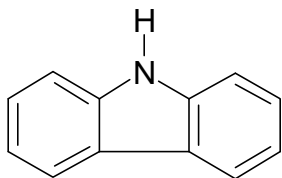


Chapter 2

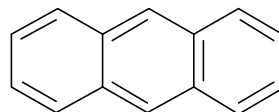
Literature Review of Carbazole and Methacrylate Based Polymers

2.1 Carbazole [86-74-8]

Carbazole (dibenzopyrrole) was discovered in 1872 by Graebe and Glaser as a by-product from the coal tar industry. High-temperature coal tar contains an average of 1.5 % carbazole; carbazole is obtained from coal tar as a co-product of anthracene. Carbazole has a higher boiling point and better solubility than anthracene in many solvents, and can be separated from anthracene by extraction with pyridine, ketones, benzene/methanol, N-methylpyrrolidone, dimethylacetamide, dialkyl sulfoxides, or dialkylformamides. Alternatively, carbazole can be separated from anthracene by azeotropic distillation with ethylene glycol. Mother liquors obtained from the preparation of pure anthracene produce carbazole by concentration and recrystallization from chlorobenzene. Alternatively, carbazole can be synthesized by the dehydrogenation and cyclization of 2-diphenylamine. Historically and to the present day, however, carbazole is commercially prepared from coal tar.³⁰



Carbazole



Anthracene

Pure carbazole is a white crystalline material with a melting point of 246°C and a molecular weight of 167.20 g/mole. It sublimes, and has a scent similar to creosote. Carbazole, an aromatic tricyclic compound, exhibits strong fluorescence and long phosphorescence upon exposure to ultraviolet light. It is readily soluble in acetone,

³⁰ Collin, G.; Höke, H., "Carbazole" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1986**, A5, 59.

slightly soluble in ether and ethanol, and barely soluble in chloroform, acetic acid, carbon tetrachloride, and carbon disulfide.³¹

The LD50 (lethal dose, 50%) of carbazole ranges from 200 mg/kg (intraperitoneal, mice) to more than 5,000 mg/kg (oral, rats), thus it is considered non-toxic.^{32,33,34} In rats and rabbits, carbazole is glucuronized and excreted in the urine.^{35,36} There is no evidence of carcinogenicity for carbazole.³⁷ Carbazole is an irritant, however, and humans can become sensitized to it. Folliculitis (skin follicle inflammation) and comedos (plugged sebaceous glands) have been reported by workers with carbazole contact.^{38,39}

Commercially, carbazole is primarily used for dye synthesis. Hydron Blue™, Naphthol™ dyes, anthraquinone vat dyes, styryl dyes, and dioxazine dyes and pigments can be synthesized from carbazole. 1,3,6,8-tetranitro-carbazole (Nirosan™) is used as an insecticide.⁴⁰ Carbazole reacts with phenols and formaldehyde in the presence of acidic catalysts to form Novalacs, which can be cured with hexamethylenetetramine to produce highly heat resistant polymers.^{41,42} It is also used to synthesize the monomer N-vinylcarbazole, which can be polymerized to form poly(vinylcarbazole).^{43,44}

³¹ Collin, G.; Höke, H., "Carbazole" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1986**, A5, 59.

³² Collin, G.; Höke, H., *ibid.*

³³ Papenfuhs, T., (Hoechst) *DE Patent*, **1971**, 2132961.

³⁴ Sax, N.J., *Dangerous Properties of Industrial Materials*, Van Norstrand Reinhold: New York, **1979**, 468.

³⁵ Collin, G.; Höke, H., *Op. Cit.*

³⁶ Johns, S.; Wright, S., *J. Med., Chem.*, **1964**, 7, 158.

³⁷ Collin, G.; Höke, H., *Op. Cit.*

³⁸ Collin, G.; Höke, H., *ibid.*

³⁹ Jirásek, L.; Stáva, Z., *Prakt. Lek.*, **1955**, 35, 34.

⁴⁰ Collin, G.; Höke, H., *Op. Cit.*

⁴¹ Collin, G.; Höke, H., *ibid.*

⁴² Omran, J., (Rütgerswerke) *DE Patent*, **1970**, 2033015.

⁴³ Collin, G.; Höke, H., *Op. Cit.*

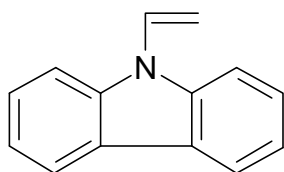
⁴⁴ Pearson, J.M.; Stolka, M., "Poly(N-vinylcarbazole)" in *Polymer Monographs No. 6*, Gordon & Breach: New York, **1981**.

2.2 Poly(N-Vinylcarbazole) [25067-59-8]

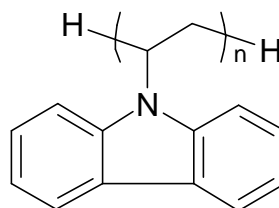
2.2.1 Physical Properties and NMR Characterization of Poly(N-vinylcarbazole)

N-Vinylcarbazole [1484-13-5] is polymerized to produce poly(vinylcarbazole) (Luvican™, Polectron™).⁴⁵ Poly(vinylcarbazole) (PVK) can be polymerized by both free radical and cationic polymerizations. The propagating chain end stabilizes electron deficient centers by resonance, involving the nonbonding electron pair on the nitrogen of the carbazole ring. N-Vinyl carbazole has not been successfully polymerized by anionic means.^{46,47}

PVK is a transparent thermoplastic material, with good thermal and chemical stability. For example, it has a softening temperature of 150°C, a reported glass transition temperature (T_g) of 211°C, and does not begin to decompose until over



N-vinylcarbazole
m.p. = 63-64°C



Poly(vinylcarbazole)
 $T_{\text{softening}} = 150^{\circ}\text{C}$ $T_g = 211^{\circ}\text{C}$

300°C.⁴⁸ Unfortunately, PVK is brittle and has poor mechanical strength. PVK has a high refractive index of 1.69.⁴⁹ PVK is also a photoconductive material; it is an insulator in the dark, and becomes electrically conductive upon exposure to ultraviolet radiation. With intense laser light, it can undergo a change in refractive index and thus is considered

⁴⁵ Pearson, J.M., "Vinylcarbazole Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, **1989**, 257.

⁴⁶ Pearson, J.M., *ibid.*

⁴⁷ Hallensleben, M.L., "Other Polyvinyl Compounds" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G., Eds., VHS: New York, **1992**, A21, 743.

⁴⁸ Pearson, J.M., *Op. Cit.*

⁴⁹ Pearson, J.M., *ibid.*

a photorefractive material. PVK also has other excellent electronic properties, such as low dielectric loss.^{50,51}

Recently, Dais, *et al.*, reported a complete and unambiguous assignment of ¹H and ¹³C NMR spectra of PVK by using gradient two dimensional NMR experiments. Figure 2.1 shows the ring assignment and the gradient correlated (gCOSY) NMR spectrum of the pendant carbazole protons. The aromatic rings of the carbazole in PVK were not electronically equivalent due to ring shielding effects in the constrained configuration of the polymer. This nonequivalence of the two aromatic rings of carbazole was attributed to the ring current effects exerted by neighboring carbazole units. In effect, the aromatic ring of the carbazole containing protons 5, 6, 7 and 8 (Figure 2.1) was more deshielded from the NMR magnetic field than the aromatic ring containing protons 1, 2, 3, and 4. The proton peaks in the more shielded ring were shifted more upfield (higher field, lower ppm) than the proton peaks in the less shielded ring. Within each aromatic ring of the carbazole, the protons in the β position from the nitrogen were shifted the furthest upfield (lower ppm) relative to the other protons within that ring.⁵² Another interpretation of the data produced by Dais is that another ring, or other adjacent rings, may have caused these differences, rather than deshielding from within the same substituent.⁵³

⁵⁰ Pearson, J.M., "Vinylcarbazole Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, **1989**, 257.

⁵¹ Hallensleben, M.L., "Other Polyvinyl Compounds" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G., Eds., VHS: New York, **1992**, A21, 743.

⁵² Karali, A.; Froudakis, G.E.; Dais, P., *Macromolecules*, **2000**, 33, 3180.

⁵³ Dorn, H., conversation, **2001**.

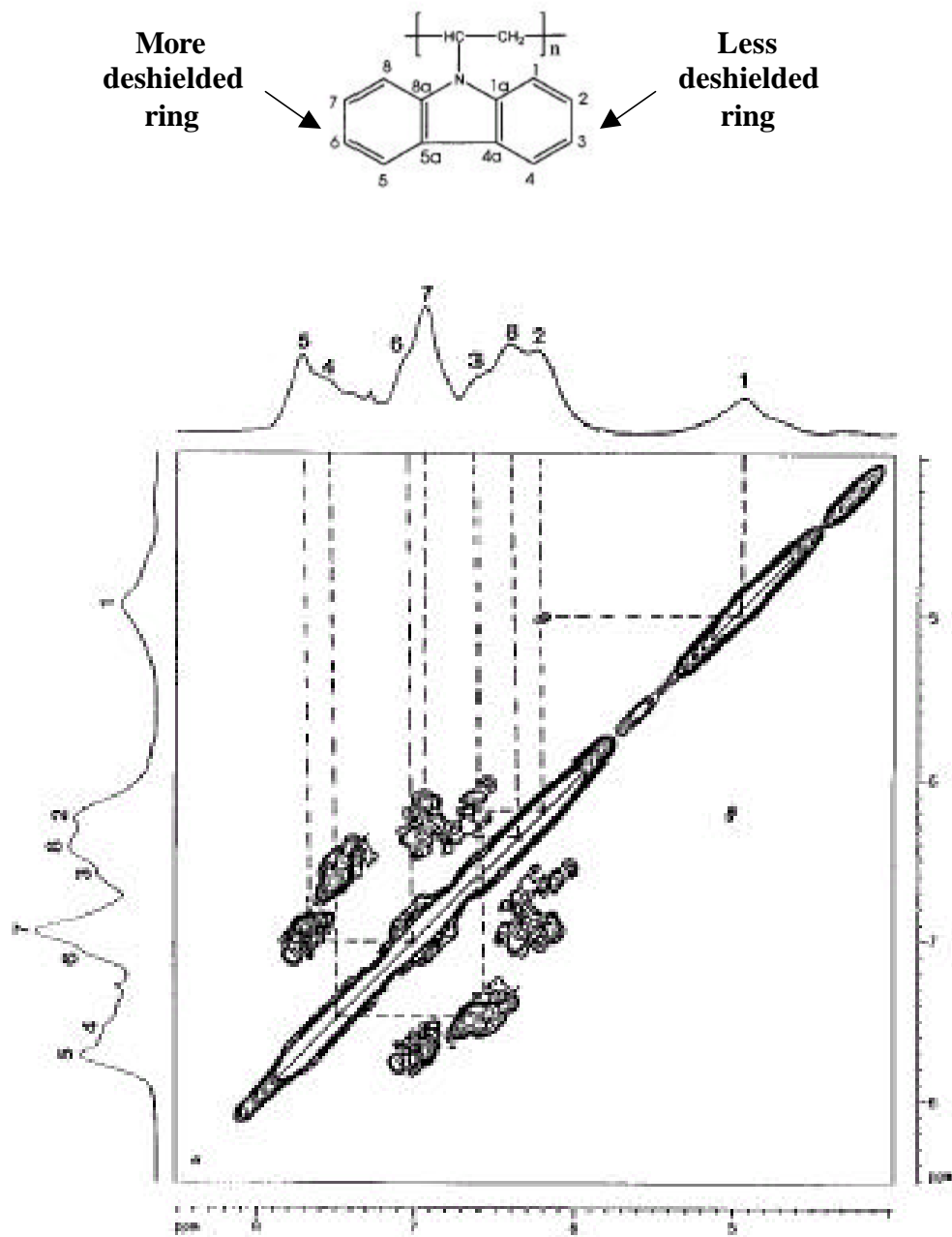


Figure 2.1 gCOSY Spectrum of the Aromatic Region of PVK⁵⁴

⁵⁴ Karali, A.; Froudakis, G.E.; Dais, P., *Macromolecules*, **2000**, *33*, 3180.

The phase sensitive gradient-selected heteronuclear multiple quantum coherence (gHMQC) NMR spectrum of PVK is depicted in Figure 2.2. This technique detects one-bond ^{13}C - ^1H connectivities, and clearly shows the peak assignments for the protonated carbazole carbons of PVK.⁵⁵ The thorough assignment of the ^1H and ^{13}C NMR spectra for PVK by Dais, Karali, and Froudakis was extremely useful for my understanding of the NMR spectra generated in the study of novel carbazole-phenoxy based methacrylates, acrylates, and dimethacrylates.

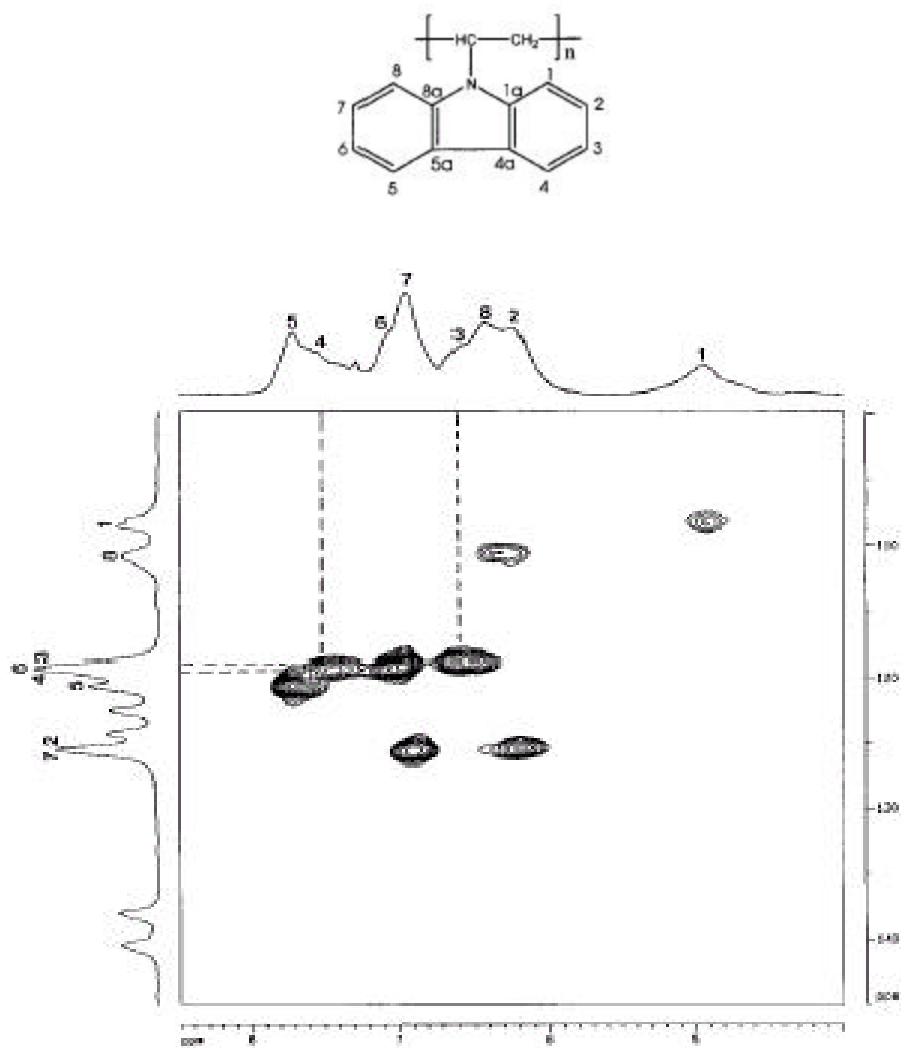


Figure 2.2 gHMQC Spectrum of the Aromatic Region of Poly(vinylcarbazole)⁵⁶

⁵⁵ Karali, A.; Froudakis, G.E.; Dais, P., *Macromolecules*, **2000**, *33*, 3180.

⁵⁶ Karali, A.; Froudakis, G.E.; Dais, P., *ibid.*

To understand how these neighboring pendant carbazole units may be influencing one another, Dais, *et al.*, used conformational calculations to molecularly model syndiotactic pentad sequences and isotactic heptad sequences (Figure 2.3). Energy minimization was performed with the semiempirical PM3 method using a Gaussian 94 program. All geometries and structural parameters were fully optimized by the PM3 method. The syndiotactic pentad assumed a helical configuration. This was similar to the 2/1 helix observed for the syndiotactic sequence from the crystal structure.^{57,58} The isotactic heptad approached a 3/1 helix.^{59,60,61} The helical configurations, particularly the “stacking” of the carbazole pendant groups in the syndiotactic polymer, would allow for many of the interesting electronic and photoconductive properties associated with PVK.⁶²

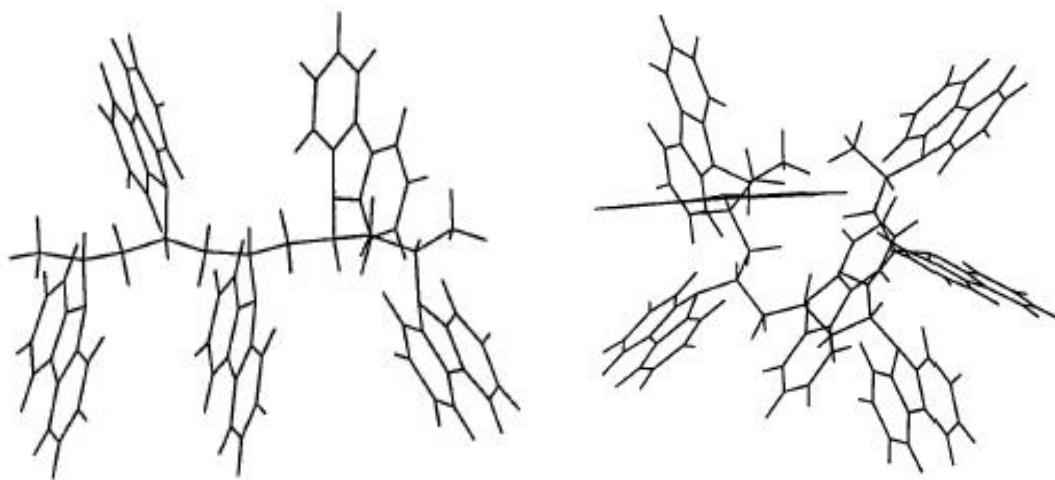


Figure 2.3 A. Minimum energy structure of syndiotactic pentad sequence, 2/1 helix.

B. Minimum energy structure of isotactic heptad sequence, 3/1 helix.⁶³

⁵⁷ Karali, A.; Froudakis, G.E.; Dais, P., *Macromolecules*, **2000**, *33*, 3180.

⁵⁸ Kimura, A.; Yoshimoto, S.; Akana, Y.; Hirata, H.; Kusabayashi, S.; Mikawa, H.; Kasai, N., *J. Polym. Sci., Polym. Phys. Ed.*, **1970**, *8*, 643.

⁵⁹ Karali, A.; Froudakis, G.E.; Dais, P., *Op. Cit.*

⁶⁰ Kimura, A.; Yoshimoto, S.; Akana, Y.; Hirata, H.; Kusabayashi, S.; Mikawa, H.; Kasai, N., *Op. Cit.*

⁶¹ Griffiths, C.H., *J. Polym. Sci., Polym. Phys. Ed.*, **1977**, *16*, 271.

⁶² Karali, A.; Froudakis, G.E.; Dais, P., *Op. Cit.*

⁶³ Karali, A.; Froudakis, G.E.; Dais, P., *ibid.*

2.2.2 Historical Uses of Poly(N-vinylcarbazole) in Xerography

Xerography was invented by Carlson in 1938, and has become the predominant form of electrophotography. In xerography, a charge pattern that replicates the original light image is formed on a photoconducting film. Pigmented, charged, thermoplastic particles, called toner, are selectively attracted to the charge pattern, which develops the pattern. This toner image is then transferred and fixed by softening and fusing the toner to paper, producing a Xerox™ copy.⁶⁴

In xerography, the photoreceptor is the device, or transducer, that converts the light pattern into an electrostatic pattern. The simplest photoreceptor consists of a photoconductive layer on a conductive substrate. Charging, the first step, produces a uniform electric field across the photoconductor layer by corona charging. In charge generation (also called exposure), the second step, photons incident on the photoreceptor are absorbed in the pattern of the image, and generate a conducting charge (electron-hole pairs). In charge transport, the third step, the electron-hole pairs drift across the photoconductor, neutralize the surface charge, and produce the electrostatic image.⁶⁵

The first organic photoreceptors consisted of a single layer charge-transfer complex composed of PVK, which was the electron-donor polymer (also called hole transporting polymer), coupled with 2,4,7-trinitofluorenone, which was the electron acceptor. The charge-transfer complex absorbed visible light and allowed charge transport of both electrons and holes. The photogeneration of this first organic photoreceptor was relatively low, and highly electric field dependent.^{66,67,68,69,70} Hole transporting PVK has

⁶⁴ Winkelmann, D.; Pai, D.; Crooks, W.; Pennington, K.; Lee, F.; Bräuninger, A.; Brabandere, L.; Verelst, J.; Frass, W.; Hoffmann, H.; Sprinsein, K.; Steppan, H.; Stoudt, T.; Allen, D., “Imaging Technology” in *Ullmann’s Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1986**, A13, 571.

⁶⁵ Winkelmann, D.; Pai, D.; Crooks, W.; Pennington, K.; Lee, F.; Bräuninger, A.; Brabandere, L.; Verelst, J.; Frass, W.; Hoffmann, H.; Sprinsein, K.; Steppan, H.; Stoudt, T.; Allen, D., *ibid.*

⁶⁶ Winkelmann, D.; Pai, D.; Crooks, W.; Pennington, K.; Lee, F.; Bräuninger, A.; Brabandere, L.; Verelst, J.; Frass, W.; Hoffmann, H.; Sprinsein, K.; Steppan, H.; Stoudt, T.; Allen, D., *ibid.*

⁶⁷ Lardon, M.; Lell-Doller, E.; Weigl, J.W., *Mol. Crystl.*, **1967**, 2, 241.

⁶⁸ Gill, W.D., *J. Appl. Phys.*, **1972**, 43, 5033.

been replaced by other electron-donor materials, such as bisphenol A poly(carbonate).⁷¹

2.2.3 Current Applications of Poly(N-vinylcarbazole)

The chemical and thermal resistance of PVK, combined with its excellent electrical properties, make it very useful in the electronics industry. It is used commercially as a paper-capacitor impregnant, and as a substitute for electrical mica. Because of its photoconductivity and photorefractivity, there is renewed interest for PVK in holography, electro-optics, electro-luminescence, non-linear optics, and electronic data storage.^{72,73,74}

2.2.3.1 Holography

Holography, or lensless photography, is a method of producing three dimensional images. The images are called holograms. Gabor developed the theoretical principles of holography in 1947, but the first actual production of holograms did not occur until the 1960s when the laser became available.⁷⁵

A hologram records not only the intensity of reflected light, like an ordinary photograph, but also the phase distribution. The holographic medium distinguishes between waves that reach the light sensitive surface while at a maximum wave amplitude, and waves that reach the surface at a minimum wave amplitude. This ability to discern waves with different phases is achieved by having a reference beam interfere with the

⁶⁹ Weiser, G., *J. Appl. Phys.*, **1972**, *43*, 5028.

⁷⁰ Melz, P.J., *J. Chem., Phys.*, **1972**, *57*, 1694.

⁷¹ Winkelmann, D.; Pai, D.; Crooks, W.; Pennington, K.; Lee, F.; Bräuninger, A.; Brabandere, L.; Verelst, J.; Frass, W.; Hoffmann, H.; Sprinsein, K.; Steppan, H.; Stoudt, T.; Allen, D., "Imaging Technology" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1986**, A13, 571.

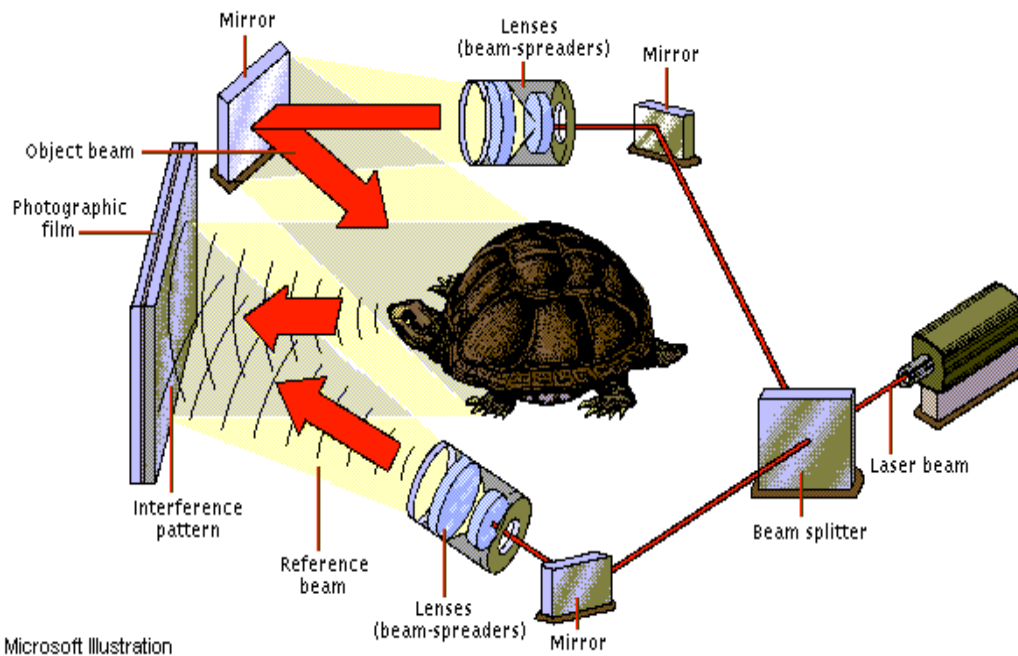
⁷² Pearson, J.M., "Vinylcarbazole Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, **1989**, 257.

⁷³ Zhang, Y.; Wada, T.; Sasabe, H., *J. Mater. Chem.*, **1998**, *8(4)*, 809.

⁷⁴ Hallensleben, M.L., "Other Polyvinyl Compounds" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G., Eds., VHS: New York, **1992**, A21, 743.

⁷⁵ "Holography" in *Microsoft® Encarta® 98 CD-ROM Encyclopedia*, Microsoft: Seattle, **1993-1997**.

reflected waves. To make a hologram, the object of interest is illuminated with a beam of coherent light, which is produced by a laser. The shape of the object determines the form of the (reflected) wave fronts, and determines the phase at which the reflected light arrives on each point of the holographic media. Simultaneously, a portion of the laser beam (coherent light) is reflected by a mirror or prism, and directed towards the holographic media. This portion, which was not reflected by the object of interest, is called the reference beam.. The wave fronts of the object-reflected and reference beam produce an interference pattern, which is recorded on the holographic media. When the hologram is viewed in coherent light, the recorded object becomes visible. When the hologram is viewed from different angles, the recorded object can be seen from different angles. The hologram reconstructs, three dimensionally, the wave fronts that were originally produced by the object of interest.⁷⁶



Microsoft Illustration
Figure 2.4 Making a Hologram⁷⁷

Holograms are made by exposing a piece of film to laser light, which is scattered by the object being holographed. The film is also exposed to light coming directly from the laser (the reference beam). The two beams of light interfere when they reach the film because they have taken different paths and are no longer in phase with each other. The film simply records this interference pattern, which is the hologram. To reconstruct (view) the image, the hologram is illuminated by a beam of light, which is diffracted by the interference pattern on the film. This reproduces the original surface pattern of the object in three dimensions.

⁷⁶ “Holography” in *Microsoft® Encarta® 98 CD-ROM Encyclopedia*, Microsoft: Seattle, **1993-1997**.

⁷⁷ “Holography” in *Microsoft® Encarta® 98 CD-ROM Encyclopedia*, *ibid.*

Electronic data storage is an important application of holography. Digital data can be recorded as bright and dark spots in holographic images. A hologram can contain a large amount of information by recording at different angles relative to the holographic media. This is why holograms can store so much digital information. By illuminating the hologram with a laser beam at different angles, the recorded information can be read out. In other words, information can be stored on the same physical area, but at different angles, allowing for the hologram to hold a multitude of information.⁷⁸

Organic photorefractive materials suitable for holography consist of two main functional components; a charge transporting agent (also called hole-transporting agent) and a linear electro-optic agent. PVK has good charge transporting properties because of its highly conjugated carbazole pendant groups. It can be sensitized by the formation of a charge transfer complex between the carbazole moiety and an acceptor molecule, such as trinitrofluorenone.^{79,80,81,82,83} High performance photorefractive effects, for example, 100 % diffraction efficiency for the readout of a hologram, has been observed for composite materials based on PVK.^{84,85}

⁷⁸ "Holography" in *Microsoft® Encarta® 98 CD-ROM Encyclopedia*, Microsoft: Seattle, **1993-1997**.

⁷⁹ Pearson, J.M., "Vinylcarbazole Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, **1989**, 257.

⁸⁰ Hallensleben, M.L., "Other Polyvinyl Compounds" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G., Eds., VHS: New York, **1992**, A21, 743.

⁸¹ Gill, W.D., *J. Appl. Phys.*, **1972**, 43, 5033.

⁸² Hoegl, H., *J. Phys. Chem.*, **1965**, 69, 755.

⁸³ Pearson, J.M.; Stolka, M., "Poly(N-vinylcarbazole)" in *Polymer Monographs No. 6*, Gordon and Breach: New York, **1981**.

⁸⁴ Zhang, Y.; Wada, T.; Sasabe, H., *J. Mater. Chem.*, **1998**, 8(4), 809.

⁸⁵ Zhao, C.; Park, C.; Prasad, P.N.; Zhang, Y.; Ghosal, S.; Burzynski, R., *Chem. Mater.*, **1995**, 7, 1237.

2.2.3.2 Optics: Refractive Index, Abbe Number, and Birefringence

Refractive index (RI or n) is the ratio of the speed of light in a vacuum, $c_0 = 3.00 \times 10^8$ m/s, compared to the speed of light through the material, c (Equation 2.1). Since all media decrease the speed of light, n is always greater than one.⁸⁶

$$\text{Refractive Index} = n = c_0/c \qquad \text{Equation 2.1}$$

Refractive indices are determined by the polarizabilities, Q , according to the Lorenz-Lorentz relationship (equation 2.2).⁸⁷ Polarizability, Q , is the concentration of molecules, N/V , with polarization, α . N is the number of molecules in a given volume V . Polarization, α , is a function of all the dipole moments from all groups in a molecule. Contributions to the refractive indices are higher for carbon atoms than for hydrogen

$$(n^2-1)/(n^2-2) = (4/3)\pi Q \qquad \text{Equation 2.2}$$

$$Q = (N/V)\alpha \qquad \text{Equation 2.3}$$

atoms. Since carbon atoms dominate the structure of most polymers, most common polymers have a refractive index near 1.5.⁸⁸ The refractive index for poly(methyl methacrylate) is 1.49, and the refractive index for poly(ethylene) is 1.51.⁸⁹ Polymers with strongly electronegative substituents usually have lower refractive indices. For

⁸⁶ Seferis, J.C., "Refractive Indices of Polymers" in *Polymer Handbook*, 4th ed., Brandrup, J.; Immergut, E.H.; Grulke, E.S., Eds., Wiley: New York, **1999**, VI/571.

⁸⁷ Elias, H., "Plastics, General Survey: Optical Properties," in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VCH: New York, **1992**, A20, 643.

⁸⁸ Elias, H., *ibid.*

⁸⁹ Seferis, J.C., *Op. Cit.*

example, the refractive index for poly(tetrafluoroethylene) is 1.37.⁹⁰ In contrast, polymers with bulky aromatic or conjugated substituents tend to have higher refractive indices. The refractive index for poly(styrene) is 1.59, and the refractive index for PVK is 1.69.⁹¹ According to the current understanding of molecular structure for all known polymers, their refractive indices should fall between 1.33 and 1.73,^{92,93} while some specialized polymers may have refractive indices as low as 1.28 and as high as 1.80.⁹⁴

Refractive index and birefringence can be measured using a modern prism coupling instrument. To determine the refractive index, the sample film is first brought into contact with the base of the prism pneumatically, creating a small air gap between the

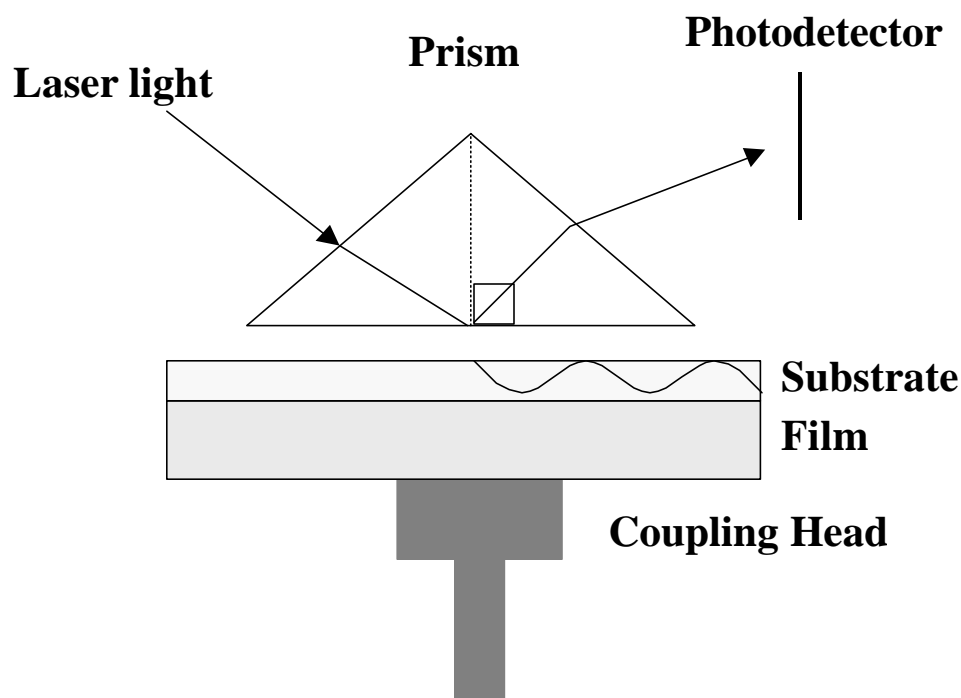


Figure 2.5 Schematic of the Metricon 2010 Prism Coupler for RI Determination⁹⁵

⁹⁰ Seferis, J.C., "Refractive Indices of Polymers" in *Polymer Handbook*, 4th ed., Brandrup, J.; Immergut, E.H.; Grulke, E.S., Eds., Wiley: New York, **1999**, VI/571.

⁹¹ Seferis, J.C., *ibid.*

⁹² Seferis, J.C., *ibid.*

⁹³ Elias, H., "Plastics, General Survey" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G., Eds. VHS: New York, **1992**, A20, 643.

⁹⁴ McGrath, J.E.; Long, T., conversations, **2001**.

⁹⁵ www.metricon.com.

film and the prism. A laser beam (coherent light at $\lambda = 633\text{nm}$) strikes the base of the prism. At certain discrete values, the incident angle, θ (also called the mode angle), the photons tunnel across the air gap into the film and enter into a guided optical propagation mode, which causes a sharp decrease in the intensity of light reaching the photodetector. The angular location of the first mode determines the refractive index of the film. The prism coupling instrument can also simultaneously measure film thickness. Angular differences between the modes determines the film thickness in films over $3,000 \text{ \AA}$.⁹⁶

The Abbe number, v_e , measures chromatic aberration by expressing the deviating effect in light of different wavelengths of an optical material (equation 2.4).⁹⁷ For eye glasses, called optical spectacles, a high Abbe number is desirable, because this reduces the “rainbow” effect. Poly(methyl methacrylate) has an Abbe number of 57.8.^{98,99,100} Polycarbonate derived from bisphenol A has an Abbe number of 29.8.¹⁰¹

$$\text{Abbe Number} = v_e = \frac{n_e - 1}{n_F - n_C} \quad \text{Equation 2.4}$$

where n_e = refractive index at λ_e of 546.1nm (green line)
 n_F = refractive index at λ_F of 480.0 nm (blue line)
 n_C = refractive index at λ_C of 643.8 nm (red line)

Birefringence, or double refraction, is the resolution or splitting of a light wave into two unequally reflected waves by an optically anisotropic medium, such calcite or quartz. Optically anisotropic polymers can also exhibit birefringence.¹⁰² Birefringence is

⁹⁶ www.metrocon.com.

⁹⁷ Hoffmann, C.; Zeiss, C., “Optical Materials” in *Ullmann’s Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., **1991**, A18, 193.

⁹⁸ Brandrup, J.; Immergut, E.H.; Grulke, E.A. Eds., *Polymer Handbook*, 4th ed., Wiley: New York, **1999**, II, 89.

⁹⁹ Matsuda, T.; Funae, Y.; Yoshida, M.; Takaya, T.; (Nippon) *US Patent*, **1990**, 4931521.

¹⁰⁰ Tsuji, S., (Canon) *US Patent*, **1990**, 4929068.

¹⁰¹ Tsuji, S., *ibid*.

¹⁰² Hoffmann, C.; Zeiss, C., *Op. Cit.*, 191.

measured by the difference in refractive indices for the unequally reflected waves.¹⁰³ Some materials split the light wave into more than two unequally reflected waves, and these materials are described as having several orders of birefringence.^{104,105} For oriented polymers, the birefringence along two orthogonal directions can be used as the measure of optical anisotropy, and consequently, orientation of the polymer. There are three birefringences, Δn_{xy} , Δn_{xz} , and Δn_{yz} , that are defined for a Cartesian (x,y,z) coordinate system (equations 2.5, 2.6, and 2.6).¹⁰⁶

$$\Delta n_{xy} = n_x - n_y \quad \text{Equation 2.5}$$

$$\Delta n_{xz} = n_x - n_z \quad \text{Equation 2.6}$$

$$\Delta n_{yz} = n_y - n_z = \Delta n_{xz} - \Delta n_{xy} \quad \text{Equation 2.7}$$

Solvent casting of thin PVK films produced oriented, optically anisotropic films. Stress introduced during the formation of the films preferentially aligned the polymer chain backbones in the plane of the film, producing birefringence. These solvent cast PVK films were found to display a high birefringence of -0.032.¹⁰⁷ In comparison, atactic polystyrene has a birefringence of only -0.006.^{108,109,110}

¹⁰³ McCrone, W., *Microscope*, **1983**, 31(2), 187.

¹⁰⁴ Hoffmann, C.; Zeiss, C., "Optical Materials" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., **1991**, A18, 191.

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