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# Ultrafast Proton Transfer in Polymer Blends Triggered by Shock Waves

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Supporting Information

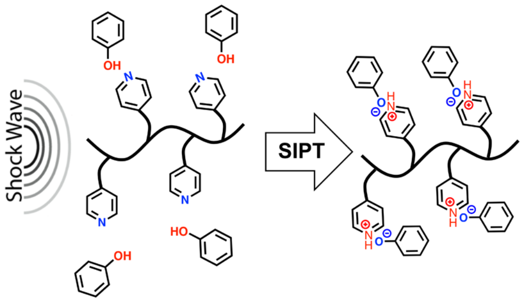
**ABSTRACT:** We describe ultrafast proton transfer in the ground electronic state triggered by the use of shock waves created by high-speed impacts. The emission of Nile Red (NR), a polarity sensing dye, was used to probe the effects of shock compression in a series of polymers, including polymer Brønsted bases blended with organic acid proton donors. NR undergoes a shock-induced red-shift due to an increase both in density and in polymer polarity. In blends with poly(4-vinylpyridine) (PVP) and phenol, NR showed an excess shock-induced red-shift with a distinct time dependence not present in controls that are incapable of proton transfer. The excess red-shift first appeared with 0.8 km·s$^{-1}$ impacts. Occurring in ca. 10 ns, this NR red-shift was caused by the formation of an ion pair created by shock-triggered proton transfer from phenol to PVP.

Proton transfer plays a fundamental role in many chemical and biological processes,[1] and extensive theoretical and experimental studies have been conducted to understand and control proton transfer in solutions and in solids.[2] The most common method for rapidly triggering proton transfer uses optical excitation of a photoacid.[3] Temperature jump[4] and infrared (IR) vibrational excitation[5] have also been used to trigger proton transfer. Here, using a recently developed tabletop shock photoemission apparatus,[6] we demonstrate that proton transfer in ground electronic states is triggered on the nanosecond time scale by shock compression.

Shock compression generally favors ion pairs over neutrals, due to the typically smaller volumes of ion pairs.[3a,7] A shock-induced polarity increase could also trigger proton transfer, since ground-state proton transfer is enabled by solvent fluctuations that increase local polarity.[8] Shock-triggered proton transfer would create an ion pair that would further increase the medium's polarity. The polarity increase in shocked water[9] is due to shock-induced dissociation of water into ion pairs.[10] In fact, Hamann and Linton proposed that the ionization of water to $H_3O^+$ and $OH^-$ can proceed nearly to completion with sufficiently strong shocks.[10,11] Shock-induced proton transfer has also been invoked as one of the key initial steps in shock initiation of high explosives. An early step in nitromethane initiation is believed to be formation of the aci ion $CH_2NO_2^-$,[12] and an early step in the initiation of nitramine explosives such as RDX[13] and HMX[14] ($[CH_2\text{-}NNO_2]_n$, $n = 3$ or 4) is believed to be the formation of HONO.

Inspired by the shock-promoted ionization of water, we hypothesized that polarization and proton transfer in solid-state polymeric materials is favored by shock waves produced by high-speed impacts, as illustrated in Scheme 1. We utilized emission from Nile Red (NR), a well-known polarity-sensing dye,[15] to investigate shock-induced polarity increases and proton transfer in polymers. The polarity-sensing ability of NR derives from the ability of polar media to lower the energy of its charge-transfer excited state.[15] In more polar media, the NR absorption and emission red-shift.

**Scheme 1. Depiction of Shock-Induced Proton Transfer (SIPT) in a Polymeric Blend Comprised of Poly(4-vinylpyridine) and Phenol in 1:1 Molar Ratio**



In a shocked polymer, there will be three sources of shock-induced red-shift. First, there is density-induced level shifting,[16] which occurs because increased density causes the excited singlet $S_1$ state to shift in energy by a different amount than the ground $S_0$ state; most commonly, the transition energy red-shifts. Second, there can be a density-induced increase in polarity due to compression, which causes the density of existing dipoles to increase and provides additional stabilization for the creation of new dipoles. The third process, the focus of this study, is the proposed additional red-shift caused by ion pairs created by shock-induced proton transfer. The first two processes have no threshold, so over a small range of impact velocity those red-shifts will be approximately linear in impact velocity.[6,17] Shock-induced proton transfer would create an excess red-shift and will exhibit an impact velocity threshold.

A first step was to identify polymers that undergo significant shock-induced polarity increases. We selected a series of commercially available polymers having the same backbone but

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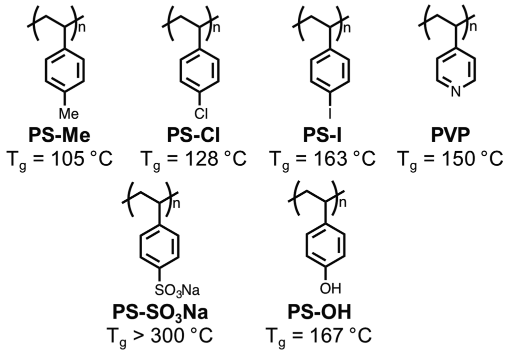
different side-chains (Scheme 2). These polymers have relatively high glass transition temperatures ($T_g$) to minimize the likelihood that shock-induced polymer softening or melting might influence NR emission (Scheme 2 and Table S1).[18] To avoid NR aggregates,[19] the NR concentration was kept at only 0.1 mol% per monomer unit of the polymer.

**Scheme 2. Chemical Structures of the Polymers Used in This Study and Their Corresponding Glass Transition Temperature ($T_g$) As Determined by Differential Scanning Calorimetry, with Heating/Cooling Rate = 10 °C/min**



The shock spectroscopy apparatus has been described previously,[6,20] and a schematic is shown in Figure S1. The shock waves were generated by laser-launched Al flyer plates 75 $\mu$m thick, which produced a steady shock drive lasting 11 ns.[21] The velocity could be varied up to 2.3 km·s$^{-1}$. A number of initial measurements were performed at 1.1 km·s$^{-1}$. The polymer samples were films 15 ± 2 $\mu$m thick on glass substrates, and the shock transit time across a film was 3−4 ns.[17] The shock pressure and temperature at 1.1 km·s$^{-1}$ depends on the properties of the polymer, but these polymers were reasonably similar mechanically and the shocks were generally about 3.4 GPa with a peak temperature of about 170 °C.[17,22] The impact velocities were measured using photon Doppler velocimetry,[21] and the photoemission spectra were measured by irradiating the NR molecules during the shock with 250 ns green laser pulses (527 nm), and acquiring one spectrum every 0.5 ns with a streak camera and spectrograph.[6,17,20]

According to the discussion above, more polar polymer media should show larger shock-induced NR red-shifts. Results showing NR used to probe shock-induced polarity increases in polymers are presented in Figure 1. Figure 1a shows a time stream of emission spectra from NR in poly(4-vinylpyridine) (PVP) with a 1.1 km·s$^{-1}$ impact. When the shock arrived, the emission red-shifted, and the maximum value of the red-shift was 47 nm. The NR emission also lost intensity and broadened slightly. In studies of the polarity-independent dye Rhodamine 6G (R6G) in poly(methyl methacrylate) (PMMA),[17] the red-shift at the same impact velocity was 30 nm and the intensity loss was caused by shock-enhanced intersystem crossing into dark triplet states.[20] Figure 1b shows time-dependent NR red-shift transients for the six polymers in Scheme 2. In PS-Me and PS-Cl, the red-shift built up during the 11 ns shock and then decayed on the 100 ns time scale. In the other polymers, due to sluggish polymer response the red-shift continued to build up until it reached a maximum around 20 ns, followed by ∼100 ns decay. Figure 1c shows the maximum red-shift versus a measure of polymer polarity, namely the ambient (unshocked) NR emission maximum. The smallest shock-induced red-shift was 35 nm for PS-Me, already greater than R6G in PMMA. The largest was 55 nm for PS-OH. A linear relation exists between the polymer's polarity, as determined from the ambient NR red-shift, and the shock-induced red-shift. The high degree of correlation between polymer polarity and NR shock red-shift was interpreted as the shock-induced polarity increase was greatest for the most polar polymers.

We then investigated the ability of NR to detect shock-induced proton transfer in polymer blends. Since temperature- and pressure-induced proton transfer had previously been observed in pyridine-based co-crystals with organic proton donors,[7,23] we selected PVP as the polymer base. We screened a series of small proton donors with a range of p$K_a$ values (Table S3), and mixed them in a 1:1 molar ratio with the NR-doped PVP. All the blends exhibited a single glass transition temperature, indicating that PVP was miscible with the proton donors (Figure S4). The donors only slightly affected the ambient NR emission (Table 1). For this reason, we believe that little, if any, proton transfer from the molecular proton donor to PVP occurred under ambient conditions. In addition, the NR red-shifts with proton donors were always at least 20 nm less than in PS-$SO_3^-Na^+$ (Table S2), a polymer salt where an ion pair is present even at ambient conditions. The lack of

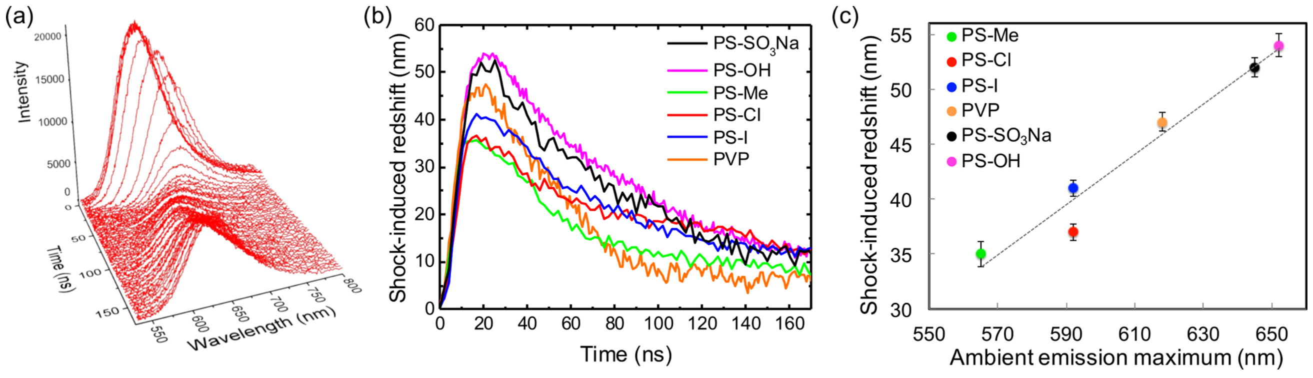


**Figure 1.** (a) Time-resolved dye photoemission from NR in PVP after impact with a 75 $\mu$m thick flyer at 1.1 km·s$^{-1}$. When the shock front arrived, NR emission lost intensity, red-shifted, and broadened slightly. After the shock wave passes, the red-shift is partially recovered. (b) Red-shift transients from NR in different polymers with 1.1 km·s$^{-1}$ impacts. (c) Correlation between polymer polarity, as judged by the ambient-pressure NR red-shift, and the shock-induced polarity increase at 1.1 km·s$^{-1}$, as judged by the shock-induced red-shift.

Table 1. Maximum Emission and Shock-Induced Red-Shift for NR in PVP Polymer and Various Proton Donors (1:1 Molar Ratio)

| proton donor used with PVP | maximum emission (nm)[a] | shock-induced red-shift (nm) |
|---|---|---|
| 3,5-dinitrobenzoic acid | 617 | 37 |
| benzoic acid | 622 | 44 |
| aniline | 612 | 49 |
| 4-methoxyphenol | 625 | 51 |
| phenol | 618 | 57 |
| 4-bromophenol | 617 | 57 |
| 4-isopropylphenol | 622 | 58 |
| none | 618 | 47 |

[a] Spectra collected under ambient temperature and pressure.

proton transfer in the donor−acceptor polymer blends was confirmed by the absence of the pyridinium ring stretch from IR spectra (Figure S3).

We subjected all the PVP-based blends to flyer plate impacts at 1.1 km·s$^{-1}$, while monitoring the maximum NR red-shift (Table 1). Our expectation was that the most acidic proton donors with the smallest p$K_a$ values would most readily undergo shock-induced proton transfer.[24] The blends with phenol, 4-bromophenol, or 4-isopropylphenol as proton donors had the largest shock-induced red-shifts. The red-shifts for 4-methoxyphenol and aniline, which have higher p$K_a$'s than phenol, were significantly smaller. With 3,5-dinitrobenzoic acid (DNBA), which had the most acidic proton donor, the red-shift was the smallest. We attribute this result to DNBA dimerization, which competes with proton transfer to the polymer.

We turned our focus to PVP−phenol, since the 1.1 km·s$^{-1}$ results with such a large NR red-shift suggested it was a likely candidate for shock-triggered proton transfer. We studied the NR red-shift as a function of impact velocity. We also looked at PVP−phenol-$d_1$ to investigate the possibility of an isotope effect, and we used pure PVP and PVP−anisole, where proton transfer is blocked by the methyl ether, as controls.

Figure 2a shows the peak NR red-shifts as a function of impact velocity from 0.3 to 2.3 km·s$^{-1}$. As expected, the NR red-shifts in PVP and PVP−anisole, where no proton transfer is possible, were linear in impact velocity, which is consistent with a NR red-shift caused mainly by density-induced NR level shifting and density-induced polarity increase of PVP. The results for PVP−phenols were dramatically different. At a threshold of ~0.8 km·s$^{-1}$, the NR red-shifts grew beyond what could be attributed to density increase alone. This excess red-shift is strongly suggestive of the polarity increase caused by proton transfer. The PVP−phenol-$d_1$ results were the same, indicating no significant kinetic isotope effect.

The NR red-shift transients in Figure 2b compare PVP and PVP−phenol below (0.6 km·s$^{-1}$) and above (1.5 km·s$^{-1}$) threshold. Below threshold, both have about the same red-shift dynamics. But above threshold, the PVP−phenol has an additional red-shift increase that starts at the end of the steadily driven shock and becomes a maximum at about 20 ns. Because of the sluggish response of the polymer to shock,[17,25] it was difficult to precisely assign a time constant for the shock-induced proton transfer, but based on Figure 2b, a reasonable estimate would be about 10 ns.

In summary, we have demonstrated shock-induced proton transfer in blends having a proton donor and acceptor (PVP−phenol): the polarity-sensing dye NR showed a shock-induced red-shift that surpassed the NR red-shifts in the controls PVP or PVP−anisole that are incapable of proton transfer. Unlike the usual shock red-shifts of dyes caused by the effects of the density increase on the dye energy levels or the increase in the polymer polarity, this excess red-shift shows a shock threshold and appeared at a threshold velocity in the 0.6−0.7 km·s$^{-1}$ range. The excess red-shift appeared with a time constant of roughly 10 ns. Based on the detailed characterization performed and the extensive controls studied, we can confidently attribute this time-delayed polarity increase to the appearance of ion pairs created by shock-triggered proton transfer.

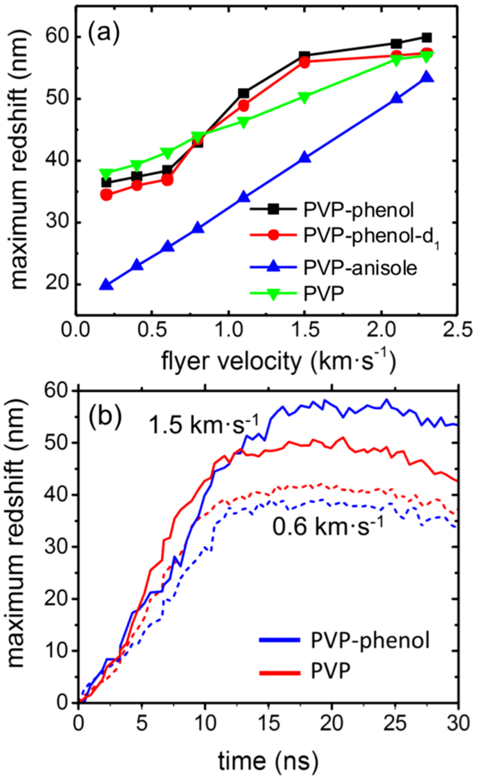


Figure 2. (a) Maximum emission red-shift of NR in different polymers versus flyer plate velocity. PVP and PVP−anisole showed the usual red-shift linearity, in flyer velocity, but PVP−phenol and PVP−phenol-$d_1$ had an excess red-shift with a threshold in the 0.6−0.7 km·s$^{-1}$ range. (b) Time-dependent red-shifts for PVP and PVP−phenol at 0.6 km·s$^{-1}$ (below threshold) and at 1.5 km·s$^{-1}$ (above threshold). The excess NR red-shift associated with proton transfer in PVP−phenol started at the end of the steady shock drive at 11 ns and was a maximum near 20 ns.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b00876.

Experimental details and data, including Tables S1−S3 and Figures S1−S6 (PDF)

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**Notes**

The authors declare no competing financial interest.

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