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Influence of acceptor functionality on charge transfer interactions in mixtures of poly(9-vinylcarbazole) with nitroaromatic compounds

Research Article

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Abstract: Charge transfer interactions in mixtures of poly(9-vinylcarbazole) with three nitro compounds (4,4'dinitrodibenzyl, ethyl 3,5-dinitrobenzoate and 2,2',4,4'-tetranitrodibenzyl) were examined.
GPC shows an increase of apparent polymer weight average molecular weight (*MW*) in mixtures compared with pure PVK. Electron acceptors show upfield ^{1}H-NMR shifts for all mixtures. The equilibrium association constants (*k*) calculated from the Benesi-Hildebrand equation are 0.511, 1.371, and 1.868 L mol^{-1} for PVK blends with DNDB, DNBE and TNDB, respectively. Shifts of (-NO$_2$) stretch vibrations in mixtures support charge transfer complex formation between PVK chains and electron acceptors
The ability to accept electrons decreases: TNDB > DNBE > DNDB.

Keywords: PVK mixtures • Electron acceptor functionality • GPC • ^{1}H-NMR • FTIR

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1. Introduction

Noncovalent forces such as hydrogen and ionic bonds, van der Walls, and hydrophobic interactions control molecular recognition [1]. Charge transfer complexes (also called electron donor-acceptor (EDA) complexes), were discovered by Benesi and Hildebrand [2], investigated by Briegleb [3] and explained in terms of valence bonds and molecular orbitals by Mulliken [4], and Dewar and Lepley [5], respectively. These interactions are based on attractive forces produced by charge transfer between an electron donor (with low ionization potential) and electron acceptor (with high electron affinity) [6,7]. CT complexation in solution depends on donor ionization potential, entropy contributions (temperature), and steric factors (spacer length) [6,9]. The binding energy does not exceed 10 kcal mol^{-1} [8]. Depending on the participating orbitals, CTC may be π-π*, π-σ*, σ-π*, σ-σ*, n-π* or n-σ* [1,9].

Poly(9-vinylcarbazole) (PVK) is a thermoplastic π-conjugated polymer with high thermal and chemical stability. It is photoconductive and transparent

with a high refractive index [10]. These characteristics are useful in electroluminescent devices and photorefractive materials [11-13]. The principal applications of PVK are in xerography [14,15].

CTC's in solution have been investigated by UV-Vis, ^{1}H-NMR and IR spectroscopy and analyzed in terms of the Benesi-Hildebrand equation or a similar form (Rose-Drago; Scott; Hammick-Wardley; Scatchard) [16].

The π-π* CTCs studied here are based on the decreased π–electron density of benzene rings containing nitro groups (electron acceptor) interacting with the π-electron rich carbazolyl groups of PVK (electron donor). The electron acceptors had different structures: monofunctional ethyl 3,5-dinitrobenzoate (DNBE), bifunctional 4,4'dinitrodibenzyl (DNDB) or 2,2',4,4'-tetranitrodibenzyl (TNDB).

The GPC data, FTIR spectra and CTC association constants (from ^{1}H-NMR) confirm that CTCs are formed and depend on the electron acceptor. The geometric requirements for CTC formation can be satisfied by parallel arrangement of the π and π* orbital planes.

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2. Experimental procedure

2.1. Materials and mixtures preparation

Poly(9-vinylcarbazole) (PVK) obtained from Sigma Aldrich has Mn of 25000-50000 g/mol and polydispersity index of about 2. It was purified by methanol precipitation from chloroform solution, then filtered and vacuum dried at 70°C for 3 hours. DNBE (Sigma Aldrich) was used as received. DNDB was synthesized by nitration of dibenzyl [17]. The TNDB synthesis has been presented elsewhere [18]. Fig. 1 shows the structures of PVK and the electron acceptors.

Deuterated chloroform (CDCl$_3$) and spectrophotometric grade tetrahydrofuran (THF) were used as received from Sigma Aldrich. CT interactions depend on the intrinsic properties of the donor and acceptor as well as environmental factors (solvent, temperature, molecular conformation). Because charge separation occurs in CTC, solvent polarity can play an important role [19]. THF and CDCl$_3$ were used to limit solvent competition.

The PVK mixtures with each electron acceptor were prepared by mixing both components in CDCl$_3$ for ^{1}H-NMR spectroscopy or THF for GPC and FTIR. The molar concentrations for ^{1}H-NMR measurements represent moles of nitroaromatic and moles of PVK repeating units.

2.2. Gel permeation chromatography

The polymer M_W and $P.I.$ were obtained by gel permeation chromatography using a Polymer Laboratories GPC instrument equipped with a PL-EMS 950 evaporative mass detector, PL gel 5 μm Mixed-C and -D columns, LC 1120 HPLC pump and 505 LC column ovens. Calibration was with polystyrene molecular weight standards from Polymer Laboratories. The M_W values for free and mixed polymer were calculated by PL Logical GPC/SEC software using Mark-Houwink constants for PVK in THF (a = 0.65 and k = 14.4×10^{-3} mL g^{-1}) [20].
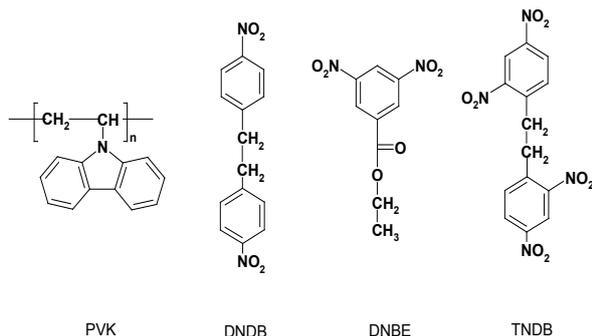
Figure 1. Chemical structures of PVK and electron acceptors.

2.3. ^{1}H-NMR spectroscopy

The ^{1}H-NMR spectra were acquired on a Bruker Avance DRX 400MHz spectrometer at 25°C following literature procedures [21]. Tetramethylsilane (Sigma Aldrich) was the reference. For binding constant estimation, the acceptor concentration was kept constant and donor concentrations varied. The donor/acceptor molar ratio in PVK-DNBE and PVK-TNDB blends varied from 5 to 50 and from 40 to 330 for the PVK-DNDB blend. Molar concentrations of DNDB, DNBE and TNDB were 0.0028 M, 0.014 M, and 0.012 M respectively.

2.4. FTIR spectroscopy

FTIR absorption spectra were obtained from solutions cast and dried on KBr discs using a Bruker Vertex-70 FTIR spectrophotometer from 400-4000 cm^{-1}.

3. Results and discussion

3.1. GPC analysis

Table 1 shows the M_W values for each PVK-acceptor pair. For an optimal (A/D) molar ratio, each pair showed a maximum value of M_W, demonstrating substantial complex formation.

Before the separation column, the solution contains three molecular species: 1- free DNDB, DNBE or TNDB molecules, 2 - uncomplexed PVK chains and 3 - complexed PVK chains. Chromatograms of PVK and PVK-DNBE blends are shown in Fig. 2. Two signals appear: one for polymer and the other for the nitroaromatic, so complexed and uncomplexed PVK molecules coelute. The polymer elution time in mixtures slowly decreases with increasing nitroaromatic concentration. An increase of M_W and a decrease of $P.I.$ values were observed for the polymer in mixtures compared to pure polymer.

We assume that the components of the mixtures act as electron donors and electron acceptors, and that changes of PVK M_W and elution time in mixtures were due to CT interactions.

Fig. 3 contains plots of f_A (acceptor signal area) vs. F_A (gravimetric fraction of acceptor) for bifunctional and monofunctional acceptors. The dashed line in this figure corresponds to behavior expected in the absence of complexation, where an increase of F_A is directly proportional to an increase of f_A.

For monofunctional PVK-DNBE mixtures the plot shows an exponential increase, with a slow, quasi-linear increase at low values of F_A. Although complexation is sterically allowed, only a few CT interactions are established. For PVK-DNBE blends,

Table 1. Chromatographic data.

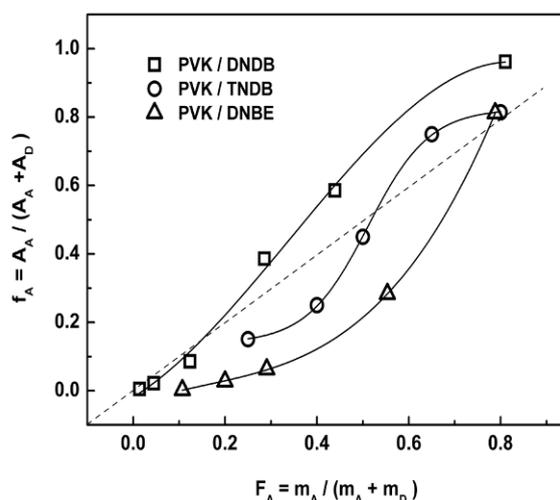| Blend in THF	Molar ratio A/D	M_W (g mol^{-1})	Ratio of signal areas A_D/A_A	F_A	f_A
PVK + DNDB	PVK	40100	-	-	-
	1/100	39000	190	0.0139	0.0052
	1/30	38200	44.4	0.0449	0.0220
	1/10	37000	10.7	0.1236	0.0855
	1/3.5	45500	1.6	0.2572	0.3846
	1/1.8	47000	0.7	0.4393	0.5882
	3/1	38400	0.4	0.8183	0.9620
PVK + DNBE	PVK	20000	-	-	-
	1/10	23500	453	0.1106	0.0022
	1/5	26100	35.7	0.1992	0.0272
	1/3	21400	14.95	0.2931	0.0627
	1/1	21000	2.53	0.5543	0.2830
	3/1	22200	0.23	0.7886	0.8117
PVK + TNDB	PVK	45000	-	-	-
	1/10	47000	5.63	0.2485	0.1508
	1/3	48300	3.02	0.3949	0.2487
	1/2	51000	1.22	0.4840	0.4504
	1/1	49200	0.33	0.6523	0.7519
	2/1	48900	0.22	0.7986	0.8197

Note: A_D and A_A represent signal areas for short and long eluting time peaks in the blend chromatogram, $f_A = A_A/(A_A + A_D)$ and F_A is the weight fraction of acceptor in the blend.
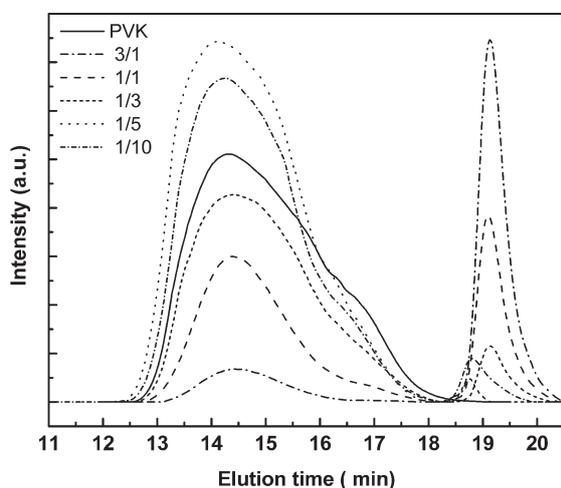
Figure 2. Chromatograms of PVK-DNBE mixtures of different A/D molar ratios.

Figure 3. $f_A = f(F_A)$ plots for mixtures in THF.

the exponential behavior is due to an increasing number of CT interactions; the single functional group of DNBE participates in charge transfer

For bifunctional PVK-DNDB and PVK-TNDB mixtures the plots are sigmoidal, suggesting that only one of the acceptor's functional groups undergoes CT interactions at low F_A values. However, when F_A increases (over 0.55 for mixtures with TNDB, and 0.18 with DNDB) the acceptor's second functionality allows new CT interactions with other carbazolyl groups.

The maximal CT interactions in THF form at molar ratios around 1:2, 1:5, and 1:2 for PVK-DNDB, PVK-

DNBE and PVK-TNDB respectively (Table 1). In all three systems, the M_W shows maximal values, corresponding to the largest fraction of CTC formation, if acceptor molecules represent 80%, 20%, or 50% of the mixture (Fig. 4).

3.2. ¹H-NMR spectroscopy data

¹H-NMR investigations of polymer charge-transfer complexes have been extensively reported [23-26], as the technique offers more information about the interaction strength. A change in electron density due to partial electron transfer will have as its effect a chemical

Table 2. Chemical shifts of DNDB, DNBE, and TNDB complexed with PVK for different molar ratios in mixtures.

Parameter / Nitro compound	$[D]_0$ (mol L^{-1})	δ (ppm)	Δ (ppm)
DNDB (H$_5$ shift)	0	8.157	0
	0.114	8.146	0.011
	0.331	8.130	0.027
	0.927	8.096	0.061
DNBE (H$_4$ shift)	0	9.228	0
	0.077	9.203	0.025
	0.232	9.151	0.077
	0.698	9.007	0.221
TNDB (H$_3$ shift)	0	8.874	0
	0.061	8.848	0.026
	0.313	8.779	0.095
	0.565	8.742	0.132

Table 3. Vibrational frequency assignments for acceptors and complexes.

Sample	Stretching band wavenumber (cm^{-1})	Assignment
DNDB	1592.90(w), 1512.56(m)	$\nu_{(-NO_2)}$ (asym)
	1340.44(s)	$\nu_{(-NO_2)}$ (sym)
PVK+DNDB (molar ratio A/D=1/1)	1595.81(w), 1518.06(m)	$\nu_{(-NO_2)}$ (asym)
	1343.39(s)	$\nu_{(-NO_2)}$ (sym)
PVK+DNDB (molar ratio A/D=1/2)	1519.62(s)	$\nu_{(-NO_2)}$ (asym)
DNBE	1542.60(s)	$\nu_{(-NO_2)}$ (asym)
	1346.96(m)	$\nu_{(-NO_2)}$ (sym)
PVK+DNBE (molar ratio A/D=1/1)	1543.65(s)	$\nu_{(-NO_2)}$ (asym)
	1347.22(m)	$\nu_{(-NO_2)}$ (sym)
PVK+DNBE (molar ratio A/D=1/5)	1538.92(m)	$\nu_{(-NO_2)}$ (asym)
TNDB	1534.86(w), 1516.72(w)	$\nu_{(-NO_2)}$ (asym)
	1344.83(m, br)	$\nu_{(-NO_2)}$ (sym)
PVK+TNDB (molar ratio A/D=1/1)	1535.04(w), 1515.85(w)	$\nu_{(-NO_2)}$ (asym)
	1344.11(m, br)	$\nu_{(-NO_2)}$ (sym)
PVK+TNDB (molar ratio A/D=1/2)	1535.42(w), 1515.48(w)	$\nu_{(-NO_2)}$ (asym)
	1345.66(m, br)	$\nu_{(-NO_2)}$ (sym)

s: strong; m: medium; w: weak; br: broad.

shift: *upfield* for the acceptor (higher electron density, more shielding) and *downfield* for the donor (lower electron density, less shielding) [22]. Because complex formation is in rapid equilibrium the observed acceptor's spectrum is a weighted average of the free and bound acceptor molecules' spectra, [27].
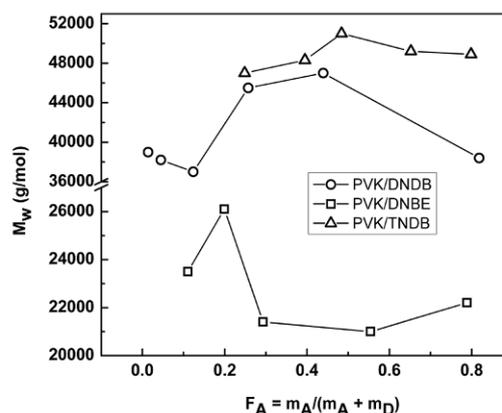
Figure 4. $F_A = f(M_w)$ plots for mixtures in THF.
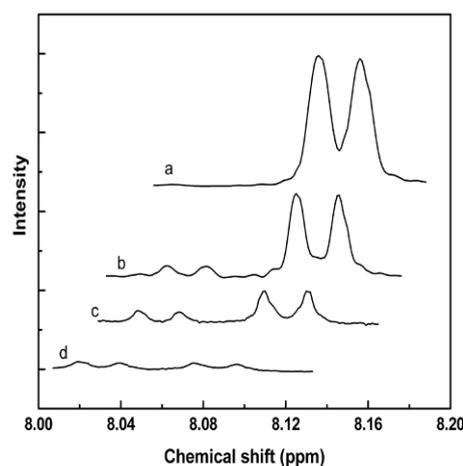
Figure 5. Expanded ^{1}H-NMR spectra for DNDB in mixtures with different PVK concentrations : (a) 0 M, (b) 0.114 M, (c) 0.331 M, and (d) 0.927 M.

For all mixtures increased shielding caused upfield shifts of the acceptor's aromatic protons, demonstrating formation of π-π* CTCs (Table 2, Figs. 5-7).

Using an expression similar to that developed by Benesi and Hildebrand from UV-Vis spectroscopy (Eq. 1), equilibrium association constants of PVK with aromatic acceptors' π-π* complexes were evaluated. A large $[D]_0/[A]_0$ molar ratio is necessary for its application (*e.g.* more than 20) [21].
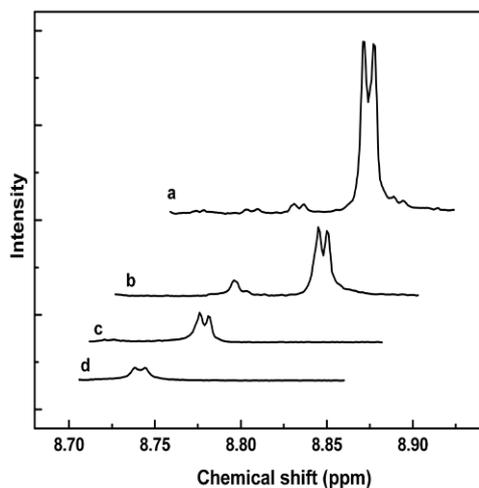
$$\frac{1}{\Delta} = \frac{1}{k}\frac{1}{[D]_0}\frac{1}{\Delta_\infty} + \frac{1}{\Delta_\infty} \quad (1)$$

k is the equilibrium association constant, $[D]_0$ the molar concentration of electron-donor, Δ the chemical shift for a specific $[D]_0/[A]_0$ molar ratio, and Δ_∞ the shift for a very small value of $[D]_0/[A]_0$.

By plotting the inverse of the acceptor's shift *versus* the inverse of donor concentration, equilibrium parameters (Δ_∞ and k) result from the intercept and
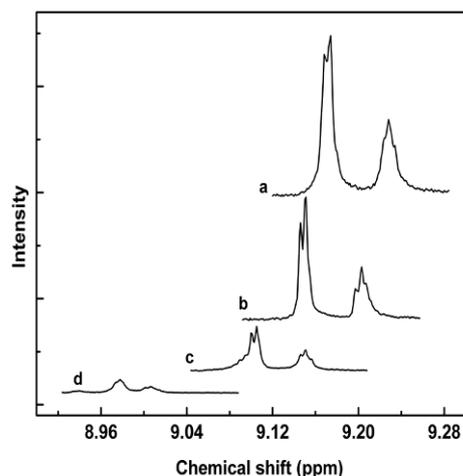
Figure 6. Expanded ^{1}H-NMR spectra for DNBE in mixtures with different PVK concentrations: (a) 0 M, (b) 0.077 M, (c) 0.232 M, and (d) 0.698 M.
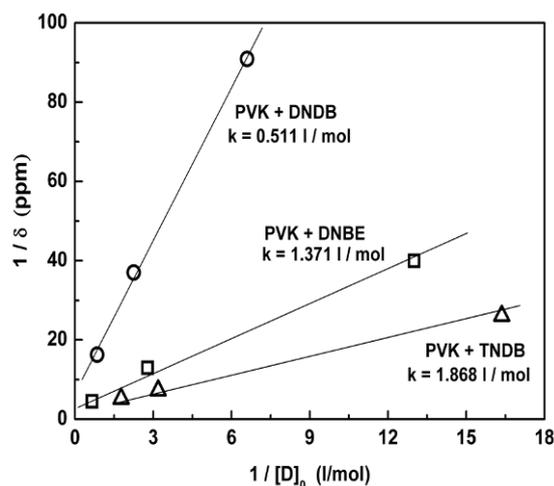

Figure 8. Benesi-Hildebrand plots from ^{1}H-NMR data.

Figure 7. Expanded ^{1}H-NMR spectra for TNDB in mixtures with different PVK concentrations: (a) 0 M, (b) 0.061 M, (c) 0.313 M and (d) 0.565 M.

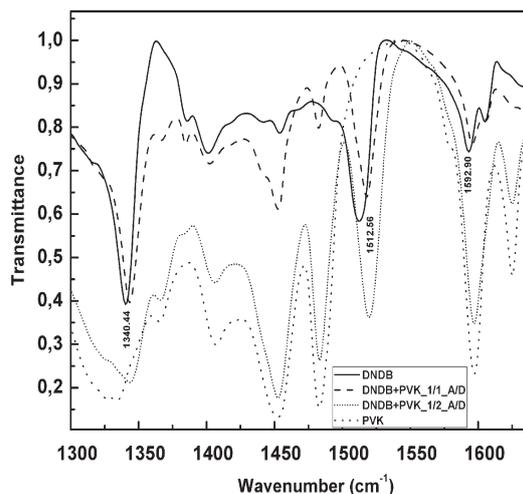**Figure 9.** Expanded FTIR spectra for DNDB, PVK and PVK-DNDB blends.

slope, as shown in Fig. 8. For the PVK-DNDB mixture, the 8.14 ppm doublet was examined as the PVK was increased. The values from the Benesi-Hildebrand equation were Δ_∞ = 0.152 ppm and k = 0.511 L mol^{-1}.

DNBE is monofunctional compared with difunctional DNDB and its π electron deficiency is larger, suggesting a stronger CT interaction. Consequently, the DNBE H_4 singlet (9.228 ppm) chemical shifts were obtained. The larger parameters (Δ_∞ = 0.260 ppm and k = 1.371 L mol^{-1}) than those from PVK-DNDB suggest stronger complexation.

For PVK-TNDB mixtures we show the Benesi-Hildebrand plot results for H_3 singlet shifts (8.874 ppm) (Δ_∞ = 0.3737 ppm and k = 1.868 L mol^{-1}). An average value of k for all protons (H_3, H_5, H_6 and CH_2) was found.

The DNDB groups can be viewed as "semi-molecules" of TNDB in a PVK-TNDB blend. These results suggest that the complex geometry corresponds to a parallel spatial arrangement of DNDB aromatic rings and CH_3 groups, centered on same axis.

3.3. FTIR spectroscopy data

The majority of IR measurements on the complexes have been concerned with shifts in the vibrational frequencies in the donor, acceptor or both. Nitroaromatic compounds exhibit (-NO_2) stretching at 1355-1320 cm^{-1} (symmetric) and 1555-1485 cm^{-1} (asymmetric) [28,29]. Assignments for acceptor molecules and their charge transfer complexes with PVK are presented in Table 3. In addition, expanded FTIR spectra of DNDB and PVK-DNDB mixtures are shown in Fig. 9.

For DNDB, the (-NO$_2$) stretches at 1592.90, 1512.56, and 1340.44 cm^{-1} are shifted to 1595.81, 1518.06 and 1343.39 cm^{-1} when it participates in charge transfer with PVK and the A/D ratio is 1. For a molar ratio of about 0.5 the polymer component predominates, and only the (-NO$_2$) asymmetric stretching band at 1519.62 cm^{-1} is observed.

The DNBE shows an (-NO$_2$) asymmetric stretch at 1542.60 cm^{-1} and (-NO$_2$) symmetric stretch at 1346.96 cm^{-1} while the corresponding bands for a complex with an A/D molar ratio of about 1 are up-shifted to 1543.65 and 1347.22 cm^{-1}, respectively. In addition, for a ratio of about 0.2, the (-NO$_2$) symmetric stretch disappears and the (-NO$_2$) asymmetric stretching vibration band is downshifted to 1538.92 cm^{-1}.

The (-NO$_2$) stretching vibration bands in TNDB are located at 1534.86, 1516.72 and 1344.83 cm^{-1}, but in complexes with PVK they are shifted by smaller amounts when compared to PVK-DNDB complexes.

4. Conclusions

GPC, ^{1}H-NMR and FTIR methods were used to evaluate CTC strength in solution and relate this to the components' structures. Although they are weak, charge transfer interactions were demonstrated in all PVK-nitroaromatic mixtures.

GPC showed increased apparent polymer M_W in mixtures compared with pure PVK, showing complex formation.

From the FTIR spectra of mixtures, acceptor (-NO$_2$) stretching shifts are related to acceptor changes in electron density when complexed with PVK chains.

The largest ^{1}H-NMR chemical shifts were obtained for the PVK-DNBE mixture, and upfield shifts in all mixtures also demonstrate complex formation. The equilibrium association constants calculated from the Benesi-Hildebrand equation imply that charge transfer interactions are strongest in the PVK-TNDB mixture. In addition, DNDB showed steric hindrance causing charge transfer interactions to be less favored in the PVK-DNDB mixture.

In mixtures with PVK, the ability of nitroaromatics to accept electrons diminishes: TNDB > DNBE > DNDB.

Acknowledgements

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