

Hydrophilic Elastomer Containing Poly(tetrahydrofuran) Segments and Viologen Units

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SYNOPSIS

Elastomeric polymer consisting of poly(oxytetramethylene) segments and viologen units was prepared by living cationic polymerization of tetrahydrofuran (THF), followed by the end capping of the living polymer by 4,4'-bipyridine. The obtained ionene-type polymer (PTV) exhibited low tensile modulus and high tensile strength with large extensibility, i.e., it is an excellent elastomer from its mechanical properties. The water swelling behavior and effects of water and the sort of counter anions on the tensile properties of PTV were investigated. PTV showed high hydrophilicity; e.g., the water content of PTV with bromide counter anions was ca. 40% after swelling in water at 25°C for 24 h. However, even for the samples with such a high water content, PTVs displayed good elastomeric properties, although the tensile modulus and tensile strength were decreased with increase of water content. The hydrophilicity of PTV was found to depend on the kind of counter anions, which in turn determined the tensile properties of PTVs in a swollen state.

INTRODUCTION

Recently, we reported the synthesis of ionene-type elastomeric polymer consisting of poly(oxytetramethylene) segments and viologen units.¹ This polymer (PTV, Scheme 1) was found to show photochromic and photomechanical behavior due to the photo-induced reduction and oxidation of the viologen groups of PTV (Scheme 2).^{1,2}

Elastomeric ionenes, elastomers carrying quaternary ammonium salts in the main chain, have characteristics such as excellent mechanical properties and hydrophilic natures.^{3,4} The present study describes the effects of water and counter anions on the tensile properties of PTV, to elucidate PTV as a hydrophilic elastomer.

EXPERIMENTAL

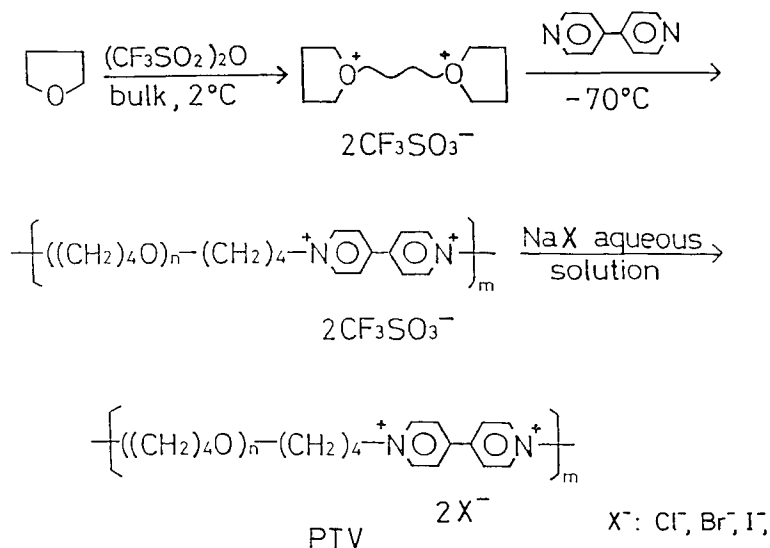
Materials

THF was distilled several times over lithium aluminum hydride before use. 4,4'-Bipyridine was re-

crystallized from toluene. Sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) was used as received. Methyl viologen dichloride was purified by recrystallization from a methanol/acetone (2 : 3 v/v) mixed solvent.

PTV was synthesized by the reaction of bifunctional living polymer of THF with 4,4'-bipyridine at -70°C .^{1,5} The reaction mixture was poured into a saturated aqueous solution of sodium bromide under vigorous stirring at room temperature (Scheme 1). The precipitated polymer was washed by distilled water and then vacuum dried. ¹H-NMR and elemental analysis of the obtained polymer were fully consistent with the structure of PTV with bromide counter anions.¹ The degree of polymerization of THF was ca. 40 as determined by gel permeation chromatography; the content of viologen groups of PTV was 1.69×10^{-4} mol/g as measured by UV spectroscopy. The intrinsic viscosity of PTV was 0.78 dL/g in 0.1M LiBr methanol solution. PTV of chloride or iodide counter anions was prepared by pouring a methanol solution of PTV with bromide ions into a saturated solution of sodium chloride or sodium iodide, respectively.⁶ The quantitative exchange of the counter anion was confirmed by elemental analysis of halogen (Cl or I) of the obtained polymers. Films of PTV were prepared by casting

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Scheme 1

its methanol solution onto Teflon mold and evaporating the solvent followed by vacuum drying.

Measurements

Absorption spectra were obtained with Beckman-Toshiba DB-G grating spectrometer. Tensile properties were determined by Shinkoh TOM-200D tensile tester at an elongation rate of 10 mm/min at room temperature. The ring-type specimens (11.6 mm inside diameter, 13.6 mm outside diameter, and ca. 0.5 mm thickness) were subjected to the measurement. Swelling test was carried out in water at 25°C and water content of the polymer was determined by the following equation:

$$\text{Water content (\%)} = \frac{100(W_S - W_D)}{W_D}$$

where W_S is the weight of swollen sample and W_D is the weight of dried sample.

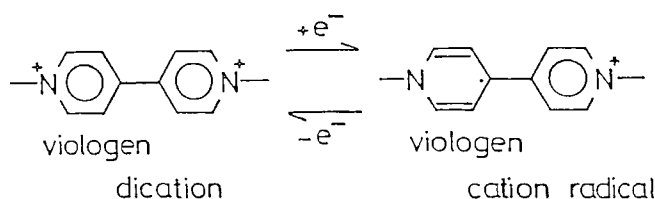
RESULTS AND DISCUSSION

Effect of Water on Tensile Properties

Figure 1 shows tensile stress-strain behavior of PTV with bromide counter anions. As shown by curve A, PTV exhibited fairly low stress up to ca. 300% elongation, but the stress increased rapidly and the tensile strength is very high with a large elongation. Thus, PTV is an excellent elastic material.

To study the effect of water, we then measured tensile properties of swollen sample of PTV; PTV film was dipped in water for 24 h and the swollen film (water content, 43.2%) was subjected to the tensile test. Figure 1, curve B, shows its stress-strain behavior. The tensile modulus, tensile strength, and elongation at break are all lower than those of the dried sample of PTV. Thus, water was found to affect greatly on the tensile properties of PTV. As indicated by curve C, after drying the swollen sample again, PTV recovered the good tensile properties almost as in the original sample.

Since PTV is a linear polymer, its elastic nature



Scheme 2

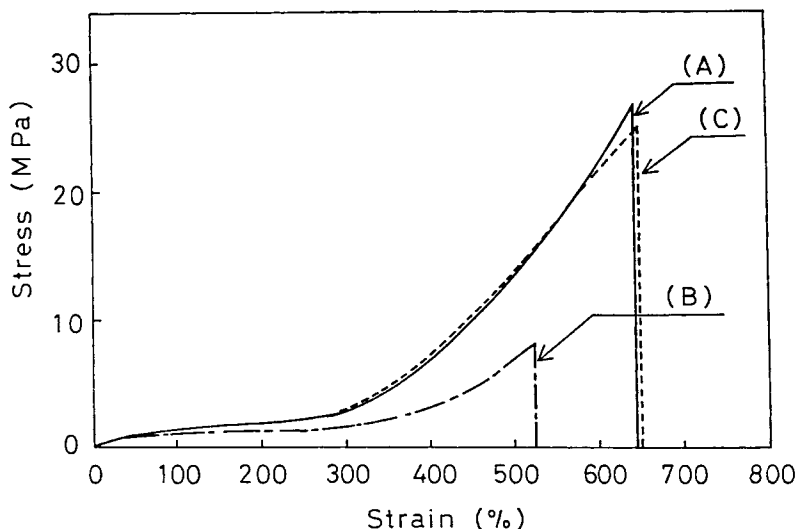


Figure 1 Tensile properties of PTV with bromide counter anion at room temperature: effect of water: (A) dried, (B) swollen (water content 43.2%), (C) redried.

probably comes from ionic clustering; the electrostatic interaction of the cationic charges of PTV molecules lead to ionic aggregation in the polymer matrix and forms ion clusters that work like cross-linking points. Therefore, water molecules were adsorbed mainly by these ion clusters and rendered

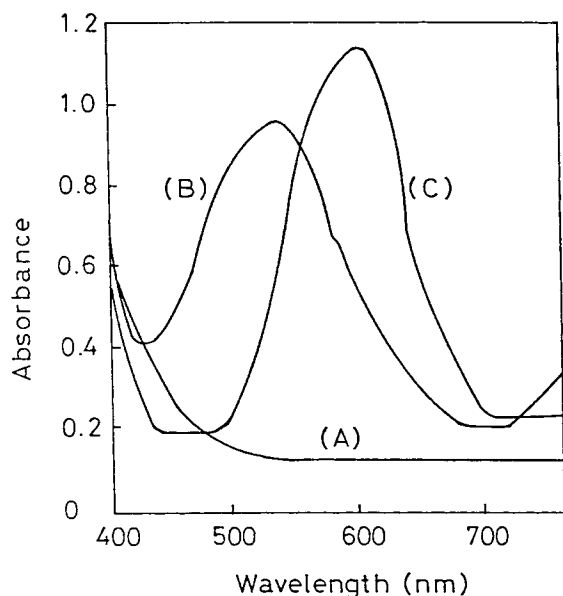


Figure 2 UV-visible spectra of films (40 μm) of PTV with bromide counter anion in (A) water and in (B) 50 mM $\text{Na}_2\text{S}_2\text{O}_4$ of phosphate buffer (pH 7.0) solution, and (C) methyl viologen dichloride in 50 mM $\text{Na}_2\text{S}_2\text{O}_4$ of phosphate buffer (pH 7.0) solution.

the ionic interactions among PTV chains weak, and hence tensile modulus and tensile strength of PTV were reduced.

The ionic agglomeration in the polymer matrix was also supported by the following spectroscopic analysis. Figure 2, curve A and B, shows UV-visible spectra of PTV films dipped in pure water and $\text{Na}_2\text{S}_2\text{O}_4$ aqueous solution, respectively. In the latter reductant solution, the spectrum shows a main absorption band around 540 nm, which is attributable to the aggregated viologen radical cation⁷ derived from the viologen groups of PTV. For comparison, the spectrum of methyl viologen dichloride in the

Table I Swelling of PTV^a in Salt Solutions^b: Effect of Salt Concentration on the Water Content and the Tensile Properties of PTV

[NaBr] (mmol/L)	Water Content (%)	M_{100} (MPa)	T_B (MPa)	E_B (%)
0	43.2 ^c	1.03	8.54	535
10	40.0	1.20	13.3	715
50	30.3	1.34	14.3	740
100	24.0	1.35	15.6	665
500	15.1	1.32	22.1	750
—	0	1.61	30.6	690

^a Counter anion: Br^- .

^b PTV films (ca. 0.5 mm) were dipped in NaBr aqueous solutions for 48 h at 25°C.

^c Dipping time, 24 h.

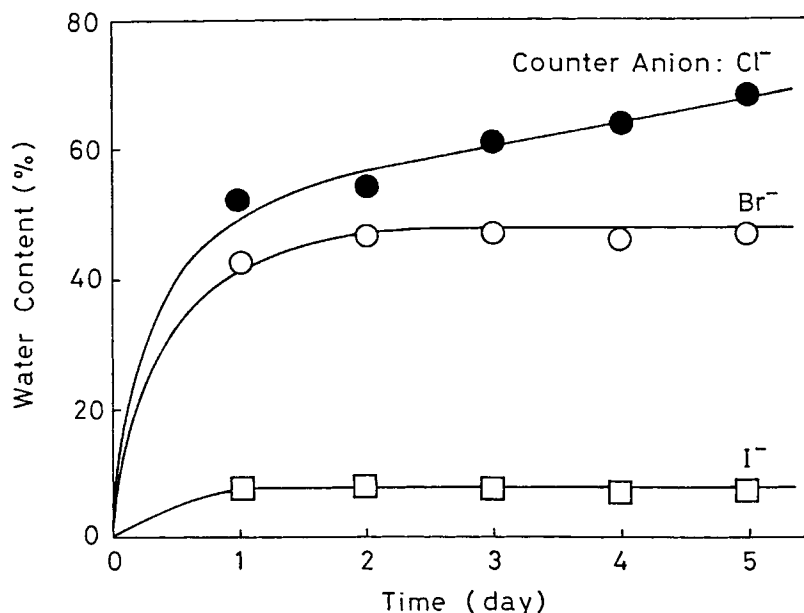


Figure 3 Swelling behavior of PTVs with different counter anions in water at 25°C. Counter anion as indicated.

same reductant solution is depicted by curve C in Figure 2. The absorption of the radical cations of the methyl viologen is observed around 600 nm, indicating the formation of monomeric viologen radical cation.⁷ Therefore, the viologen groups of PTV may cluster in a state of film.

The water content of PTV dipped in Na₂S₂O₄ aqueous solution (50 mM) for 24 h at 25°C was found to be 19.8 wt %, which is much less value than that in pure water under the same conditions (43.2 wt %). Transformation of the viologen dications of PTV into viologen radical cations by the reducing agent decreases the number of ionic sites, and hence the adsorption sites for water molecules.

To study the effect of water further, PTV films

Table II Swelling of PTVs with Different Counter Anions in Water^a: Effect of Counter Anions on the Tensile Properties of PTV

Counter Anion	Water Content (%)	M_{100} (MPa)	T_B (MPa)	E_B (%)
Cl ⁻	53.1	0.92	16.0	760
Br ⁻	43.2	1.03	8.54	535
I ⁻	8.8	1.21	30.9	680

^a PTV films (ca. 0.5 mm) were dipped in water for 24 h at 25°C.

were dipped in NaBr aqueous solutions of various concentrations and swollen films of different water content were prepared for the tensile test. Table I shows the results. When PTV adsorbed 15 wt % water, the tensile modulus at 100% elongation (M_{100}) was much reduced and retained almost the same value until 30% water content. In contrast, the tensile strength (T_B) decreased monotonously with increasing water content of the films. The elongation at break (E_B) did not change much in the range of water content studied. At present, however, the reason why the water content can be controlled by the NaBr concentration is not clear.

Effect of Counter Anions on the Hydrophilic Properties

Figure 3 shows the effect of counter anions of PTV on its swelling behavior in water. The water content of PTV films depend on the sort of counter anions and decrease in the following order: Cl⁻ > Br⁻ > I⁻. PTV with iodide ions exhibited much less hydrophilicity (water content, 8.8%) than the chloride and bromide counterparts. Therefore, the counter anion is considered to affect a state of the ionic clustering among the viologen groups of PTV molecules, and hence hydrophilicity of the ion clusters in the polymer.

Table II shows tensile properties of swollen films of PTVs with different counter anions. Tensile

modulus, M_{100} , is higher for PTV with lower water content. However, PTV with chloride ions exhibited higher T_B than PTV with bromide ions, although the water content of the chloride polymer was even higher than that of the bromide PTV. The iodide polymer showed highest T_B due to its low water content.

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