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# SYNTHESIS AND PHOTOCHROMIC BEHAVIOR OF ELASTOMERIC IONENE CONTAINING VIOLOGEN UNITS

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Ionene-type polymer containing viologen units was synthesized by the reaction of dicationic living poly(tetrahydrofuran) with 4,4'-bipyridine at -70 °C. This viologen polymer (PTV) was easily formed into a thin, tough, and highly elastic film. The methanol solution of PTV with ethylenediaminetetraacetic acid tetrasodium salt (EDTA) and proflavine, the N-methyl-2-pyrrolidone solution of PTV, and the thin film of PTV containing poly(N-vinyl-2-pyrrolidone) showed the photochromic property, i.e., color change by the irradiation of light.

In recent years much efforts have been paid to the incorporation of organic photochromic groups into polymers.[1-18] The methods included the physical mixing of the functional compounds in polymers,[3,4] and the chemical binding of the group to side chains or backbone of the polymers,[5-17] or at the crosslinking points.[18] This report describes the synthesis and properties of the ionene polymer containing viologen groups in its main chains.

Figure 1 shows the synthetic route of PTV. The polymerization of tetrahydrofuran (THF) with trifluoromethanesulfonic acid anhydride was already reported.[19,20] The reaction of living dicationic poly(THF) with 4,4'-bipyridine was successfully carried out at -70 °C to produce PTV having $CF_3SO_3^-$ as a counter anion. The living poly(THF) was introduced to the THF solution of bipyridine maintained at -70 °C, and the mixture was allowed to react at that temperature for one hour. It is noted

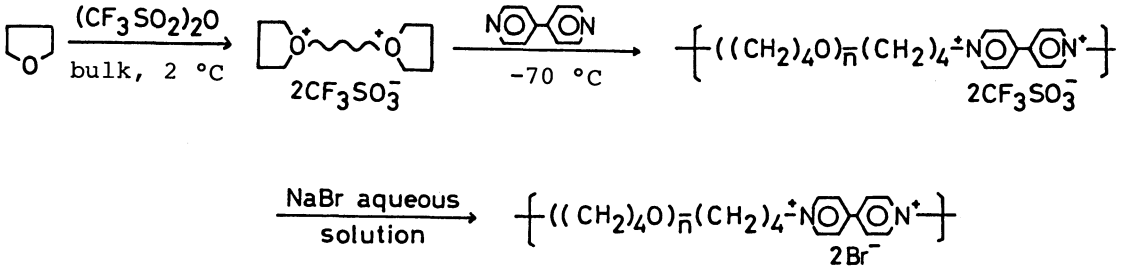



Fig. 1. Synthetic route of PTV.

Table 1. The Reaction Conditions and the Characterization of PTV and PTP

| | Cationic polymn[a] | | Reaction with amine[b] | Elemental analysis[c]/% | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | [THF]/[I][e] | Time min | [amine]/[I][e] | C | | H | | N | |
| | | | | obsd | calcd | obsd | calcd | obsd | calcd |
| PTV | 100 | 15 | 1.0 | 63.75 | 64.12 | 10.51 | 10.38 | 0.87 | 0.88 |
| PTP | 100 | 13 | 2.0 | - | - | - | - | 0.62 | 0.80 |

| | Br | | $[\eta]$[d] dl g |
|---|---|---|---|
| | obsd | calcd | |
| PTV | 4.79 | 5.02 | 0.78 |
| PTP | 4.98 | 5.02 | 0.14 |

a) Initiator, I was $(CF_3SO_2)_2O$: at 2 °C in bulk. b) 4,4'-Bipyridine for PTV and pyridine for PTP: at -70 °C for 1 h. c) Calcd values assuming n in Fig. 1 to be 40. d) Intrinsic viscosity measured in 0.1-M LiBr methanol solution at 30 °C. e) Mole ratio.

that Cunliffe et al. failed to couple bipyridine though they did not specify the reaction conditions.[21] The bromide salt, which was used through this study, was prepared by pouring the sulfonic acid salt into a large amount of the saturated aqueous solution of NaBr. The overall yield was ca. 30%.

Table 1 shows the polymerization conditions and the characterizations of PTV together with those of PTP, i.e., a model polymer of PTV which is produced by the reaction of dicationic poly(THF) with pyridine instead of bipyridine. The large intrinsic viscosity of PTV indicates that the considerable chain-extension reaction occurs when bipyridine is used in comparison with pyridine. PTV was soluble in dimethylformamide, methanol and N-methyl-2-pyrrolidone (NMP). The viscosity in methanol showed the characteristics of polyelectrolytes.[20,22] This finding and the non-polyelectrolyte behavior in the presence of LiBr (see Table 1) evidenced the formation of a polycation.

Elemental analysis (Table 1) and IR spectra of PTV and PTP were fully consistent with the assumed structures, so were the $^1$H-NMRs[23] with reference to those of poly(THF) and methylviologen. UV spectra showed an absorption peak at 260 nm in accord with that of methylviologen. Assuming the same absorption coefficient as that of methylviologen ($\varepsilon_{260}$ = 1.95 x $10^4$; lit. $\varepsilon_{254}$ = 1.39 x $10^4$ in $H_2O$[13]), the concentration of viologen units in PTV was found: 1.69 x $10^{-4}$ mol $g^{-1}$.

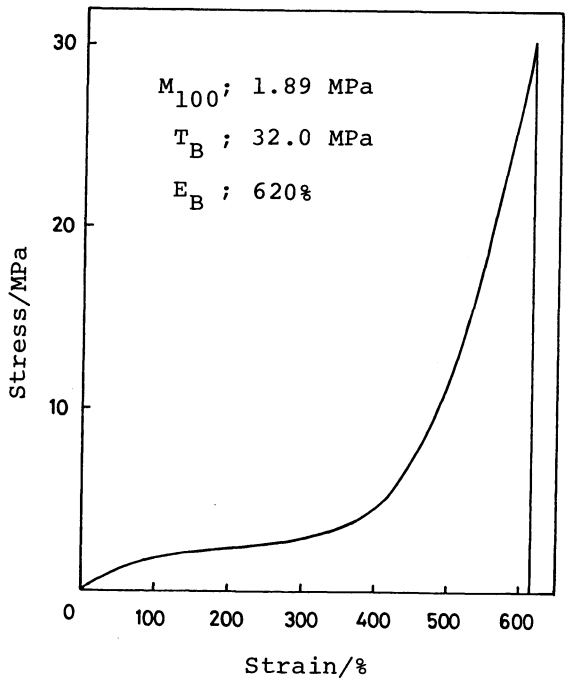
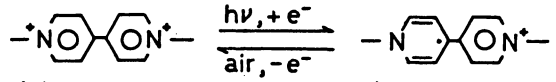



Fig. 2. Tensile properties of PTV film. $M_{100}$, stress at 100-% elongation; $T_B$, tensile strength; $E_B$, elongation at break.

In Fig. 2 is shown the tensile stress strain behavior of PTV film. The film was made by the casting method from methanol

solution, and was very flexible, i.e., fairly low stress up to ca. 400-% elongation, but the tensile strength was very high. This high strength is ascribable to the stress-induced crystallization of poly(THF) segments.[24]

Viologen is known to be a kind of oxidation-reduction chromophore, and is a typical organic photochromic material.[1,2,6] The results of the observation of




viologen cation (colorless) ⇌ viologen cation radical (green to violet)

photochromism of PTV are shown in Table 2. The light irradiation was carried out by a 150-W halogen lamp without any filters. It is noticeable that the pyrrolidone groups (NMP in Entry 3 and PVP in Entry 5) were effective accelerators for PTV to undergo color change. Similar behavior for viologen dichloride was explained by the electron transfer from chloride anion,[3] and it may also be the case for the bromide.

Table 2. Photochromism of PTV in Solutions[a] and Solid States[b]

| Entry | Solvent | [PTV][c] / % | Sensitizer or accelerator | Color observation |
|---|---|---|---|---|
| 1 | $CH_3OH$ | 1.3 | none | remains colorless |
| 2 | " | 0.18 | EDTA,[d] proflavine[e] | yellow – deep green |
| 3 | NMP[f] | 1.2 | none | yellow – deep green |
| 4 | none | – | EDTA,[d] proflavine[e] | brown – deep brown |
| 5 | none | – | PVP[g] | light yellow – green |

a) Entry Nos. 1-3. b) Entry Nos. 4 and 5. c) Concentration in g of PTV/100 $cm^3$ of solvent. d) Ethylenediaminetetraacetic acid tetrasodium salt. e) Mole ratio of [viologen]/[EDTA]/[proflavine] was 1/1.4/0.14. f) N-methyl-2-pyrrolidone. g) Poly(N-vinyl-2-pyrrolidone, 1.1 wt% of PTV.

The properties of PTV especially in solid state are now under further investigation, and shall be reported later.

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23) $^{1}$H-NMR peaks (200 MHz, in $CD_3OD$) of PTV and methylviologen (MV) are given as follows. PTV; $\delta$ 1.6 and 3.4 (methylene protons in THF units, $\beta$ and $\alpha$ to ether oxygen, respectively), $\delta$ 4.8 (methylene protons adjacent to $N^+$), $\delta$ 8.6 and 9.1 (protons in pyridinium ring, $\beta$ and $\alpha$ to $N^+$, respectively): MV; $\delta$ 4.8 (methyl protons on $N^+$), $\delta$ 8.6 and 9.1 (protons in pyridinium ring, $\beta$ and $\alpha$ to $N^+$, respectively).
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