. Reference 12 contains an excellent description of the model with examples. This is a relatively simple model and treats the polymer as an assembly of non-interacting, rigid rods in a deformable box. Shown in Fig. 5 is the relationship between dichroic ratio and stretch ratio for the model as well as for a broad range of KE samples. In this analysis, the model's prediction for A_z/A_y was based on the assumption that the transition moment vector is coincident with the molecular chain axis. As a result, the value for the dichroic ratio, calculated at a given stretch ratio, will be the maximum value attainable within the assumptions of the model. For the KE data, the reported dichroic ratios were measured at 560 nm, and the pre-stretch for these samples ranged from 2.6X to 4.8X. The abscissa represents

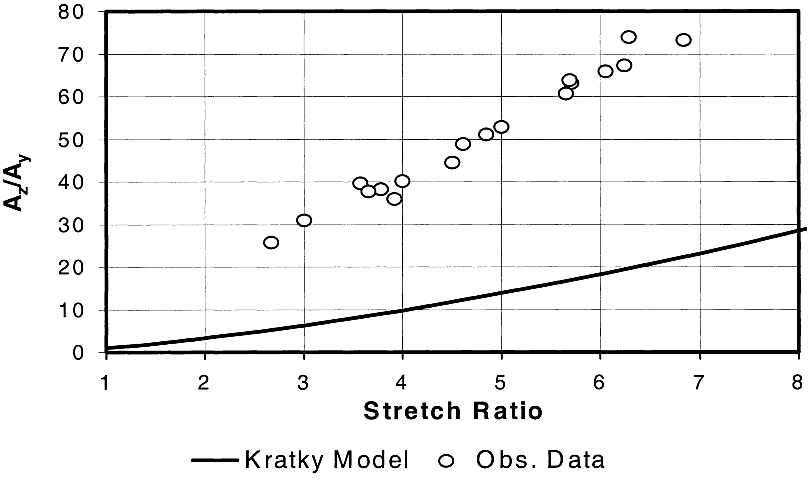

Fig. 5: Comparison of observed and predicted dichroic ratios as a function of stretch ratio. The data for KE represent the combined effects of pre-stretch and restretch.

the total combined stretch ratio. It is obvious from the figure that the model severely underestimates the dichroic ratios for this system. The lack of agreement is not surprising given that the model ignores the fact that real polymer systems often consist of amorphous and crystalline phases, and these have a multitude of intermolecular interactions which will have a profound effect upon the dynamics of the orientation process.

To gain insight on the orientation distribution for the PAC chromophore within the PVA matrix, we attempt to estimate the absorbance in the thickness direction, A_x. Specifically, we are interested in whether or not the polyacetylene blocks are distributed uniaxially about the stretch direction. Uniaxial symmetry requires that $A_x = A_y$, and estimates of A_x can be achieved from recording polarized spectra from a sample tilted over a range of angles, θ. To do this we have used two different sample geometries. In the first, the initial sample orientation is the same as that used to measure A_z and the sample is rotated about the sample y-axis. In this orientation the x and z-axes of the sample will be coplanar with the incident electric field, and we designate the absorbance for a given tilt angle as $A(z,\theta)$. The second geometry is similar to the first, except the polarization is parallel to A_y, and the sample is rotated about its z-axis. Data obtained in this configuration are denoted as $A(y,\phi)$. For these two geometries A_x can be calculated from the following relationships$^{12)}$:

$$A(y,\phi) = A_y\cos^2(\phi) + A_x\sin^2(\phi) \quad (1)$$
$$A(z,\theta) = A_z\cos^2(\theta) + A_x\sin^2(\theta)$$

Polarized UV/Vis data measured at 560 nm from tilting a representative KE sample are shown in Fig. 6. Within experimental error, both sets of data are seen to converge to one common point, i.e., A_x, as θ or ϕ approaches 90°. Of greater interest is the result that $A_x = A_y$, and this is a clear indication that the PAC chromophore is distributed uniaxially about the stretch direction.

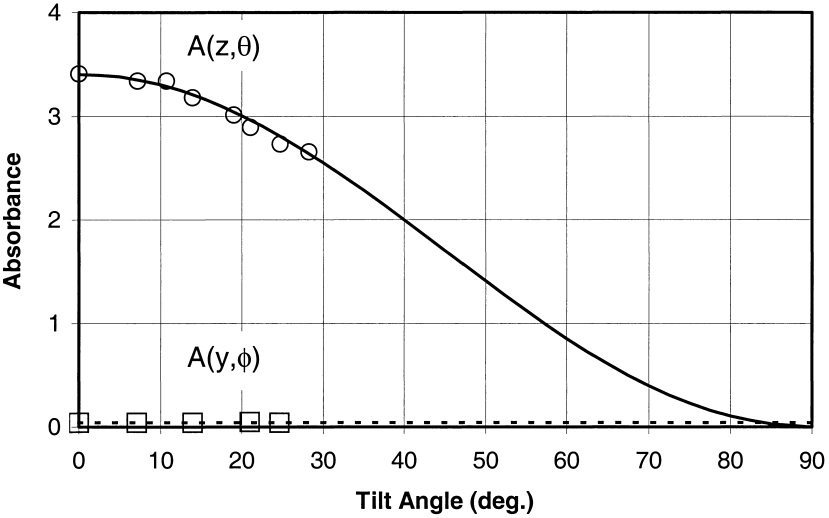

Fig. 6: A(z,θ) and A(y,ϕ) at 560 nm for KE as a function of tilt angle.

Just as PVA's transparency in the UV/Vis presented us with the opportunity to isolate the spectral features arising from the PAC component, an analogous situation arises in the IR. Since the concentration of PAC in the PVA matrix is only ~1%, then IR spectra for Raw-K are found to be indistinguishable from those of the parent PVA. However for the KE polarizer, the IR spectra are modified relative to either Raw-K or PVA due to additional absorption bands caused from the presence of boric acid and borax in the matrix. For simplicity in what follows, only IR data for Raw-K will be presented; however, it should be understood that all subsequent results and conclusions apply to both the stretched PVA and KE polarizer. In Fig. 7 are shown the A_y and A_z polarized spectra for a 4.5X stretched sample of Raw-K. Significant dichroism is observed with most of the bands in the spectrum exhibiting perpendicular dichroism, i.e., maximum absorption occurs when the plane of polarization of the incident beam is parallel to the transverse direction of the sample.

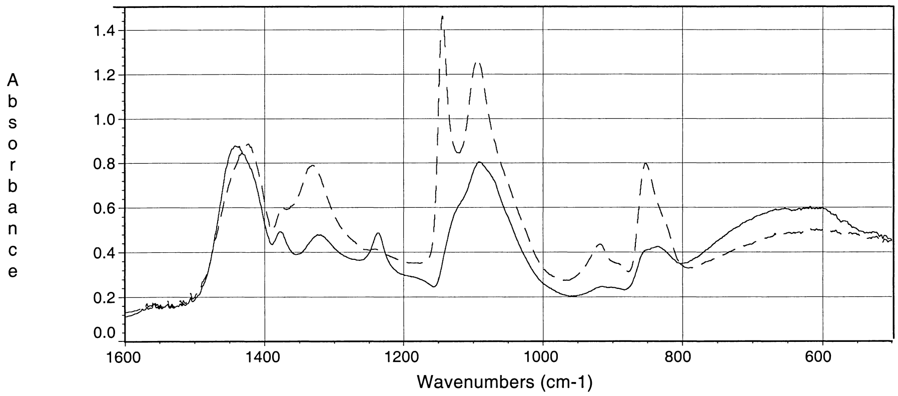

Fig. 7: A_z(—) and A_y(----) IR spectra for 4.5X stretched Raw-K.

As was the case for PAC, we are interested in the orientation distribution of the PVA, and have applied the same sample tilting methodology used in the UV/Vis for the determination of A_x in the infrared. Figs. 8 and 9 show the A(y,ϕ) and A(z,θ) spectra as a function of tilt angle, respectively. The arrows shown in the figures are to assist in indicating the direction of change for a given IR band. Examination of the A(y,ϕ) spectra in Fig. 8 indicates that in both

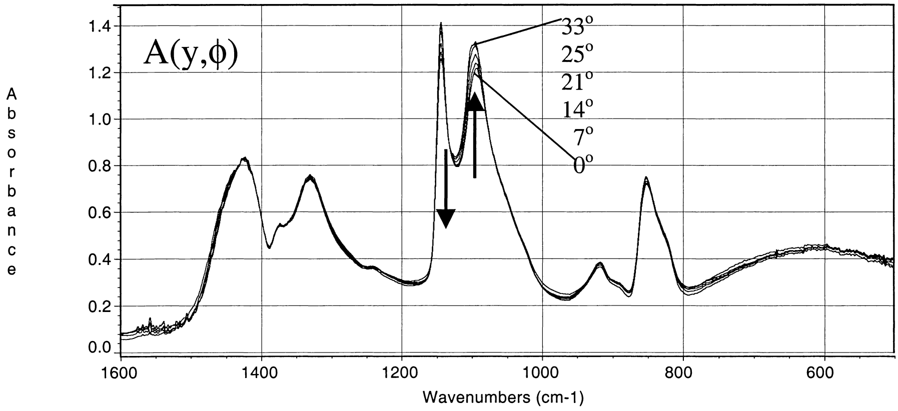

Fig. 8: A(y,ϕ) spectra at the designated tilt angles for 4.5X stretched Raw-K.

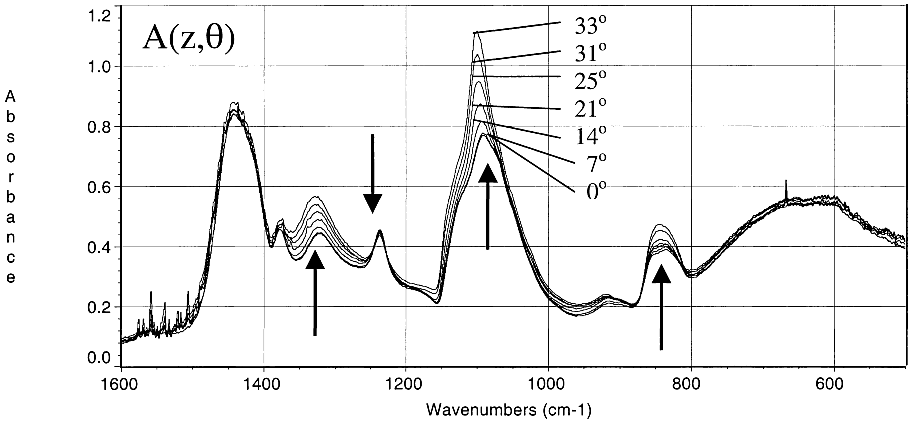

Fig. 9: A(z,θ) at the designated tilt angles for 4.5X stretched Raw-K

the 1600-1200 cm^{-1} and 1000-500 cm^{-1} regions the differences are quite small and do not change systematically with tilt angle. This suggests that the transition dipole moments for these vibrational modes are uniaxially distributed about the fiber axis. In contrast, for the 1200-1000 cm^{-1} region the differences are larger and do change with tilt angle. Similar analysis of the A(z,θ) spectra in Fig. 9 show that virtually all IR bands change with tilting. The absorbance vs. tilt angle data for IR bands in the 1600-1200 cm^{-1} and 1000-500 cm^{-1} regions is similar to the profile of Fig. 6.

Of particular interest are the changes occurring to the A(y,ϕ) and A(z,θ) spectra in the 1200-1000 cm^{-1} region. A plot of the absorbance versus tilt angle for the 1144 cm^{-1} and 1093 cm^{-1} bands is shown in Fig. 10(a) and (b), respectively.

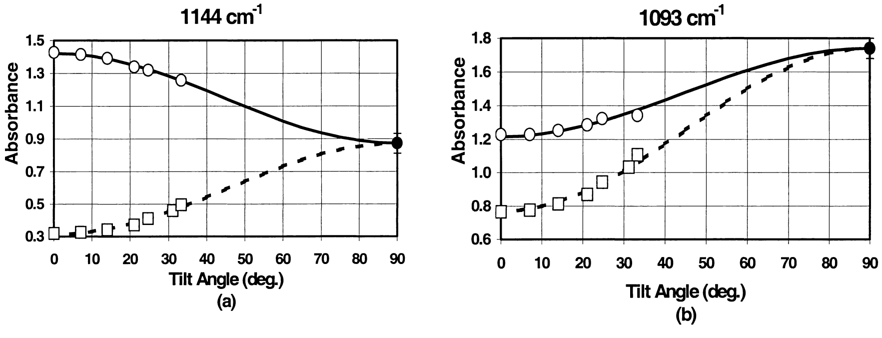

Fig. 10: A(y, ϕ) and A(z,θ) vs. tilt angle at 1144 cm^{-1} (a) and 1093 cm^{-1} (b) for 4.5X Raw-K.

For the 1144 cm^{-1} band $A_z < A_x < A_y$, and for the 1093 cm^{-1} band $A_z < A_y < A_x$. Taken together these results indicate that these two transition moments are not uniaxially distributed about the fiber axis. It is difficult to reconcile this result with that observed for the rest of the infrared where $A_x = A_y$. The fact that $A(y,\phi)$ decreases with tilt angle for the 1144 cm-1 band and increases for the 1093 cm-1 band indicates that it is unlikely that a systematic error is involved with either the sample tilting or the corrections applied for reflection or refraction. The result may be indicative of a two-phase system, one which is uniaxial, and the other which can be characterized as having preferred or biaxial orientation. The bands in this region of the IR are the result of highly coupled vibrational modes involving C-C and C-O bond stretching as well as valence angle bending the same bonds. The band at 1144 cm^{-1} is unusually sharp relative to the other bands in this spectral region, and it is both tempting and speculative to assign it to a vibration of the crystalline phase. Further work, e.g., X-ray pole figure analysis, is required to elucidate origins of this spectral behavior to sample tilting.

Finally, the stability at 80°C/90% relative humidity of the PVA/PAC copolymer comprising the KE polarizer is shown in Fig. 11(a) and (b) for the polarizer transmittance and polarization efficiency, respectively.

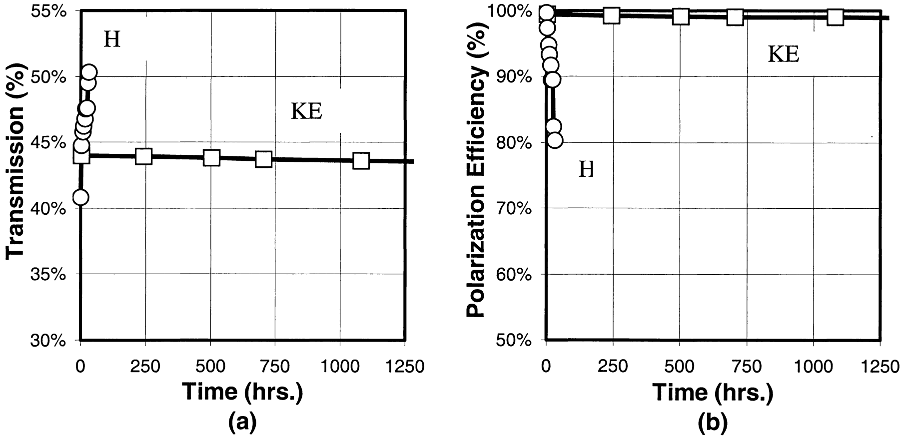

Fig. 11: Comparison of the stability of H and KE polarizers at 80°C/90% RH for transmission (a) and polarization efficiency (b).

The data in Fig. 11 were obtained using an unpolarized white light source, and as a result, the transmission and efficiency data represent an average across the visible spectrum. The difference in stability between the two polarizers at high temperature and humidity is dramatic. For the H-type there is a rapid increase in transmission with a concomitant decrease in polarization efficiency. This is caused by the dissociation of the PVA-polyiodide complex, and in as little as 200 hours the H polarizer will become totally faded or bleached. In contrast, the KE polarizer is inherently stable under these conditions. We routinely test KE polarizers at these conditions as well as at 105°C for an excess of 7000 hours, and we have not seen any degradation in its optical performance. Similarly, we note that KE is stable to most organic solvents, such as alcohols and ketones. We have coated a broad range of solvent-based adhesive formulations on this polarizer without any detrimental effects.

Conclusions

A new stable and high efficiency polarizer that is formed from the acid catalyzed thermal dehydration of oriented PVA films is described. The product of this reaction is a block copolymer of vinylalcohol and acetylene, and the latter functions as the light absorbing chemical entity in the ultraviolet and visible spectral regions. The distribution of PAC conjugation lengths in this copolymer are controlled by the initial stretch ration of the PVA, and the ultimate attainment of high polarization efficiency is achieved by a subsequent restretch step in aqueous, boric acid and borax. Only ~1% of the PVA is converted to PAC; however, this is sufficient to yield a polarizer with both high light transmission (40-41%) and polarization efficiency (99.9%).

Analysis of a KE polarizer with polarized UV/Vis spectroscopy in combination with sample tilting indicates that the PAC chain segments are highly oriented and are distributed uniaxially about the stretch direction of sample. Similar results are also found in polarized IR analyses, and the exception to this is the 1200-1000 cm^{-1} spectral region. The response of both bands in this region (1144 and 1093 cm^{-1}) to sample tilting indicates that there is some preferred or biaxial orientation associated with these vibrational modes. Compared to conventional H-type polarizers, KE polarizers are inherently stable, showing no degradation in optical performance after 7000 hours of testing at 80°C/90% RH.

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